

Title 18 WAC

AIR POLLUTION

CHAPTERS

- 18-02** **Recordkeeping, reporting and public availability of emission data.** 18-04-080
- 18-06** **Sensitive areas.**
- 18-20** **Establishing requirements for the receipt of state financial aid.**
- 18-24** **Assumption of jurisdiction over motor vehicles--Emission control systems.**
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Reviser's note: All rules filed within this title subsequent to January 1, 1971 are rules filed by the department of ecology. (Chapter 43.21 RCW.) See also Title 173 WAC, Department of Ecology; Title 371, Pollution Control Hearings Board; Title 372, Water Pollution Control Commission.

DISPOSITION OF CHAPTERS FORMERLY CODIFIED IN THIS TITLE

Chapter 18-04

GENERAL REGULATIONS FOR AIR POLLUTION SOURCES

- 18-04-010 Purpose. [Order 72-6, § 18-04-010, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-010.
- 18-04-020 Applicability. [Order 72-6, § 18-04-020, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-020.
- 18-04-030 Definitions. [Order 72-6, § 18-04-030, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-030.
- 18-04-040 General standards for maximum permissible emissions. [Order 72-29, § 18-04-040, filed 1/22/73; Order 72-6, § 18-04-040, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-040.
- 18-04-050 Minimum emission standards for combustion and incineration sources. [Order 72-6, § 18-04-050, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-050.
- 18-04-060 Minimum emission standards for general process sources. [Order 72-6, § 18-04-060, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-060.
- 18-04-070 Minimum standards for certain source categories. [Order 72-29, § 18-04-070, filed 1/22/73; Order 72-6, § 18-04-070, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-070.
- 18-04-075 Emission standards for sources emitting hazardous air pollutants. [Order DE 76-11, § 18-04-075, filed 4/14/76; Order DE 76-10, § 18-04-075, filed 2/25/76; Order 74-16, § 18-04-075, filed 7/22/74.]

- Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-075.
- Compliance schedules. [Order 72-29, § 18-04-080, filed 1/22/73; Order 72-6, § 18-04-080, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-080.
- 18-04-090 Sensitive area designation. [Order 72-6, § 18-04-090, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-090.
- 18-04-100 Registration. [Order 74-16, § 18-04-100, filed 7/22/74; Order DE 73-17, § 18-04-100, filed 9/5/73; Order 72-19, § 18-04-100, filed 7/18/72; Order 72-6, § 18-04-100, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-100.
- 18-04-110 Notice of construction. [Order 74-16, § 18-04-110, filed 7/22/74; Order DE 73-17, § 18-04-110, filed 9/5/73; Order 72-6, § 18-04-110, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-110.
- 18-04-115 Standards of performance for new stationary sources. [Order DE 74-39, § 18-04-115, filed 1/27/75.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-115.
- 18-04-120 Monitoring and special reporting. [Order 72-6, § 18-04-120, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-120.
- 18-04-130 Regulatory actions. [Order 72-6, § 18-04-130, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-130.
- 18-04-140 Appeals. [Order 72-6, § 18-04-140, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-140.
- 18-04-150 Variance. [Order 72-6, § 18-04-150, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-38, filed 12/21/76. Later promulgation, see WAC 173-400-150.

Chapter 18-08

EMERGENCY EPISODE PLAN

- 18-08-010 Purpose. [Order 72-4, § 18-08-010, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-21, filed 10/31/77. Later promulgation, see chapter 173-435 WAC.
- 18-08-020 Definitions. [Order 72-4, § 18-08-020, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-21, filed 10/31/77. Later promulgation, see chapter 173-435 WAC.
- 18-08-030 Episode stage criteria. [Order 72-4, § 18-08-030, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-21, filed 10/31/77. Later promulgation, see chapter 173-435 WAC.
- 18-08-040 Source emission reduction plans. [Order 72-4, § 18-08-040, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-21, filed 10/31/77. Later promulgation, see chapter 173-435 WAC.
- 18-08-050 Action procedures. [Order 72-4, § 18-08-050, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-21, filed 10/31/77. Later promulgation, see chapter 173-435 WAC.

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18-08-060 Enforcement. [Order 72-4, § 18-08-060, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-21, filed 10/31/77. Later promulgation, see chapter 173-435 WAC.

**Chapter 18-12
OPEN BURNING**

18-12-010 Purpose. [Order 72-2, § 18-12-010, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-020 Applicability. [Order DE 73-16, § 18-12-020, filed 9/5/73; Order 72-2, § 18-12-020, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-030 Definitions. [Order DE 73-16, § 18-12-030, filed 9/5/73; Order DE 73-1, § 18-12-030, filed 2/9/73; Order 72-2, § 18-12-030, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-035 Episodes. [Order DE 73-16, § 18-12-035, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-040 Permits and restrictions. [Order DE 73-1, § 18-12-040, filed 2/9/73; Order 72-2, § 18-12-040, filed 1/24/72, 2/2/72.] Repealed by Order DE 73-16, filed 9/5/73.

18-12-045 Prohibited materials. [Order DE 73-16, § 18-12-045, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-050 Department of natural resources—Smoke management plan. [Order 72-2, § 18-12-050, filed 1/24/72, 2/2/72.] Repealed by Order DE 73-16, filed 9/5/73.

18-12-055 Exceptions. [Order DE 73-16, § 18-12-055, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-060 Notice of violation. [Order 72-2, § 18-12-060, filed 1/24/72, 2/2/72.] Repealed by Order DE 73-16, filed 9/5/73.

18-12-065 Residential open burning. [Order DE 73-16, § 18-12-065, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-070 Remedies. [Order 72-2, § 18-12-070, filed 1/24/72, 2/2/72.] Repealed by Order DE 73-16, filed 9/5/73.

18-12-075 Commercial open burning. [Order DE 73-16, § 18-12-075, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-080 Exemptions. [Order DE 73-1, § 18-12-080, filed 2/9/73; Order 72-2, § 18-12-080, filed 1/24/72, 2/2/72.] Repealed by Order DE 73-16, filed 9/5/73.

18-12-085 Agricultural open burning. [Order DE 73-16, § 18-12-085, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-090 Alternate technology. [Order DE 73-1, § 18-12-090, filed 2/9/73.] Repealed by Order DE 73-16, filed 9/5/73.

18-12-095 No burn area designation. [Order DE 73-16, § 18-12-095, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-100 Delegation of agricultural open burning program. [Order DE 73-16, § 18-12-100, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-110 Certification of alternatives to open burning. [Order DE 75-19, § 18-12-110, filed 9/3/75; Order DE 73-16, § 18-12-110, filed 9/5/73.] Repealed by Order

DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-120 Department of natural resources—Smoke management plan. [Order DE 73-16, § 18-12-120, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-130 Notice of violation. [Order DE 73-16, § 18-12-130, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

18-12-140 Remedies. [Order DE 73-16, § 18-12-140, filed 9/5/73.] Repealed by Order DE 77-19, filed 10/24/77. Later promulgation, see chapter 173-425 WAC.

Chapter 18-16

BURNING OF FIELD AND TURF GRASSES GROWN FOR SEED

18-16-010 Purpose. [Order 73-18, § 18-16-010, filed 9/5/73; Order 72-5, § 18-16-010, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-20, filed 11/9/77. Later promulgation, see chapter 173-430 WAC.

18-16-020 Definitions. [Order 74-2, § 18-16-020, filed 4/1/74; Order 72-5, § 18-16-020, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-20, filed 11/9/77. Later promulgation, see chapter 173-430 WAC.

18-16-030 Compliance program. [Order 73-18, § 18-16-030, filed 9/5/73; Order 72-5, § 18-16-030, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-20, filed 11/9/77. Later promulgation, see chapter 173-430 WAC.

18-16-040 Mobile field burners. [Order 72-5, § 18-16-040, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-20, filed 11/9/77. Later promulgation, see chapter 173-430 WAC.

18-16-050 Other approvals. [Order 72-5, § 18-16-050, filed 1/24/72, 2/2/72.] Repealed by Order DE 77-20, filed 11/9/77. Later promulgation, see chapter 173-430 WAC.

18-16-060 Study of alternates. [Order 73-18, § 18-16-060, filed 9/5/73.] Repealed by Order DE 77-20, filed 11/9/77. Later promulgation, see chapter 173-430 WAC.

18-16-070 Fees. [Order 73-18, § 18-16-070, filed 9/5/73.] Repealed by Order DE 77-20, filed 11/9/77. Later promulgation, see chapter 173-430 WAC.

18-16-080 Certification of alternates. [Order 73-18, § 18-16-080, filed 9/5/73.] Repealed by Order DE 77-20, filed 11/9/77. Later promulgation, see chapter 173-430 WAC.

Chapter 18-32

CARBON MONOXIDE

18-32-009 Preamble. [Order 72-7, § 18-32-010 (codified as WAC 18-32-009), filed 1/24/72.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. See chapter 173-475 WAC.

18-32-010 Definitions. [Order 72-7, § 18-32-020 (codified as WAC 18-32-010), filed 1/24/72, 2/2/72; Order 6, § 18-32-010, filed 2/18/69.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. Later promulgation, see WAC 173-475-020.

18-32-020 Air quality standard. [Order 72-7, § 18-32-030 (codified as WAC 18-32-020), filed 1/24/72, 2/2/72; Order 6, § 18-32-020, filed 2/18/69.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. Later promulgation, see WAC 173-475-030.

18-32-030 Air quality objective. [Order 72-7, § 18-32-040 (codified as WAC 18-32-030), filed 1/24/72, 2/2/72; Order 6, § 18-32-030, filed 2/18/69.]

- 18-32-040 Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. Later promulgation, see WAC 173-475-030.
- 18-32-050 Method of measurement. [Order 6, § 18-32-040, filed 2/18/69.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. Later promulgation, see WAC 173-475-040.
- 18-32-060 Reporting of data. [Order 72-7, § 18-32-060 (codified as WAC 18-32-050), filed 1/24/72, 2/2/72; Order 6, § 18-32-050, filed 2/18/69.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. Later promulgation, see WAC 173-475-050.
- 18-32-060 Method of determination and reporting for continuous infrared analysis. [Order 72-7, § 18-32-070 (codified as WAC 18-32-060), filed 1/24/72, 2/2/72; Order 6, § 18-32-060, filed 2/18/69.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120.
- 18-32-990 Appendix A—Suggested method of assembly. [Order 6, Appendix A (codified as WAC 18-32-990), filed 2/18/69.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120.
- 18-32-99001 Appendix B—Suggested construction. [Order 6, Appendix B (codified as WAC 18-32-99001), filed 2/18/69.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120.

Chapter 18-36

KRAFT PULPING MILLS

- 18-36-010 Statement of policy and purpose. [Order DE 76-2, § 18-36-010, filed 2/5/76; Order 74-17, § 18-36-010, filed 7/22/74; Order 8, § 18-36-010, filed 6/18/69.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-011 Statement of policy and purpose. [Order DE 76-22, § 18-36-011, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-011.
- 18-36-020 Definitions. [Order DE 76-2, § 18-36-020, filed 2/5/76; Order 74-17, § 18-36-020, filed 7/22/74; Order 8, § 18-36-020, filed 6/18/69.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-021 Definitions. [Order DE 76-22, § 18-36-021, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-021.
- 18-36-030 Specific emission standards. [Order DE 76-2, § 18-36-030, filed 2/5/76; Order 8, § 18-36-030, filed 6/18/69.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-031 Specific emission standards. [Order DE 76-22, § 18-36-031, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-031.
- 18-36-035 General emission standards and nuisance control measures. [Order DE 76-2, § 18-36-035, filed 2/5/76.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-036 General emission standards and nuisance control measures. [Order DE 76-22, § 18-36-036, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-036.
- 18-36-040 Compliance. [Order DE 70-14, § 18-36-040, filed 2/9/71, effective 3/12/71; Order 8, § 18-36-040, filed 6/18/69.] Repealed by Order DE 76-35, filed 12/28/76.
- 18-36-045 Compliance schedules—Individual mills. [Order 9, § 18-36-045, filed 3/17/70.] Repealed by Order DE 70-14, filed 2/9/71, effective 3/12/71.
- 18-36-050 Public hearing. [Order 8, § 18-36-050, filed 6/18/69.] Repealed by Order DE 76-2, filed 2/5/76.
- 18-36-060 More restrictive emission standards. [Order DE 76-2, § 18-36-060, filed 2/5/76; Order 8, § 18-36-060, filed 6/18/69.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-061 More restrictive emission standards. [Order DE 76-22, § 18-36-061, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-061.
- 18-36-070 Monitoring and reporting. [Order DE 76-2, § 18-36-070, filed 2/5/76; Order 8, § 18-36-070, filed 6/18/69.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-071 Monitoring and reporting. [Order DE 76-22, § 18-36-071, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-071.
- 18-36-075 Report of startup, shutdown, breakdown or upset condition. [Order DE 76-2, § 18-36-075, filed 2/5/76.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-076 Report of startup, shutdown, breakdown or upset condition. [Order DE 76-22, § 18-36-076, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-076.
- 18-36-080 Notice of construction. [Order DE 76-2, § 18-36-080, filed 2/5/76; Order 74-17, § 18-36-080, filed 7/22/74; Order 8, § 18-36-080, filed 6/18/69.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-081 Notice of construction. [Order DE 76-22, § 18-36-081, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-081.
- 18-36-090 Special studies. [Order DE 76-2, § 18-36-090, filed 2/5/76; Order 8, § 18-36-090, filed 6/18/69.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-091 Special studies. [Order DE 76-22, § 18-36-091, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-091.
- 18-36-100 Exemption. [Order DE 76-2, § 18-36-100, filed 2/5/76; Order 8, § 18-36-100, filed 6/18/69.] Repealed by Order DE 76-22, filed 6/28/76.
- 18-36-101 Exemption. [Order DE 76-22, § 18-36-101, filed 6/28/76.] Repealed by Order DE 76-35, filed 12/28/76. Later promulgation, see WAC 173-405-101.

Chapter 18-38

SULPHITE PULPING MILLS

- 18-38-010 Statement of policy and purpose. [Order DE 76-3, § 18-38-010, filed 2/5/76; Order 72-1, § 18-38-010, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-011 Statement of policy and purpose. [Order DE 76-23, § 18-38-011, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-011.
- 18-38-020 Definitions. [Order DE 76-3, § 18-38-020, filed 2/5/76; Order 72-1, § 18-38-020, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-021 Definitions. [Order DE 76-23, § 18-38-021, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-021.
- 18-38-030 Specific emission standards. [Order DE 76-3, § 18-38-030, filed 2/5/76; Order 72-1, § 18-38-030, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-031 Specific emission standards. [Order DE 76-23, § 18-38-031, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-031.

- 18-38-035 General emission standards and nuisance control measures. [Order DE 76-3, § 18-38-035, filed 2/5/76.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-036 General emission standards and nuisance control measures. [Order DE 76-23, § 18-38-036, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-036.
- 18-38-040 More restrictive emission standards. [Order DE 76-3, § 18-38-040, filed 2/5/76; Order 72-1, § 18-38-040, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-041 More restrictive emission standards. [Order DE 76-23, § 18-38-041, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-041.
- 18-38-050 Compliance. [Order DE 76-3, § 18-38-050, filed 2/5/76; Order 72-1, § 18-38-050, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-051 Compliance. [Order DE 76-23, § 18-38-051, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-051.
- 18-38-060 Monitoring and reporting. [Order DE 76-3, § 18-38-060, filed 2/5/76; Order 72-1, § 18-38-060, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-061 Monitoring and reporting. [Order DE 76-23, § 18-38-061, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-061.
- 18-38-065 Report of startup, shutdown, breakdown or upset condition. [Order DE 76-3, § 18-38-065, filed 2/5/76.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-066 Report of startup, shutdown, breakdown or upset condition. [Order DE 76-23, § 18-38-066, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-066.
- 18-38-070 Special studies. [Order 72-1, § 18-38-070, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-36, filed 12/28/76.
- 18-38-080 Exemptions. [Order DE 76-3, § 18-38-080, filed 2/5/76; Order 72-1, § 18-38-080, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-081 Exemptions. [Order DE 76-2, § 18-38-081, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-091.
- 18-38-090 Notice of construction. [Order DE 76-3, § 18-38-090, filed 2/5/76; Order 74-17, § 18-38-090, filed 8/29/74; Order 74-17, § 18-38-090, filed 7/22/74; Order 72-1, § 18-38-090, filed 1/24/72, 2/2/72.] Repealed by Order DE 76-23, filed 6/28/76.
- 18-38-091 Notice of construction. [Order DE 76-23, § 18-38-091, filed 6/28/76.] Repealed by Order DE 76-36, filed 12/28/76. Later promulgation, see WAC 173-410-081.

Chapter 18-46

PHOTOCHEMICAL OXIDANT--HYDROCARBONS--NITROGEN DIOXIDE

- 18-46-010 Preamble. [Order 72-3, § 18-46-010, filed 1/24/72, 2/2/72.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. See chapter 173-475 WAC.
- 18-46-020 Definitions. [Order 72-3, § 18-46-020, filed 1/24/72, 2/2/72.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and

- 70.120.120. Later promulgation, see WAC 173-475-020.
- 18-46-030 Air quality standards. [Order 72-3, § 18-46-030, filed 1/24/72, 2/2/72.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. Later promulgation, see WAC 173-475-030.
- 18-46-040 Measurement. [Order 72-3, § 18-46-040, filed 1/24/72, 2/2/72.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. Later promulgation, see WAC 173-475-030 and 173-475-040.
- 18-46-050 Reporting of data. [Order 72-3, § 18-46-050, filed 1/24/72, 2/2/72.] Repealed by 80-03-071 (Order DE 79-36), filed 2/29/80. Statutory Authority: RCW 43.21A.080, 70.94.331, 70.120.030, and 70.120.120. Later promulgation, see WAC 173-475-050.

Chapter 18-52

PRIMARY ALUMINUM PLANTS

- 18-52-010 Statement of purpose. [Order 12, § 18-52-010, filed 5/18/70.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-010.
- 18-52-015 Objectives. [Order DE 76-4, § 18-52-015, filed 2/5/76; Order 12, § 18-52-015, filed 5/18/70.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-016 Objectives. [Order DE 76-24, § 18-52-016, filed 6/28/76.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395.
- 18-52-020 Definitions. [Order DE 76-4, § 18-52-020, filed 2/5/76; Order 12, § 18-52-020, filed 5/18/70.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-021 Definitions. [Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331. 80-04-048 (Order DE 80-6), § 18-52-021, filed 3/21/80; Order DE 76-24, § 18-52-021, filed 6/28/76.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-020.
- 18-52-030 Emission standards. [Order DE 76-4, § 18-52-030, filed 2/5/76; Order 14, § 18-52-030, filed 5/28/70; Order 12, § 18-52-030, filed 5/18/70.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-031 Emission standards. [Order DE 76-24, § 18-52-031, filed 6/28/76.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-030.
- 18-52-035 Nuisance control measures. [Order DE 76-4, § 18-52-035, filed 2/5/76.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-036 Nuisance control measures. [Order DE 76-24, § 18-52-036, filed 6/28/76.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395.
- 18-52-040 Revision of emission standards. [Order DE 76-4, § 18-52-040, filed 2/5/76; Order 12, § 18-52-040, filed 5/18/70.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-041 Revision of emission standards. [Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331. 80-04-048 (Order DE 80-6), § 18-52-041, filed 3/21/80; Order DE 76-24, § 18-52-041, filed 6/28/76.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395.
- 18-52-050 Compliance. [Order DE 70-14, § 18-52-050, filed 2/9/71, effective 3/12/71; Order 12, § 18-52-050, filed 5/18/70.] Repealed by 80-04-048 (Order DE

- 18-52-051 80-6), filed 3/21/80. Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331. Standards of performance. [Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331. 80-04-048 (Order DE 80-6), § 18-52-051, filed 3/21/80.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-040.
- 18-52-056 New source review. [Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331. 80-04-048 (Order DE 80-6), § 18-52-056, filed 3/21/80.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-050.
- 18-52-060 Monitoring. [Order DE 76-4, § 18-52-060, filed 2/5/76; Order 12, § 18-52-060, filed 5/18/70.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-061 Monitoring. [Order DE 76-24, § 18-52-061, filed 6/28/76.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-060.
- 18-52-070 Reporting. [Order DE 76-4, § 18-52-070, filed 2/5/76; Order 74-17, § 18-52-070, filed 7/22/74; Order 12, § 18-52-070, filed 5/18/70.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-071 Reporting. [Order DE 76-24, § 18-52-071, filed 6/28/76.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-060.
- 18-52-075 Report of startup, shutdown, breakdown or upset condition. [Order DE 76-4, § 18-52-075, filed 2/5/76.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-076 Report of startup, shutdown, breakdown or upset condition. [Order DE 76-24, § 18-52-076, filed 6/28/76.] Repealed by 80-04-048 (Order DE 80-6), filed 3/21/80. Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331.
- 18-52-077 Abnormal operations or upset conditions. [Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331. 80-04-048 (Order DE 80-6), § 18-52-077, filed 3/21/80.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-070.
- 18-52-080 Special studies. [Order 12, § 18-52-080, filed 5/18/70.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395.
- 18-52-086 Emission inventory. [Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331. 80-04-048 (Order DE 80-6), § 18-52-086, filed 3/21/80.] Repealed by 80-11-028 (Order DE 80-17), filed 8/14/80. Statutory Authority: RCW 70.94.331 and 70.94.395. Later promulgation, see WAC 173-415-080.
- 18-52-090 Notice of construction. [Order DE 76-4, § 18-52-090, filed 2/5/76; Order 74-17, § 18-52-090, filed 7/22/74.] Repealed by Order DE 76-24, filed 6/28/76.
- 18-52-091 Notice of construction. [Order DE 76-24, § 18-52-091, filed 6/28/76.] Repealed by 80-04-048 (Order DE 80-6), filed 3/21/80. Statutory Authority: RCW 43.21A.080, 70.94.110, 70.94.152, and 70.94.331.
- 18-60-010 Policy and purpose. [Order DE 70-14, § 18-60-010, filed 2/9/71; effective 3/12/71.] Repealed by 83-09-013 (Order DE 83-12), filed 4/11/83. Statutory Authority: Chapters 43.21A and 70.94 RCW. Later promulgation, see WAC 173-403-010.
- 18-60-020 Definitions. [Order DE 70-14, § 18-60-020, filed 2/9/71; effective 3/12/71.] Repealed by 83-09-013 (Order DE 83-12), filed 4/11/83. Statutory Authority: Chapters 43.21A and 70.94 RCW. Later promulgation, see WAC 173-403-030.
- 18-60-030 Procedure. [Order DE 70-14, § 18-60-030, filed 2/9/71; effective 3/12/71.] Repealed by 83-09-013 (Order DE 83-12), filed 4/11/83. Statutory Authority: Chapters 43.21A and 70.94 RCW. Later promulgation, see chapter 173-403 WAC.
- 18-60-040 Penalty. [Order DE 70-14, § 18-60-040, filed 2/9/71; effective 3/12/71.] Repealed by 83-09-013 (Order DE 83-12), filed 4/11/83. Statutory Authority: Chapters 43.21A and 70.94 RCW. Later promulgation, see chapter 173-403 WAC.
- 18-60-050 Public information. [Order DE 70-14, § 18-60-050, filed 2/9/71; effective 3/12/71.] Repealed by 83-09-013 (Order DE 83-12), filed 4/11/83. Statutory Authority: Chapters 43.21A and 70.94 RCW. Later promulgation, see chapter 173-403 WAC.

Chapter 18-02 WAC

RECORDKEEPING, REPORTING AND PUBLIC AVAILABILITY OF EMISSION DATA

WAC

18-02-010	Purpose.
18-02-020	Classification.
18-02-030	Recordkeeping and reporting.
18-02-040	Public availability of emission data.
18-02-050	Definitions.

WAC 18-02-010 Purpose. The purpose of this regulation is to:

(1) Require owners or operators of stationary sources of air contaminants to maintain records of, and periodically report to the state information on, the nature and amounts of emissions and other information as may be necessary to determine whether such sources are in compliance with applicable emission limitations and other control measures.

(2) Provide for public availability of emission data reported to the state by stationary source owners or operators or otherwise obtained by the state, as correlated with applicable emission limitations. [Order 72-18, § 18-02-010, filed 7/18/72.]

WAC 18-02-020 Classification. The director of the department of ecology finds that the types of emissions from sources within the following listed classes may cause or contribute to air pollution, in that such emissions may result in the presence in the outdoor atmosphere of air contaminants so as to affect adversely human health; other biological values; the enjoyment of life; and the value, physical conditions and enjoyment of property:

- (1) Agricultural drying and dehydrating operations;
- (2) Asphalt plants;
- (3) Cattle feedlots;
- (4) Chemical plants;
- (5) Ferrous foundries;

Chapter 18-60
ESTABLISHING PROCEDURES FOR IMPLEMENTING
REGULATIONS APPLICABLE TO EMISSIONS FROM
PARTICULAR TYPES AND CLASSES OF AIR CONTAMINANT
SOURCES--REGULATORY ORDERS CONTAINING
COMPLIANCE SCHEDULES

- (6) Fertilizer plants;
- (7) Grain handling, seed processing, pea and lentil processing;
- (8) Mineralogical processing plants;
- (9) Nonferrous foundries;
- (10) Oil refineries;
- (11) Other metallurgical processing plants;
- (12) Power boilers using coal, hog fuel or oil;
- (13) Rendering plants;
- (14) Scrap metal operations;
- (15) Veneer dryers;
- (16) Wood waste incinerators including wigwam burners.

The classifications above set forth apply throughout the state and include all stationary sources within any listed class wherever located in the state. [Order 72-18, § 18-02-020, filed 7/18/72.]

WAC 18-02-030 Recordkeeping and reporting. (1) The owner or operator of any stationary source in the state which is within a classification listed in the preceding section shall, upon notification by the director of the department of ecology, maintain records of the nature and amounts of emissions from such source and/or other information deemed necessary by the director to determine whether such source is in compliance with applicable emission limitations and other control measures.

(2) The information recorded pursuant to subsection (1) hereof shall be reported to the director of the department of ecology on forms supplied by said department. Such reports shall be filed semiannually during January, and July, commencing January, 1973.

(3) Whenever the director of the department of ecology shall determine that record-keeping and reporting of emission data from any stationary source or stationary source-type in the state, not listed in WAC 18-02-020, is needed for the investigation of causes, effects, prevention, abatement or control of air pollution or otherwise necessary to effectuate the purposes of chapter 70.94 RCW, said director shall notify the owner(s) or operator(s) of such source or sources. Such notification shall constitute an order to maintain records and submit reports on emissions in the manner set forth in subsections (1) and (2) of this section. [Order 72-18, § 18-02-030, filed 7/18/72.]

WAC 18-02-040 Public availability of emission data. Emission data obtained by the department of ecology from owners or operators of stationary sources pursuant to the preceding section or otherwise obtained by said department will be correlated with applicable emission limitations and other control measures and will be available to the public during normal business hours at said department's offices. [Order 72-22, § 18-02-040, filed 11/10/72; Order 72-18, § 18-02-040, filed 7/18/72.]

WAC 18-02-050 Definitions. As used in this chapter, the following words and phrases shall have the following meanings:

- (1) "Department" means department of ecology.
- (2) "Director" means director of department of ecology.
- (3) "Emission" means a release of air contaminants into the ambient air.
- (4) "Stationary source" means any building, structure, facility or installation which releases emissions. [Order 72-18, § 18-02-050, filed 7/18/72.]

Chapter 18-06 WAC SENSITIVE AREAS

WAC	Purpose.
18-06-010	Purpose.
18-06-020	Applicability.
18-06-030	Definitions.
18-06-040	Sensitive areas designated.
18-06-050	Standards.
18-06-900	Appendix A—Map.

WAC 18-06-010 Purpose. Pursuant to chapter 70.94 RCW, the Washington Clean Air Act, and in order to implement WAC 18-04-090, this regulation is for the purpose of designating certain geographical areas of the state as sensitive areas in light of population concentrations, intensity of human activity and recreational and scenic values; and for the purpose of providing for the imposition of more stringent standards and compliance requirements for certain stationary source categories within such areas than apply to such categories outside sensitive areas. [Order 72-23, § 18-06-010, filed 11/22/72.]

WAC 18-06-020 Applicability. The sensitive areas designated herein are located only in geographical areas not presently subject to the regulatory control of any activated air pollution control authority. Should any air pollution control authority hereafter be activated whose jurisdictional boundaries include all or any part of a sensitive area designated herein, such area or part thereof would not thereby be abrogated but such area or part would remain in effect, although such newly activated authority could adopt more stringent standards for such areas. [Order 72-23, § 18-06-020, filed 11/22/72.]

WAC 18-06-030 Definitions. (1) "Department" means department of ecology.

(2) "Director" means director of the department of ecology.

(3) "Sensitive area" means an area in which more stringent standards and compliance requirements apply to specified stationary source categories than apply to such source categories outside such area.

(4) "Stationary source" means any building, structure, facility or installation which emits or may emit any contaminants to the ambient air. [Order 72-23, § 18-06-030, filed 11/22/72.]

WAC 18-06-040 Sensitive areas designated. Based on a consideration of present and predicted ambient air

quality in light of population density and trends, intensity of highway usage and scenic and recreational values, the following areas are designated as sensitive areas:

(1) All cities within the state with a population of 1,000 or more which are not presently subject to the regulatory control of any activated air pollution control authority, together with those lands extending one mile outward from the present city limits in all directions as measured on a horizontal plane from such limits. These cities are presently:

- (a) Pullman
- (b) Wenatchee
- (c) Ellensburg
- (d) Clarkston
- (e) Othello
- (f) Omak
- (g) Colville
- (h) Colfax
- (i) Dayton
- (j) Goldendale
- (k) Chelan
- (l) Okanogan
- (m) Cashmere
- (n) Ritzville
- (o) Pomeroy
- (p) Cle Elum
- (q) White Salmon
- (r) Oroville
- (s) Newport
- (t) Coulee Dam
- (u) Davenport
- (v) Chewelah
- (w) Leavenworth

- (x) Brewster
- (y) Wilbur
- (z) Odessa

(2) Those portions of state highways designated on the map which is hereby incorporated herein as Appendix A [WAC 18-06-900], together with a strip of land bordering each side of such designated portions of highways extending one mile outward from the edge of the right of way measured on a horizontal plane from each such edge, plus all incorporated cities or towns bordering such designated portions of highways.

(3) Any area on either side of Columbia, Snake, or Spokane Rivers in this state which is within one mile measured on a horizontal plane from the line of mean high water. [Order 72-23, § 18-06-040, filed 11/22/72.]

WAC 18-06-050 Standards. Stationary sources within sensitive areas must comply with all applicable emission limitations set forth in Title 18 WAC. In addition, the following more restrictive standards shall apply within such areas to stationary sources within the categories listed.

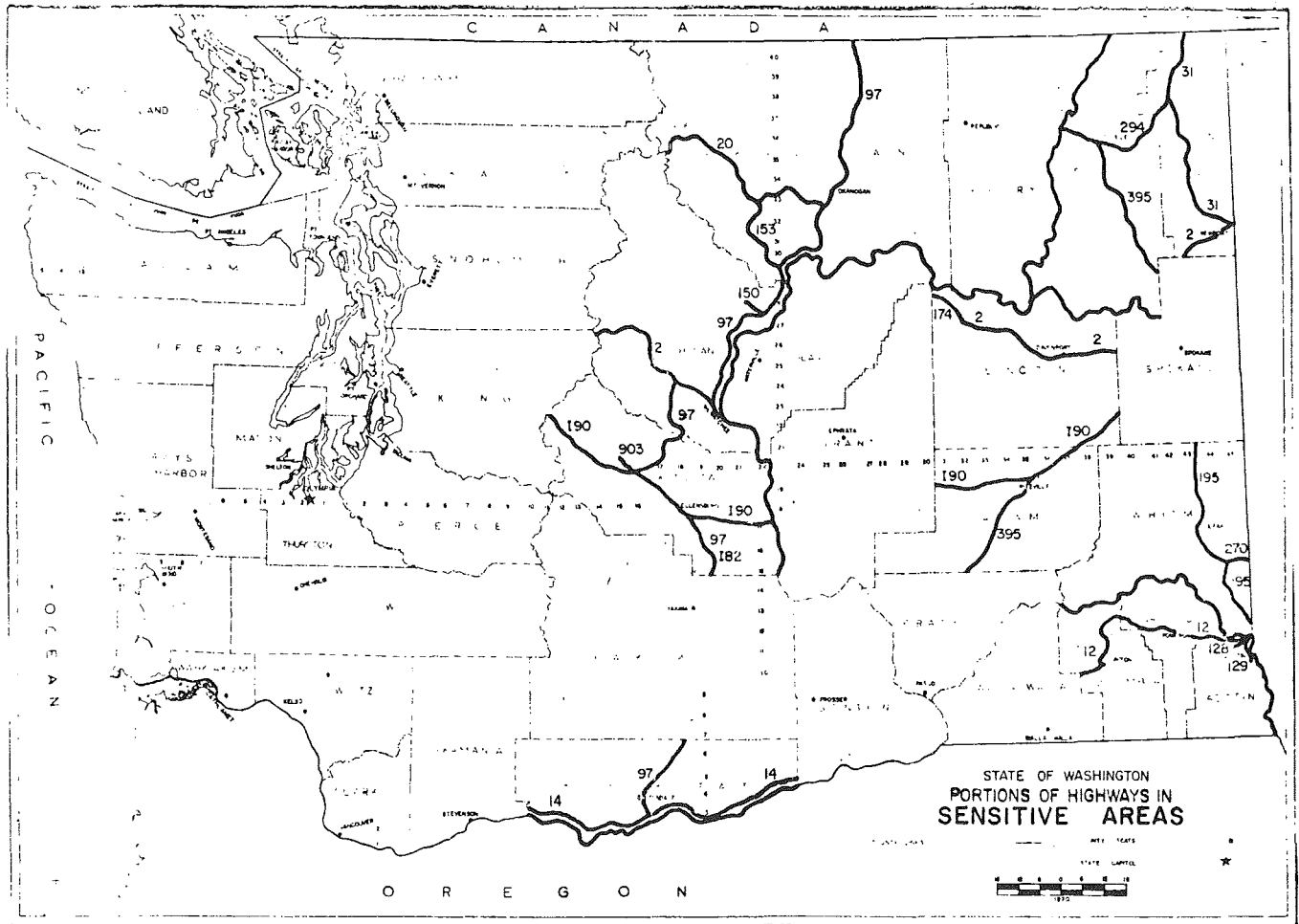
(1) Wigwam burners.

(a) All wigwam burners shall meet all the provisions of WAC 18-04-040. Wigwam burners will be considered to be in compliance with WAC 18-04-040(1) if they meet the requirements contained therein except during a startup period not to exceed 30 minutes in any eight consecutive hours.

(b) All wigwam burners shall apply best practicable technology in order to reduce emissions to the lowest possible level. [Order 72-23, § 18-06-050, filed 11/22/72.]

WAC 18-06-900 Appendix A--Map.

APPENDIX A



[Order 72-23, Appendix A (codified as WAC 18-06-900), filed 11/22/72.]

Chapter 18-20 WAC
ESTABLISHING REQUIREMENTS FOR THE
RECEIPT OF STATE FINANCIAL AID

WAC

- 18-20-010 Standards of purpose and applicability.
- 18-20-020 Definitions.
- 18-20-030 Limitations.
- 18-20-040 Applications.
- 18-20-050 Workable program.
- 18-20-060 Grant conditions.
- 18-20-070 Payments.
- 18-20-080 Changes, amendments and supplemental state financial aid.
- 18-20-090 Termination.
- 18-20-100 Federal grants.

WAC 18-20-010 Standards of purpose and applicability. These rules and regulations are enacted under the provisions of the 1969 amendments to the Washington Clean Air Act (RCW 70.94.143, chapter 168, section 18, Laws of 1969 ex. sess., and RCW 70.94.385, section

37, chapter 168, Laws of 1969 ex. sess.) to establish standard of eligibility for the granting of state financial aid to applicant air pollution control agencies. [Order 7, § 18-20-010, filed 6/18/69; Regulation 18-20-010, filed 1/3/68.]

WAC 18-20-020 Definitions. (1) "State board" means the state air pollution control board.

(2) "Air pollution control agency" means any activated air pollution control authority.

(3) "Applicant" means an air pollution control agency applying for state financial aid under the provisions of chapter 70.94 RCW.

(4) "Grantee" means an applicant for whom state financial aid has been approved by the state board.

(5) "Locally funded portion" or "local funds" means the funds provided to the applicant agency from sources available to it under chapter 70.94 RCW exclusive of state financial aid or federal funds designated specifically for air pollution.

(6) "Workable program" means a comprehensive statement of objectives for the prevention and control of air pollution and the existing and proposed measures to achieve these objectives as described in WAC 18-20-050.

(7) "Payment ratio" means the ratio of the amount of approved state financial aid to the local funds provided by the grantee. [Order 7, § 18-20-020, filed 6/18/69; Regulation 18-20-020, filed 1/3/68.]

WAC 18-20-030 Limitations. State financial aid shall be granted to air pollution control agencies qualifying under these regulations subject to the following limitations:

(1) State financial aid shall not exceed an amount equal to fifty percent of the locally funded portion of the annual expenditures of such air pollution control agency in each of the first three years during which state financial aid is utilized by the agency and shall not exceed an amount equal to one hundred percent of the locally funded portion in each year thereafter.

(2) The state board may limit the amount of financial aid available to a grantee when it becomes necessary due to the lack of sufficient funds available for distribution to meet the needs of all qualified grantees throughout the state.

(3) The state board may limit the amount of financial aid to less than the amount for which the applicant applies when the state board determines that proposed items of expenditure are not consistent with air pollution control program needs in the applicant's area of jurisdiction, or are not in the best interests of a coordinated statewide air pollution control program, or where such items of expenditure duplicate the responsibilities and activities of the state board. [Order 7, § 18-20-030, filed 6/18/69; Regulation 18-20-030, filed 1/3/68.]

WAC 18-20-040 Applications. Applications for state financial aid shall be prepared and submitted on forms specified by the board under the following conditions:

(1) Applications shall be filed with the executive director at least fourteen days prior to presentation to the board at a regular or special meeting. The board shall take action as to the disposition of an application within 65 days of its first presentation to the board. Applications shall be approved, denied, or deferred: *Provided*, That where action is deferred the applicant shall be advised of the reasons for such deferral and action shall be taken within a reasonable time.

(2) Applications must contain a statement of need for air pollution prevention and control in the applicant's jurisdiction.

(3) The applicant must describe a workable program and its objectives together with a description of the existing or proposed organization and operational elements through which the program objectives will be attained, together with a proposed timetable of accomplishment. Program goals and proposed budgets shall be included for at least two years beyond the proposed grant period.

(4) The application shall contain the budget of the agency showing all anticipated revenue and sources of revenue, including requested state financial aid, and shall show proposed expenditures covering salaries, equipment and accessories, expendable supplies, travel, and such other information as may be deemed necessary by the board.

(5) Any air pollution control activity conducted by the applicant, agency or constituent local governments during the twelve-month period immediately prior to the proposed grant period shall be described in the application, including funds budgeted and expended.

(6) It shall be the policy of the state board in reviewing applications for state financial aid and in administering such financial aid to take into consideration the following factors:

(a) The implementation of coordinated statewide air pollution prevention and control.

(b) The responsibilities of the state board with respect to its jurisdiction over any areas or type of air contaminant sources and for monitoring the movement of air contaminants throughout the state.

(c) The needs and financial capability of the air pollution control authorities in the various areas of the state and the relative effectiveness of the authorities.

(d) The capability and reasonable potential of the authorities to perform.

(7) The state board will, from time to time, determine or estimate the amount of state financial aid that will be available and advise the applicants, or potential applicants, as to the availability of such aid or supplemental aid. [Regulation 18-20-040, filed 1/3/68.]

WAC 18-20-050 Workable program. The applicant must provide sufficient information to show that its workable program is designed to provide for effective prevention and control of air pollution through an orderly progression of development, establishment, and improvement of air pollution control programs.

(1) The initial activity of an applicant shall be the development of a plan designed to provide an evaluation of existing and potential air pollution within the jurisdiction of the applicant, including a general inventory of the types of air contaminant sources and their relative contribution to the air pollution problem; to provide for the initiation of air quality surveillance appropriate to the air contaminant sources over which the applicant will have jurisdiction; and to provide for the development of regulations appropriate to the existing air contaminant sources or those which may be reasonably anticipated.

(2) The establishment and improvement of air pollution control programs which constitute the operating control activity of an applicant, shall be oriented to attaining compliance with requirements and regulations of the applicant with respect to air contaminant sources under its jurisdiction.

(3) Sampling and monitoring programs shall be oriented to surveillance for control purposes with respect to

those air contaminant sources under the applicant's jurisdiction, except as may be requested by the state board to supplement the statewide monitoring program.

(4) Budget for personnel, equipment and other operating expenses must be adequate to carry out the program during the grant period for which state financial aid is requested. Total funding from all sources shall provide, as a minimum, for the equivalent of one full time person: *Provided*, That the state board may approve the sharing of personnel with another agency, the utilization of part time staff, or persons under contract when these methods can be demonstrated as an effective means of carrying out the program and the purposes of the Washington Clean Air Act.

(5) The locally funded portion of the annual operating cost, budgeted and expended in any grant period for which application is made for state financial aid, shall not be less than the locally funded annual expenditure for air pollution control during the twelve-months' period immediately preceding the proposed grant period, unless it can be demonstrated by the applicant that there were necessary nonrecurring expenditures in the previous period or that the program objectives and the purposes of the Washington Clean Air Act can reasonably be met with a reduced expenditure. [Regulation 18-20-050, filed 1/3/68.]

WAC 18-20-060 Grant conditions. (1) No grant of state funds shall be made to any grantee for a period in excess of twelve months.

(2) Any state financial aid granted shall be used solely for carrying out the program outlined in the approved application or approved amendment as provided in section WAC 18-20-040 and 18-20-080.

(3) The grantee shall provide for and maintain such accounting, budgetary, and other fiscal procedures so as to assure the proper and efficient administration of funds. The fiscal records shall be such as to reflect currently the receipt and disposition of all funds including state financial aid. Such records and documents pertinent to the receipt and disposition of funds shall be kept available for review and audit.

(4) The grantee shall submit quarterly financial and progress reports to the state board. [Order 7, § 18-20-060, filed 6/18/69; Regulation 18-20-060, filed 1/3/68.]

WAC 18-20-070 Payments. (1) "Payment period" means the period of time for which money for state financial aid is paid to the grantee upon receipt and approval by the state department of health of a properly executed voucher.

(2) Grantees shall initiate requests for payment of state financial aid for the appropriate payment period utilizing properly executed vouchers furnished by the state department of health. The voucher shall state the requested amount of state financial aid and the expenditure of local funds during the payment period. Local

funds expended for any item may be shown as the appropriate portion of the total expenditure when the expenditure properly includes the use of, or anticipates, reimbursement with federal or state grant funds.

(3) Upon approval of the voucher by the executive director and the state department of health, payment for the appropriate payment period shall be authorized.

(4) Payments of state financial aid shall be made by way of reimbursement and shall be in an amount determined by multiplying the payment ratio by the amount of local funds expended by the grantee during the payment period. Such payments may be increased or decreased by the amount that prior payments of state financial aid exceed or are less than the appropriate state share of the costs as may have been determined by subsequent review of audit.

(5) Final payment of state financial aid shall be based upon approved vouchers properly reflecting the payment ratio applied to the entire grant period.

(6) Vouchers for the final payment period during a grant period ending in an odd-numbered year must be submitted by the grantee by the 12th day of July of that year.

(7) The executive director may withhold approval of the vouchers submitted by the grantee if he finds that said grantee has failed to comply with any of the grant conditions or any other requirement or condition imposed by these regulations or chapter 70.94 RCW, for a period not to exceed thirty days. If at the end of such period the matter has not been resolved and the executive director has not approved said vouchers, the grantee may request an administrative hearing before the state board pursuant to the provisions of chapter 18-08 WAC. [Regulation 18-20-070, filed 1/3/68.]

WAC 18-20-080 Changes, amendments and supplemental state financial aid. (1) Changes in the workable program of a grantee during the grant period which would not substantially affect the workable program, nor increase the total cost to the state, and which are for the purpose of improving the operation and performance of the workable plan, may be made: *Provided*, That written approval in advance is obtained from the executive director of the state board.

(2) Changes in the workable program of a grantee during the grant period which would significantly alter the workable program shall not be made until the grantee has submitted to, and the state board has approved, an amendment to the original application.

(3) Application for supplemental state financial aid may be made by the grantee when notice is given by the state board that such supplemental funds have become available. The application shall be made as an amendment to the previously approved workable program of the grantee and shall include proposed additions in or improvements to the workable program and proposed changes in the budget including the additional local funds to be provided. The state board may approve additional financial aid to the extent such funds become available having considered the needs of all grantees

throughout the state. [Order 7, § 18-20-080, filed 6/18/69; Regulation 18-20-080, filed 1/3/68.]

WAC 18-20-090 Termination. The state board may terminate state financial aid, in whole or in part, to any grantee when it finds, after reasonable notice and opportunity for hearing under the provisions of chapter 18-08 WAC that the grantee has failed to comply with any of the conditions of the approved application or amendments thereto or any of the requirements or conditions imposed by or pursuant to these regulations or the Washington Clean Air Act.

Upon the effective date of termination, the grantee shall promptly render an accounting and final statement as would similarly be required for request for payment of state financial aid under WAC 18-20-070. The state board may authorize payment of the state's share of the amount required to settle at minimum cost any contractual obligations properly incurred by the grantee prior to the date of termination, if the state board finds that the grantee acted in good faith in incurring the obligations. [Regulation 18-20-090, filed 1/3/68.]

WAC 18-20-100 Federal grants. The standards and requirements of these regulations establishing the eligibility of air pollution control authorities for state financial aid shall be equally applicable to the applications of such agencies for federal grants under the provisions of the 1969 amendments to the Washington Clean Air Act (chapter 70.94 RCW, section 18, chapter 168, Laws of 1969 ex. sess.). [Order 7, § 18-20-100, filed 6/18/69; Regulation 18-20-100, filed 1/3/68.]

Chapter 18-24 WAC

ASSUMPTION OF JURISDICTION OVER MOTOR VEHICLES--EMISSION CONTROL SYSTEMS

WAC

18-24-010	Statement of purpose and applicability.
18-24-020	Definitions.
18-24-030	Assumption of jurisdiction.
18-24-040	Standards of motor vehicles.

DISPOSITION OF SECTIONS FORMERLY CODIFIED IN THIS CHAPTER

18-24-050	Effective date. [Order 74-8, § 18-24-050, filed 5/17/74, effective 8/15/74; Order, § 18-24-050, filed 5/7/68.] Repealed by Order DE 75-13, filed 6/18/75.
18-24-060	Delegation. [Order 74-8, § 18-24-060, filed 5/17/74, effective 8/15/74; Order 73-12, § 18-24-060, filed 10/10/73.] Repealed by Order DE 75-13, filed 6/18/75.
18-24-070	Applicability of complex source provisions. [Order 74-8, § 18-24-070, filed 5/17/74, effective 8/15/74; Order 73-12, § 18-24-070, filed 10/10/73.] Repealed by Order DE 75-13, filed 6/18/75.
18-24-080	Fee. [Order 73-12, § 18-24-080, filed 10/10/73.] Repealed by Order DE 75-13, filed 6/18/75.
18-24-090	Review of proposed construction or modification. [Order 74-8, § 18-24-090, filed 5/17/74, effective 8/15/74; Order 73-12, § 18-24-090, filed 10/10/73.] Repealed by Order DE 75-13, filed 6/18/75.

18-24-100	Duration of approval orders. [Order 74-8, § 18-24-100, filed 5/17/74, effective 8/15/74; Order 73-12, § 18-24-100, filed 10/10/73.] Repealed by Order DE 75-13, filed 6/18/75.
18-24-110	General responsibilities. [Order 74-8, § 18-24-110, filed 5/17/74, effective 8/15/74; Order 73-12, § 18-24-110, filed 10/10/73.] Repealed by Order DE 75-13, filed 6/18/75.
18-24-120	Information in environmental impact statements. [Order 73-12, § 18-24-120, filed 10/10/73.] Repealed by Order DE 75-13, filed 6/18/75.
18-24-130	Sanctions. [Order 73-12, § 18-24-130, filed 10/10/73.] Repealed by Order DE 75-13, filed 6/18/75.

WAC 18-24-010 Statement of purpose and applicability. These regulations are enacted under the provisions of the Washington Clean Air Act to provide for the assumption of jurisdiction by the department of ecology over motor vehicles as defined herein, for the purpose of preventing and controlling air contaminant emissions resulting from the operation of motor vehicles. [Order 73-12, § 18-24-010, filed 10/10/73; Order, § 18-24-010, filed 5/7/68.]

WAC 18-24-020 Definitions. (1) "Department" means the department of ecology.

(2) "Motor vehicle" means any operating vehicle or one capable of being operated which has its own self-contained sources of motive power, is designed for the transportation of people or property, and is of the type for which a license is required for operation on a highway. [Order DE 75-13, § 18-24-020, filed 6/18/75; Order 74-8, § 18-24-020, filed 5/17/74, effective 8/15/74; Order 73-12, § 18-24-020, filed 10/10/73; Order, § 18-24-020, filed 5/7/68.]

WAC 18-24-030 Assumption of jurisdiction. The department finding that the prevention and control of air pollution from motor vehicles should be regulated on a state-wide basis, hereby assumes jurisdiction over motor vehicles for the purpose of controlling air contaminant emissions from the operation of such motor vehicles. [Order DE 75-13, § 18-24-030, filed 6/18/75; Order 73-12, § 18-24-030, filed 10/10/73; Order, § 18-24-030, filed 5/7/68.]

WAC 18-24-040 Standards of motor vehicles. No person shall remove or render inoperable any devices or components of any systems on a motor vehicle installed as a requirement of federal law or regulation in the purpose of controlling air contaminant emissions, subject to the following conditions:

(1) The components or parts of emission control systems on motor vehicles may be disassembled or reassembled for the purpose of repair and maintenance in proper working order.

(2) Components and parts of emission control systems may be removed and replaced with like components and parts intended by the manufacturer for such replacement.

(3) The provisions of this section (WAC 18-24-040) shall not apply to salvage operations on wrecked motor vehicles when the engine is so damaged that it will not

be used again for the purpose of powering a motor vehicle on a highway. [Order, § 18-24-040, filed 5/7/68.]

Chapter 18-28 WAC

INFORMATIONAL REPORTING BY THERMAL POWER PLANTS--ALUMINUM PLANTS-- CHEMICAL WOOD PULP MILLS

WAC

18-28-010	Statement of purpose and applicability.
18-28-020	Definitions.
18-28-030	Submission of information.
18-28-040	Interim procedure.
18-28-050	Confidential information.

WAC 18-28-010 Statement of purpose and applicability. These rules are enacted under the provisions of the "Washington Clean Air Act" to provide a basis for the obtaining and compiling of necessary information to enable the state air pollution control board to establish standards for certain types or classes of air contaminant sources for the purpose of preventing and controlling air pollution and prescribing interim procedures with respect to new construction or major alteration of certain types or classes of air contaminant sources. [Order 4, § 18-28-010, filed 6/6/68.]

WAC 18-28-020 Definitions. (1) "State board" means the state air pollution control board.

(2) "Thermal power reduction" means the production of electrical energy through the use of any fuel, including nuclear materials, for distribution through private and public power agencies for public use.

(3) "Chemical wood pulping" means the production of pulp by digestion of wood with solutions of various chemicals to obtain separation of lignin from cellulose wood fibers.

(4) "Primary aluminum reduction" means the production of aluminum from alumina in electrolytic cells. [Order 4, § 18-28-020, filed 6/6/68.]

WAC 18-28-030 Submission of information. The owner, manager, or other person operating or responsible for operating chemical wood pulping mills and primary aluminum reduction plants, shall submit information to the state board under the following conditions:

(1) Information shall be on forms provided by, or in a manner acceptable to, the executive director of the state board.

(2) Information shall be submitted within ninety days after the effective date of this regulation for existing installations.

(3) The information shall include:

(a) Ownership, address, location, and name of manager of the plant.

(b) A description of the primary process and ancillary or complementary processes at the same location together with a description of air contaminant sources.

(c) Description and quantities of raw materials used and products produced.

(d) A description of available data on the emission of air contaminants as to kind and quantity from each source, size and height of emission points, the concentration of air contaminants in the carrying gas stream, and a description of the method of measurement or estimation used in developing the data.

(e) A description of available data obtained through measurements of air contaminants in the ambient air, vegetation or other environmental media, as they relate to the operation of the air contaminant source(s), and a description of the measurement methods used or proposed.

(f) A description of the systems, methods, and equipment used for controlling or preventing the release of air contaminants and available data on efficiency of air contaminant removal.

(4) The available data as described under subsection (3)(d), (e), and (f) above shall be furnished to the executive director of the state board when such data is requested by him. [Order 4, § 18-28-030, filed 6/6/68.]

WAC 18-28-040 Interim procedure. (1) Until such time as the state board adopts regulations setting forth standards and requiring the submission of plans, specifications and other pertinent information as a condition precedent to the construction, installation, establishment, or major alteration of air contaminant sources, the person operating or responsible for the operation of chemical wood pulping mills, primary aluminum reduction plants, and thermal power plants shall submit to the state board information equivalent to that required under WAC 18-28-030 for the purpose of review and consultation as to the adequacy of the proposed control measures and conformance with good industrial practice.

(2) The required information shall be submitted not later than sixty days prior to start of construction. [Order 4, § 18-28-040, filed 6/6/68.]

WAC 18-28-050 Confidential information. Information submitted to the state board in accordance with this regulation shall be handled as provided in the Washington Clean Air Act, where applicable, with respect to confidential information. [Order 4, § 18-28-050, filed 6/6/68.]

Chapter 18-40 WAC

SUSPENDED PARTICULATE

WAC

18-40-010	Preamble.
18-40-020	Definitions.
18-40-030	Air quality standard.
18-40-040	Air quality objective.
18-40-050	Method of measurement.
18-40-060	Reporting of data.
18-40-990	Appendix I—High volume sampling schedule.
18-40-991	Appendix II—Method of determination and reporting.

WAC 18-40-010 Preamble. In the interest of the people of the state of Washington, it is the objective of the department of ecology to obtain and maintain the

cleanest air possible, consistent with the highest and best practicable control technology.

In areas where existing concentrations are lower than concentrations allowed by the standards enumerated below, degradation of the atmosphere should be minimized. The highest and best practicable control technology should be applied to all sources unless it is determined by the responsible air pollution control agency that application of lesser technology is justified. Air quality standards should not be construed to encourage degradation of existing air quality. [Order 72-7, § 18-40-010, filed 1/24/72, 2/2/72; Order 10, § 18-40-010, filed 5/18/70.]

WAC 18-40-020 Definitions. (1) Ambient air – The surrounding outside air.

(2) Air quality objective – The concentration and exposure time of a contaminant or multiple contaminants in the ambient air below which, according to available knowledge, undesirable effects will not occur.

(3) Air quality standard – An established concentration, exposure time, and frequency of occurrence of a contaminant or multiple contaminants in the ambient air which shall not be exceeded.

(4) Primary air mass station suspended particulate (PAMS-SP) – A type of station designed to measure contamination in an air mass, and representing a relatively broad area. The sampling site shall be representative of the general area concerned. The sampler shall be a minimum of fifteen feet and a maximum of one hundred fifty feet above ground level. Actual elevation will vary, depending upon surrounding buildings and terrain. The filter shall be placed a minimum of three feet above a supporting rooftop.

(5) Particle – A small discrete mass of solid or liquid matter. (For air pollution usage, sizes generally range from submicron to over two thousand microns.)

(6) Suspended particulates – Those airborne particulates, collected on eight inch by ten inch sheets of flash-fired glass fiber filter web of specified collection efficiency, using a high-volume air sampler or other particulate collection equipment equivalent to the high volume sampler and glass fiber filter. [Order 72-7, § 18-40-020, filed 1/24/72, 2/2/72; Order 10, § 18-40-020, filed 5/18/70.]

WAC 18-40-030 Air quality standard. Suspended particulate in the ambient air shall not exceed the standards enumerated below at the conditions stated.

(1) The suspended particulate concentration measured at any primary air mass station shall not exceed:

(a) Sixty micrograms per cubic meter of air as an annual geometric mean.

(b) 150 micrograms per cubic meter of air – maximum 24-hour concentration not to be exceeded more than once per year.

(2) In recognition of natural dust loading in some areas of the state, the following exceptions shall apply to areas east of the Cascade Mountain crest:

(a) If concentrations, measured at approved background locations, exceed thirty micrograms per cubic

meter of air on individual sample days, the concentration of suspended particulate matter measured at any primary air mass station shall not exceed 120 micrograms per cubic meter of air plus background as a maximum 24-hour concentration not to be exceeded more than once per year.

(b) If concentrations, measured at approved background locations, exceed twenty micrograms per cubic meter of air as an annual geometric mean, the concentration of suspended particulate matter at any primary air mass station shall not exceed forty micrograms per cubic meter of air, plus background, as an annual geometric mean.

(3) Sampling shall be conducted on a schedule approved by, and on file with, the department of ecology. Only those samples taken in compliance with an approved schedule may be used to determine compliance with the air quality standards. A maximum of two makeup samples may be taken each month to meet the required sample frequency. (A typical sample schedule is attached as Appendix I [WAC 18-40-990].) [Order 72-7, § 18-40-030, filed 1/24/72, 2/2/72; Order 10, § 18-40-030, filed 5/18/70.]

WAC 18-40-040 Air quality objective. In recognition of the need for continuing improvement of the quality of the air resource, it is the intent of the department of ecology to work toward achievement of the following objective for suspended particulate: Concentrations measured at primary air mass stations shall not exceed thirty micrograms per cubic meter of air for more than fifty percent of the samples collected in any calendar year. [Order 72-7, § 18-40-040, filed 1/24/72, 2/2/72; Order 10, § 18-40-040, filed 5/18/70.]

WAC 18-40-050 Method of measurement. Sampling and analysis for suspended particulates shall be conducted according to methods approved by and on file with, the department of ecology. Methods equivalent in sensitivity, accuracy, reproducibility, and selectivity to the approved standard method may be used after approval by the department of ecology. [Order 72-7, § 18-40-050, filed 1/24/72, 2/2/72; Order 10, § 18-40-050, filed 5/18/70.]

WAC 18-40-060 Reporting of data. (1) Local and regional agencies. Local and regional air pollution control agencies sampling for suspended particulates shall notify the state department of ecology of all results exceeding the adopted standards. Notification shall be made quarterly. A semi-annual summary of all samples exceeding the standards shall be submitted by February 1 for the six-month period ending December 31 and by August 1 for the six-month period ending June 30. Quarterly data shall include:

(a) Location of sampler.

(b) Time span involved (day or year).

(c) Standard exceeded (daily, annual).

(d) Concentrations recorded. All samples greater than 150 mg/m³ shall be reported.

(e) The geometric mean if the annual standard is exceeded (first quarter report only for previous calendar year).

(2) If particulate values in excess of the standards are detected by the department of ecology, the appropriate local agency shall be notified quarterly after validation of the results. This notification shall include:

(a) Standard exceeded.

(b) Location.

(c) Time or time span involved.

(d) Concentrations recorded. [Order DE 73-1, § 18-40-060, filed 2/9/73; Order 72-7, § 18-40-060, filed 1/24/72, 2/2/72; Order 10, § 18-40-060, filed 5/18/70.]

WAC 18-40-990 Appendix I--High volume sampling schedule.

APPENDIX I

High Volume Sampling Schedule

January, 1970

Saturday	3
Wednesday	7
Sunday	11
Thursday	15
Monday	19
Friday	23
Tuesday	27
Saturday	31

February, 1970

Wednesday	4
Sunday	8
Thursday	12
Monday	16
Friday	20
Tuesday	24
Saturday	28

March, 1970

Wednesday	4
Sunday	8
Thursday	12
Monday	16
Friday	20
Tuesday	24
Saturday	28

July, 1970

Thursday	2
Monday	6
Friday	10
Tuesday	14
Saturday	18
Wednesday	22
Sunday	26
Thursday	30

August, 1970

Monday	3
Friday	7
Tuesday	11
Saturday	15
Wednesday	19
Sunday	23
Thursday	27
Monday	31

September, 1970

Friday	4
Tuesday	8
Saturday	12
Wednesday	16
Sunday	20
Thursday	24
Monday	28

April, 1970

Wednesday	1
Sunday	5
Thursday	9
Monday	13
Friday	17
Tuesday	21
Saturday	25
Wednesday	29

May, 1970

Sunday	3
Thursday	7
Monday	11
Friday	15
Tuesday	19
Saturday	23
Wednesday	27
Sunday	31

June, 1970

Thursday	4
Monday	8
Friday	12
Tuesday	16
Saturday	20
Wednesday	24
Sunday	28

October, 1970

Friday	2
Tuesday	6
Saturday	10
Wednesday	14
Sunday	18
Thursday	22
Monday	26
Friday	30

November, 1970

Tuesday	3
Saturday	7
Wednesday	11
Sunday	15
Thursday	19
Monday	23
Friday	27

December, 1970

Tuesday	1
Saturday	5
Wednesday	9
Sunday	13
Thursday	17
Monday	21
Friday	25
Tuesday	29

Samples are to be run from midnight to midnight on the dates indicated.

[Order 10, Appendix I (codified as WAC 18-40-990), filed 5/18/70.]

WAC 18-40-991 Appendix II--Method of determination and reporting.

APPENDIX II

Method of Determination and Reporting

[Bibliographic references noted in the text of the following appendix were not filed with the appendix]

GENERAL:

Samples of air-borne particulates are collected on 8" x 10" tared sheets of flash-fired glass fiber filter web for 24 ± 2 hours, using a high volume air sampler, and weighed to determine total air particulate collected on the filter.

APPARATUS:

1. High volume air sampler, with frame adapter for 8" x 10" sheets of filter web. [References] (2, 3, 4)
2. Housing which allows for vertical positioning of the air sampler and provides a minimum of 65 square inches and a maximum of 100 square inches in area to permit a

uniform flow of ambient air into space above the filter. [References] (2, 3, 4)

3. Flowmeter calibrated in cubic feet per minute. A constant flow regulator or continuous flow recorder is recommended if flow rate during sampling period decreases more than 10% due to particulate loading. [References] (2, 4, 5)

4. Timer switch, 7 day.

5. Elapsed time indicators (recommended).

6. Analytical balance, capable of weighing to 1.0 mg, and a weighing chamber large enough to accommodate an open full-sized 8" x 10" filter web. If the balance is to be used as a multipurpose balance, it is recommended it be capable of weighing to 0.1 mg and have a capacity of 160 to 200 grams. [References] (1, 4, 7)

7. Large desiccating and/or humidifying chamber, such as a converted oven, refrigerator or incubator with trays for holding dessicant and racks for holding filters. [References] (1, 4, 7)

8. A constant temperature (20–24°C) and humidity (less than 50% r.h.) balance room for equilibrating and weighing samples. If a balance room is not available, it is recommended that a humidity chamber be placed immediately adjacent to the balance in a room held at constant temperature (20–24°C). Saturated solutions of sodium nitrite (NaNO_2) (50% r.h. at 21°C) or calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) (46% r.h. at 23°C) may be used to provide constant relative humidity in the chamber. [References] (2, 4, 6, 7)

9. Flash-fired glass fiber filter web, 8" x 10". [References] (2, 4, 6)

10. A 6-wheel numbering device.

11. Paper supplies:

(a) Manila tag cards, 9–1/2" x 11".

(b) Envelopes, 5" x 11–1/2".

(c) File folder, 9" x 12".

PRELIMINARY FILTER PREPARATION:

1. Each filter will be screened over a light table for "pin holes" and other visible defects. The filter will be discarded if defects are found.

2. The last two filter sheets from each group of 25 of a specific manufacturer's lot will be analyzed as blanks. [References] (2, 4)

3. Number the filter web on two diagonally opposite corners, one on front and one on reverse, and outside the area to be exposed, using the numbering device with gentle pressure. A series of filters assigned at one time to one location should be numbered consecutively, weighed and placed on top of one another in a folder with manila tag cards separating them. [References] (1, 4)

4. Weigh the 8" x 10" filter, full size, to the nearest milligram after a minimum 16 hour equilibration in an air conditioned room or chamber at a temperature of 20–24°C and a relative humidity below 50%. [References] (2, 4, 6, 7)

SAMPLING PROCEDURE: For general metals sampler; procedure with minor modifications is applicable to other acceptable sampling devices. Care should be taken while handling filter to prevent damage or contamination.

1. Secure the high volume air sampler in a vertical position in a shelter at the sampling site. The sampler should be allowed to run to seat the brushes and insure a representative flow rate. It is helpful to position the shelter so that the lid provides a windbreak during installation of the filter.

2. Set the time switch for the desired sampling period.

3. Remove the frame from the filter holder and position the prenumbered and weighed filter with rough side out, making certain the filter is centered on its holder. [References] (1, 2, 4)

4. Turn the sampler on and then replace the filter holder. Secure the wing nuts diagonally and finger tight so the frame holder is not put in a bind which may cause air leaks. Close the roof of the shelter. [References] (2, 4)

5. Allow the sampler to run for several minutes, then connect the calibrated flowmeter to the sampler and take a flow reading with the flowmeter in a vertical position. Read the top of the flowmeter ball estimating to the nearest whole number. Make a record of the time the time switch will start and the flowmeter reading. [References] (2, 4)

6. Turn the sampler off, remove the flowmeter and make sure the clock and time switch are operational.

7. After a 24-hour sample has been obtained, measure the air flow as in Step 5 above. Turn the sampler on for several minutes before taking the reading. Record the stop time and the final flowmeter reading.

8. Stop the motor, remove the filter, fold once lengthwise with the dirty side in, place in a folded manila tag card and finally into an envelope. Return the packaged filter to the laboratory.

ANALYSIS:

1. Equilibrate the sample at 20–24°C and 50%, or less, relative humidity in an air conditioned room or humidity chamber for a minimum of 16 hours. If it is necessary to remove excess moisture from the filter, dry it in a desiccating chamber at room temperature for 24 hours prior to equilibration. Weigh the filter sample to the nearest milligram. [References] (1, 2, 4, 6, 7)

2. For further analysis, aliquot the filter sample across the 8" dimension using a plastic template designed for the purpose. [References] (2, 3)

a. Organic materials; half the sample is used for extraction.

b. Nonmetals; a 3/4" wide strip representing 8% of the sample is used for water extraction, nitrate, and sulfate determinations.

c. Metals; a 2" wide strip representing 22% of the sample is used.

3. Water soluble constituents are extracted by placing the 8% aliquot filter strip in a 125 ml boiling flask containing 50 ml of distilled water. The filter is refluxed for a minimum of 90 minutes, cooled and filtered through Whatman #1, or equivalent, paper. Repeat the extraction with 10–15 ml of water for a few minutes without a condenser. Pass the additional extract through the same Whatman filter. Wash the boiling flask and sample filter to insure good quantitative transfer. [References] (2, 3, 4, 10)

a. Sulfates are determined by the Sulfa Ver Turbidimetric or Turbidimetric Barium Sulfate Method.

b. Nitrates are determined by the 2, 4 Xylenol Method. [References] (2, 3, 4, 10)

4. Organic constituents are extracted with benzene. [References] (2, 3, 4, 10)

a. Fold the sample into a small bundle such that the particulate matter is entirely enclosed within the filter. Tie the bundle with copper wire and place in a 125 ml Soxhlet extraction apparatus.

b. Add about 80 ml of redistilled reagent grade benzene and extract for a minimum of 6 hours. Concentrate the extract to approximately 5 ml and quantitatively transfer through a medium porosity fritted disc funnel into a pre-weighed vial. Rinse the extraction flask three times, using about 5 ml of benzene in each rinse. Transfer the wash through the funnel and into the vial.

c. Evaporate the benzene in an explosion proof, ventilated oven at 62°C.

d. Transfer the vial to a constant humidity chamber, equilibrate overnight and weigh to the nearest milligram.

CALCULATIONS - TOTAL WEIGHT:

1. Correct field flowmeter readings to true air flow from calibration curve.

2. Calculate the average air flow (cfm):

$$\frac{\text{start flow} + \text{stop flow}}{2}$$

3. Calculate the total hours of sampling time: Stop time - start time.

4. Calculate the total air flow: Average air flow (cfm) x total hours sample time (to nearest tenth of one hour) x 1.7 + total air volume (to the nearest whole number in cubic meters (m³)).

5. Report as micrograms per cubic meter (μg/M³) to the nearest microgram.

$$\frac{\text{grams of collected material (nearest 1.0 mg)} \times 10^6}{\text{air volume (M}^3)} = \mu\text{g/M}^3$$

[References] (1, 4)

SAMPLER LOCATION:

1. The sampler may be located at a primary air mass station or at a primary ground level monitoring station adhering to the requirements of these locations.

2. Other stations, designated as special stations, shall be evaluated to be representative of the pollution information desired. The placement of the sampling unit shall minimize biased results from eddy currents, etc., to the fullest extent possible. The filter should be approximately 3 to 4 feet above mounting level. [References] (2, 9)

3. A sampling site report form shall be completed for each site.

SAMPLING SCHEDULE:

1. All samples shall be taken on a midnight to midnight schedule. [Reference] (4)

2. The number of samples to be taken shall be within consideration of limits of:

a. Approximately 250 to 300 days on a random schedule per year could be required to produce accurate estimates of monthly means (i.e. ± 20%).

b. Twenty-six bi-weekly random samples are sufficient to determine a site's annual mean (± 20% of the true mean). [References] (11, 12, 13)

3. Determination of seasonal and monthly estimates of means is best accomplished by sampling on a systematic basis; example, every fourth day. Any bias introduced into the selection of the starting date may be removed by selecting the starting date for the first week of sampling from a table of random numbers. [Reference] (11)

4. Sampling schedules on file with the Washington state air pollution control board and Oregon state sanitary authority require a minimum number of samples and allow make-up sampling as follows: A minimum of 85 samples shall be collected in a calendar year and a minimum of seven samples shall be taken each calendar month. A maximum of two make-up samples may be taken each month. It is desirable, but not mandatory, that make-up samples be taken the same day of the week as the missed samples.

5. For a community sampling program all high-volume samplers should operate during the same time period to provide for comparison of the suspended particulate pollution within the area. [Reference] (11)

DATA RECORDING:

The type of data form utilized shall be compatible with the type of data processing used.

Weather observations shall be recorded with each sample if not available elsewhere. Record any unusual happenings which may affect sampling results.

DATA REPORTING:

1. All suspended particulate data obtained with the high-volume air sampler shall be reported in a micrograms per cubic meter.

2. Data reporting should relate to the effects that are caused by the contaminant and should reflect how the data relates to standards.

3. Total suspended particulate data shall be reported to the nearest whole number and shall include:

a. All sample results including dates of sampling and type of stations.

b. Minimum, maximum and median values.

c. Number of samples > 100 μg/M³ (PAMS, PGLMS ONLY).

CALIBRATION PROCEDURE:

GENERAL:

High volume samplers operated with regular use should be calibrated every six months and after each motor change. Calibration can be performed either in the field or laboratory using a National Air Sampling Network (NASN) type orifice calibration assembly.

EQUIPMENT:

1. National Air Sampling Network (NASN) type calibration orifice and calibration curve.
2. Manometer, fillings and tubing.
3. Flowmeter and small wrenches for adjustment.
4. Variable voltage transformer.
5. Graph paper.

PRECALIBRATION CHECKS:

- 163 1. Replace flowmeter tubing if dirty.
2. Clean or replace flowmeter. A soft pipe cleaner and Stoddard solvent is good for cleaning.
3. Check the system for leaks. (See leak test procedure under post calibration checks.)
4. If new brushes have been installed, run the sampler for 30 minutes to seat the brushes. (Leak check can be done at this time.)

CALIBRATION:

1. Remove filter head from sampler and install the calibration orifice. Make sure the joint is air tight.
2. Set up the manometer and attach the tubing from manometer to the pressure tap on the side of the calibration orifice.
3. Plug sampler into output plug of the variable voltage transformer.
4. Adjust the scaler on the manometer to zero.
5. Check all connections (electrical and tubing) and plug the variac into 120 VAC power line.
6. Adjust variable voltage transformer such that the manometer read the inches of water equivalent to 50 cfm as shown on the orifice calibration curve. Adjust the flowmeter to read 50 cfm by turning the orifice screw at the top of the flowmeter. If a constant flow regulator is to be used in the sampler, the manometer and flowmeter should be set at 35 cfm.
7. Tighten the lock nut and put a drop of sealant, i.e., Duco cement, to assure the setting is not changed. Re-check to assure a 50 cfm flow at the proper manometer setting. (35 cfm for constant flow regulator use)
8. Run a standard calibration from 15 to 65 cfm in intervals of 5 cfm, recording the inches of water at each interval.
9. Using the orifice calibration data draw a flow curve so that a best fit line is drawn through the points. On the ordinate of the graph, plot the true air flow as taken from the orifice data and on the abscissa, plot the flowmeter readings. The curve should approximate a 45° angle from 40 to 60 cfm (30 to 40 cfm for constant flow regulator). If not, all connections should be checked and another calibration run.

POST-CALIBRATION CHECKS:

1. Remove calibration orifice and return equipment to operational configuration.
2. Place an 8" x 10" piece of tag board into the filter holder and tighten the wing nuts.
3. Start the motor to check for leaks. If the flowmeter does not stay on zero a leak exists. Tighten the holder adaptor connection and retest. CAUTION! Do not leave the motor running with the tag board on the filter holder as they will damage the motor.
4. Remove tag board and replace with a clean filter.

5. Start the sampler, record the air flow through the clean filter (should not be greater than 65 cfm).
6. Information should be recorded on the calibration curve to include the following:
 - a. Sampler number
 - b. Date
 - c. Date of previous calibration
 - d. Clean air filter flow
 3. Flowmeter set — cfm
 - f. Calibrated by -----
 - g. Remarks
 - h. Pressure regulator number (if used).

[Order 10, Appendix II (codified as WAC 18-40-991), filed 5/18/70.]

Chapter 18-44 WAC PARTICLE FALLOUT

WAC

18-44-010	Preamble.
18-44-020	Definitions.
18-44-030	Air quality standard.
18-44-040	Air quality objective.
18-44-050	Method of measurement and analysis.
18-44-060	Reporting of data.
18-44-990	Appendix I—Collection and analysis of particle fallout.

WAC 18-44-010 Preamble. In the interest of the people of the state of Washington, it is the objective of the department of ecology to obtain and maintain the cleanest air possible, consistent with the highest and best practicable control technology.

In areas where existing concentrations are lower than concentrations allowed by the standards enumerated below, degradation of the atmosphere should be minimized. The highest and best practicable control technology should be applied to all sources unless it is determined by the responsible air pollution control agency that application of lesser technology is justified. Air quality standards should not be construed to encourage degradation of existing air quality. [Order 72-7, § 18-44-010, filed 1/24/72, 2/2/72; Order 11, § 18-44-010, filed 5/18/70.]

WAC 18-44-020 Definitions. (1) Air quality objective — The concentration and exposure time of a contaminant or multiple contaminants in the ambient air below which, according to available knowledge, undesirable effects will not occur.

(2) Air quality standard — An established concentration, exposure time, and frequency of occurrence of a contaminant or multiple contaminants in the ambient air which shall not be exceeded.

(3) Particle — A small discrete mass of solid or liquid matter. (For air pollution usage, sizes generally range from submicron to over two thousand microns.)

(4) Primary air mass station (PAMS-PFO) — A type of station designed to measure contamination in an air mass and representing a relatively broad area. The sampling site shall be representative of the general area

concerned. The jar opening shall be a minimum of fifteen feet and a maximum of one hundred fifty feet above ground level. Actual elevation should vary to prevent adverse exposure conditions caused by surrounding buildings and terrain. When mounting on rooftops, the minimum height of jar opening shall be at least five feet above the rooftop.

(5) Primary ground level monitoring station (PGLMS-PFO) – Stations designed to provide information on contaminant concentrations near the ground and provide data valid for the immediate area only. The sampler shall be six to fifteen feet above ground level with a desired optimum height of ten feet. The jar opening shall be at least five feet above the rooftop. The sampling site shall be representative of the immediate area.

(6) Special stations – Any station that does not meet the criteria or purpose of the standard stations is defined as a special station. [Order 72-7, § 18-44-020, filed 1/24/72, 2/2/72; Order 11, § 18-44-020, filed 5/18/70.]

WAC 18-44-030 Air quality standard. Particle fallout shall not exceed the standards enumerated below at the conditions stated.

(1) The particle fallout rate measured at a primary air mass station, ground level monitoring station or special station shall not exceed:

(a) Ten grams per square meter per month in an industrial area, or

(b) Five grams per square meter per month in an industrial area if visual observations show a presence of wood waste and the volatile fraction of the sample exceeds seventy percent.

(c) Five grams per square meter per month in residential and commercial areas.

(d) Three and one-half grams per square meter per month in residential and commercial areas if visual observations show the presence of wood waste and the volatile fraction of the sample exceeds seventy percent.

(2) In recognition of natural dust loading in some areas of the state, the following exceptions shall apply to areas east of the Cascade Mountain crest. If concentrations measured at approved background locations exceed three and one-half grams per square meter per month, the particle fallout rate measured at a primary air mass station, ground level monitoring station or special station, shall not exceed:

(a) Six and one-half grams per square meter per month plus background in an industrial area, or

(b) One and one-half grams per square meter per month plus background in residential and commercial areas.

The provisions of WAC 18-44-030(1)(b) and (1)(d) pertaining to wood waste shall continue to apply regardless of background. [Order 11, § 18-44-030, filed 5/18/70.]

WAC 18-44-040 Air quality objective. In recognition of the need for continuing improvement of the

quality of the air resource, it is the intent of the department of ecology to work toward the achievement of the following objective for particle fallout: The particle fallout rate shall not exceed two and a half grams per square meter per month. [Order 72-7, § 18-44-040, filed 1/24/72, 2/2/72; Order 11, § 18-44-040, filed 5/18/70.]

WAC 18-44-050 Method of measurement and analysis. Sampling and analysis for particle fallout shall be conducted according to methods approved by, and on file with, the department of ecology. Methods equivalent in sensitivity, accuracy, reproducibility and selectivity to the approved standard method may be used after approved by the department of ecology. [Order 72-7, § 18-44-050, filed 1/24/72, 2/2/72; Order 11, § 18-44-050, filed 5/18/70.]

WAC 18-44-060 Reporting of data. (1) Local and regional agencies. Local and regional air pollution agencies sampling for particle fallout shall notify the state department of ecology of all results exceeding the adopted standard. Monthly summaries shall be submitted annually by March 1st and shall provide the following information:

(a) Location of sampler.

(b) Type of station (air mass – PAMS-PFO), ground level (PGLMS-PFO) or special station.

(c) Time span involved.

(d) Standard exceeded.

(e) Concentrations recorded.

(2) If a violation of the standards is detected by the state department of ecology, the appropriate local agency shall be notified after validation of the results. This notification shall include:

(a) Standard exceeded.

(b) Location.

(c) Time span involved.

(d) Concentrations recorded. [Order 72-7, § 18-44-060, filed 1/24/72, 2/2/72; Order 11, § 18-44-060, filed 5/18/70.]

WAC 18-44-990 Appendix I--Collection and analysis of particle fallout.

APPENDIX I

COLLECTION AND ANALYSIS OF PARTICLE FALLOUT

General: Collection of particle fallout in the Pacific Northwest must be adapted to fulfill the requirements of the local region. Particle sizes exceed those found in other parts of the country. The predominance of wig-wam waste burners and other lumber operations within the state necessitates procedures for detection of large cinders and fly ash particulates. The screening method recommended by ASTM, APCA and ASPHS therefore cannot be utilized in this analysis.

The use of a wet collection method was selected due to regional climatic conditions where collection of dry samples is virtually impossible except during the summer months. The following recommendations incorporate

specific variations in the accepted standards of particle fallout collection and analyses methods for the needs of the area.

Sampling equipment: (1) Collector jar:

(a) Jar should be made of polyethylene. Glass, stainless steel, or other nonreactive material may be used. For convenience in shipping and storage, jar should be equipped with a water-tight cover.

(b) Top opening of not less than six inches in diameter.

(c) Height between two to three times diameter of top opening.

At present a five and one-half quart tupperware jumbo canister is being used for sample collection. The recommended design for a new standard collector is shown in Figure 1. Until this unit is available from plastic manufacturers, it is recommended that the present tupperware collector be used.

When necessary an algaecide may be added to the distilled water placed in the collector. Dowicide B is recommended - five milliliters of 0.2% solution per sampler is sufficient. Use of any type of antifreeze should be discouraged unless absolutely necessary.

(2) Sampler support: Suitable unrestricted holder with a bird ring or other attachments, when necessary to preserve sampling purity.

Sampling station criteria: (1) Location: Station be freely exposed and not subject to interference from local sources or adjacent buildings and high objects. The top of any building, structure or natural growth should not be on a line exceeding 30° angle above the sampling position from the horizontal. Concur with other conditions as stated under PAMS and PGLMS criteria.

(2) Height: Not less than eight feet or over 150 feet above ground level following the criteria of PAMS, PGLMS and special stations. When mounting on roof tops the minimum height of the jar opening shall be five feet above the roof level.

Sampling procedure: (1) Add distilled water to the jar. The amount of water can vary to meet existing climatic conditions.

(2) Remove lid from the collecting jar and mount the jar in the support assembly.

(3) The sampling duration time of PRIMARY stations shall be one calendar month \pm two days. Special sampling time duration shall be as needed to document the problem.

Laboratory equipment: (1) Analytical balance - 160 gram capacity, sensitivity 0.1 milligram.

(2) Steam bath.

(3) Drying oven - Temperature regulation of $\pm 2^\circ\text{C}$. at 105°C .

(4) Evaporating dish - Coors capable of holding 150-200 milliliters of sample.

(5) Electric stirrer.

(6) Rubber policeman broad tip.

(7) Desiccator.

(8) Laboratory furnace with temperature at 800°C .

(9) Waring blender - One-gallon capacity. (Optional method)

Laboratory analysis: (1) Selectively remove all insects, leaves, and other substances that are not considered fallout material.

(2) Scrub down the inside of the jar and quantitatively transfer to a suitable beaker.

(3) Adjust the volume of the sample by evaporation, or the addition of distilled water to exactly 500 ml.

(4) Using a stirrer, remove 100 ml. of sample for the chemical analysis, 100 ml. for soluble-insoluble analysis (if desired). The remainder is used for the determination of total particulate, ash and volatile. If chemical and soluble-insoluble analysis are not desired, the whole sample should be used to determine the total particulate, etc.

(5) To determine total particulate, ash and volatile, transfer to a preweighed evaporating dish and evaporate at 105°C . for twenty minutes, desiccate and weigh to determine the total ash weight. Calculate volatile portion (%).

Optional method (from (2) above): (3a) Adjust the volume of the sample to less than 500 ml. by evaporation, or by the addition of distilled water.

(4a) Quantitatively transfer to a Waring blender for mixing. Blend and transfer to a 500 ml. graduate using the blender wash water to adjust the volume to 500 ml. Mix thoroughly.

(5a) Pipet 200 ml. from the graduate and transfer to a preweighed evaporating dish. Evaporate at 105°C . to dryness, desiccate and weigh to determine the total weight.

(6a) Place the evaporating dish in a muffle furnace at 800°C . for twenty minutes, desiccate and weigh to determine the total ash weight (% volatile).

(7a) Transfer the remaining 300 ml. from (4) into a beaker, heat and vacuum filter through a Buechner funnel. Adjust the volume of the filtrate to exactly 300 ml.

(8a) Transfer 100 ml. of the filtrate to a storage bottle for later chemical analysis.

(9a) Transfer the remaining 200 ml. from (7) to a preweighed evaporating dish, evaporate to dryness at 105°C . Desiccate and weigh to determine the total soluble weight.

(10a) Place the soluble weight evaporating dish from (9a) in a muffle furnace at 800°C . for twenty minutes, desiccate and weigh to determine the soluble ash weight.

Calculations: Total particulates and chemical analyses shall be expressed in gram, per square meter per month. Other units may be used to suit individual needs. Total particulate will be reported to the nearest 0.1 grams per square meter per month for values under 10. For values 10 or above, the data will be reported to the nearest whole number.

Volatile fractions will be reported as a percent of the total weight to the nearest one percent.

Chemical analyses, solubles and insoluble fractions will be reported to the nearest hundredth of a gram per square meter per month.

REFERENCES

(1) ASTM Standards on Methods of Atmospheric Sampling and Analysis, ASTM Committee D-22, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa., October, 1962.

(2) Recommended Standard Method for Continuing Dustfall Survey, Committee on Air Pollution Measurements of the Air Pollution Control Association (APM - 1, Revision 1), J. Air Poll. Control Assoc. 16:372, 1966.

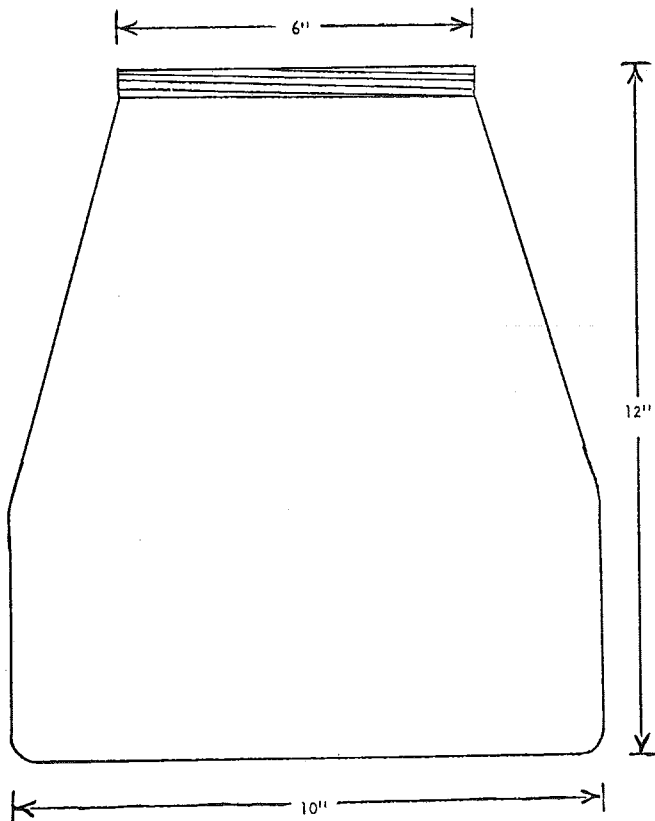
(3) J. S. Nader, Dust Retention Efficiencies of Dustfall Collectors, J. Air Pollution Control Assoc. 8:35, 1958.

(4) H. P. Sanderson; P. Bradt; M. Katz, A Study of Dustfall on the Basis of Replicated Latin Square Arrangements of Various Types of Collectors, J. Air Poll. Control Assoc. 10:461, 1963.

(5) J. Stockham; S. Radner; E. Grove, The Variability of Dustfall Analysis Due to the Container and the Collecting Fluid, J. Air Poll. Control Assoc. 16:263, 1966.

(6) S. Hochheiser, Determination of Dustfall, Approved by the Interbranch Chemical Advisory Committee, March, 1967.

Figure 1
Suggested Design
for
Particle Fallout Collection



With Plastic Screw Cap
Should Be Leak-Proof

[Order 11, Appendix I (codified as WAC 18-44-990), filed 5/18/70.]

Chapter 18-48 WAC FLUORIDES

WAC

18-48-080	Preamble.
18-48-090	Policy limitations.
18-48-100	Definitions.
18-48-110	Intent of regulations.
18-48-120	Forage standards.
18-48-130	Ambient air standards.
18-48-140	Compliance with standards.
18-48-150	Sampling and analysis.
18-48-900	Appendix I—Methods of collection and analysis for fluorides in forage and ambient air.

Reviser's note: WAC 18-48-080 through 18-48-150 are rules as filed by the department of ecology (chapter 43.21A RCW).

DISPOSITION OF SECTIONS FORMERLY CODIFIED IN THIS CHAPTER

18-48-010	Policy limitations. [Order 15, § 18-48-010, filed 5/28/70.] Repealed by Order DE 70-9, filed 1/5/71.
18-48-020	Definitions. [Order 15, § 18-48-020, filed 5/28/70.] Repealed by Order DE 70-9, filed 1/5/71.
18-48-030	Intent of regulations. [Order 15, § 18-48-030, filed 5/28/70.] Repealed by Order DE 70-9, filed 1/5/71.
18-48-040	Forage standards. [Order 15, § 18-48-040, filed 5/28/70.] Repealed by Order DE 70-9, filed 1/5/71.
18-48-050	Ambient air standards. [Order 15, § 18-48-050, filed 5/28/70.] Repealed by Order DE 70-9, filed 1/5/71.
18-48-060	Compliance with standards. [Order 15, § 18-48-060, filed 5/28/70.] Repealed by Order DE 70-9, filed 1/5/71.
18-48-070	Sampling and analysis. [Order 15, § 18-48-070, filed 5/28/70.] Repealed by Order DE 70-9, filed 1/5/71.

WAC 18-48-080 Preamble. In the interest of the people of the state of Washington, it is the objective of the state department of ecology to obtain and maintain the cleanest air possible, consistent with the highest and best practicable control technology.

In areas where existing concentrations are lower than concentrations allowed by the standards enumerated below, degradation of the atmosphere should be minimized. The highest and best practicable control technology should be applied to all sources emitting fluorides to the atmosphere unless it is determined by the responsible air pollution control agency that application of lesser technology is justified. Air quality standards should not be construed to encourage degradation of existing air quality. [Order DE 70-9, § 18-48-080, filed 1/5/71.]

WAC 18-48-090 Policy limitations. The standards set forth within these regulations are intended to protect livestock and vegetation. All sampling to measure compliance with said standards will be conducted in areas and during time periods appropriate to protect vegetation and livestock. [Order DE 70-9, § 18-48-090, filed 1/5/71.]

WAC 18-48-100 Definitions. (1) Forage – Grasses, pasture and other vegetation that is consumed or is intended to be consumed by livestock.

(2) Cured forage – Hay, straw, ensilage that is consumed or is intended to be consumed by livestock.

(3) Ambient air – The surrounding outside air.

(4) Ambient air quality standard – An established concentration, exposure time and frequency of occurrence of a contaminant or multiple contaminants in the ambient air which shall not be exceeded.

(5) Standard conditions – Sixty degrees Fahrenheit and fourteen and seven-tenths pounds per square inch absolute. [Order DE 70-9, § 18-48-100, filed 1/5/71.]

WAC 18-48-110 Intent of regulations. Two standards are established by these rules. One shall be for the fluoride content of forage and the other for gaseous fluorides in the ambient air. No person shall cause, let, permit, or allow any emission of elemental or chemically combined fluorine, which either alone or in combination with other fluorides that may be present in forage or the ambient air, to be in excess of the standards in WAC 18-48-120 and 18-48-130. [Order DE 70-9, § 18-48-110, filed 1/5/71.]

WAC 18-48-120 Forage standards. (1) The fluoride content of forage calculated by dry weight shall not exceed:

(a) Forty parts per million fluoride ion (40 ppm F⁻) average for any twelve consecutive months.

(b) Sixty parts per million fluoride ion (60 ppm F⁻) each month for more than two consecutive months.

(c) Eighty parts per million fluoride ion (80 ppm F⁻) more than once in any two consecutive months.

(2) In areas where cattle are not grazed continually, but are fed cured forage part of the year, the fluoride content of the cured forage shall be used as the forage fluoride content for as many months as it is fed to establish the yearly average.

(3) Cured forage grown for sale as livestock feed shall not exceed forty parts per million fluoride ion (40 ppm F⁻) by dry weight after curing or preparing for sale. [Order DE 70-9, § 18-48-120, filed 1/5/71.]

WAC 18-48-130 Ambient air standards. Gaseous fluorides in the ambient air calculated as HF at standard conditions shall not exceed:

(1) Three and seven-tenths micrograms per cubic meter (3.7 µg/m³) average for any twelve consecutive hours;

(2) Two and nine-tenths micrograms per cubic meter (2.9 µg/m³) average for any twenty-four consecutive hours;

(3) One and seven-tenths micrograms per cubic meter (1.7 µg/m³) average for any seven consecutive days;

(4) Eighty-four one hundredths micrograms per cubic meter (0.84 µg/m³) average for any thirty consecutive days;

(5) Five-tenths micrograms per cubic meter (0.5 µg/m³) average for the period March 1 through October 31 of any year. [Order DE 70-9, § 18-48-130, filed 1/5/71.]

WAC 18-48-140 Compliance with standards. When requested by the director of the department of ecology, persons emitting fluorides to the atmosphere shall be required to establish their compliance with WAC 18-48-120 and 18-48-130 by conducting a monitoring program approved in writing by the director of the department of ecology and submitting all data obtained to the director. [Order DE 70-9, § 18-48-140, filed 1/5/71.]

WAC 18-48-150 Sampling and analysis. (1) Forage samples shall be taken once each calendar month at intervals of twenty-five to thirty-five days, to determine compliance with WAC 18-48-120.

(2) Gaseous fluoride shall be sampled according to the approved monitoring program, using the sodium bicarbonate tube method.

(3) Samples shall be analyzed by the Technicon Auto Analyzer or the Modified Willard-Winter Distillation Method. The Orion probe may be used to analyze the gaseous ambient air sample when the fluoride is in soluble form.

(4) Sampling and analysis shall be in accordance with techniques approved by and on file with the department of ecology. Other sampling and methods of analysis which are equivalent in accuracy, sensitivity, reproducibility and applicability under similar conditions may be used after approval by the department. [Order DE 70-9, § 18-48-150, filed 1/5/71.]

WAC 18-48-900 Appendix I--Methods of collection and analysis for fluorides in forage and ambient air.

Reviser's note: Appendix I Methods of collection and analysis for fluorides in forage and ambient air was filed with the now repealed WAC 18-48-010 through 18-48-070, Order 15, filed 5/28/70.

APPENDIX I

METHODS OF COLLECTION AND ANALYSIS FOR FLUORIDES IN FORAGE AND AMBIENT AIR

[Footnotes and bibliographical references noted in the text of the following appendix are found at the end of the Appendix I.]

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SAMPLING AND ANALYSIS FOR FLUORIDE IN AMBIENT AIR AND FORAGE.

DISCUSSION. These methods are adapted, with modification, from procedures which have been used successfully by industry and government laboratories. [References](1, 2, 7, 10)

Gaseous fluoride is absorbed from an air sample by passing the air across a film of sodium bicarbonate on the inside surface of a glass sampling tube. The coating is removed from the tube by solution in water and the fluoride content determined using a specific ion electrode method.

Particulate matter containing fluorine is collected on a membrane filter. The soluble fluorine compounds are dissolved in water and the fluoride content is determined with a specific ion electrode. The fluorine in the water-insoluble particulate is isolated by steam distilling from sulfuric acid at 165°C and from perchloric acid at 135°C. The fluoride in the distillate is measured by titrating with thorium nitrate to a standard color end point.

Forage samples are dried and ignited to an ash. The fluorine in the ash is isolated by steam distilling from perchloric acid at 135°C and the fluorine content of the distillate is determined spectrophotometrically after reacting with a zirconium-SPADNS reagent.

Automatic analysis of these samples can be made if the results can be shown to compare favorably with those given by the recommended manual methods. [Reference](13)

GENERAL PRECAUTIONS. Fluorine is one of the more common elements and occurs in at least trace amounts in virtually all natural and manufactured materials. Contamination by extraneous fluoride may, therefore, come from such sources as sampling and laboratory apparatus, reagents, and from exposure to laboratory dust and fume. Care must be exercised in the selection, purification and testing of reagents and apparatus, and only minimal exposures of samples should be permitted.

Vessels used for evaporation, ashing, or caustic fusion of samples are first rinsed with warm, dilute acid solution (hydrochloric or nitric), then with distilled water and air dried under clean toweling. Inconel crucibles

used for fusion of the ash may require additional cleaning by boiling in 10 percent (w/v) NaOH for one hour. Glassware is washed with hot detergent solution followed by a rinse in warm, dilute acid. It is finally rinsed with distilled water and dried. All sampling devices, containers, volumetric glassware, reagent solutions, etc. are stored under suitable conditions of protection from airborne dusts and fumes, and are reserved for exclusive use in low-fluoride analysis.

Before proceeding with analysis of samples, blank determinations are repeated until satisfactorily low values (5 µg, or less, total fluoride per determination) are consistently obtained. Calibration standards are analyzed whenever new batches of reagent solutions are prepared. In addition, one blank and one standard determination are carried through the entire analytical procedure with each set of 10 or fewer samples. If samples are handled in larger sets, the ratio of one blank and one standard per 10 samples must be maintained.

FLUORIDE IN AMBIENT AIR AND FORAGE SAMPLING METHODS.

AMBIENT AIR SAMPLING [Reference](1)

DISCUSSION. These methods provide a means of separating gaseous and particulate fluorine compounds.

[Beginning of original Page 4 of Appendix I]

The reactive gaseous fluorides such as hydrogen fluoride are removed from the air stream with sodium bicarbonate coated on the inside wall of a glass tube. The particulate matter, if collected, is removed by filtration at the tube outlet.

APPARATUS AND REAGENTS. (1) Filter paper – Whatman No. 32 or equivalent.

(2) Filter paper holder – Constructed out of aluminum, with all metal parts coated on the inside with Tygon paint mixed 1:10 with thinner. This coating will prevent pickup of fluorine and fluorine compounds by the metal surface. Other holders which are inert to fluorine compounds can be used. An example is the Millipore Swinnex-47 holder made of polypropylene.

(3) Glass tubing – 4 foot lengths of 7 mm. I.D. tubing with the ends fire polished.

(4) Sample station – A cabinet at the bottom of the sampling station accommodates the motor, pump and filter holder. A chimney supports and protects the glass tube. A conical rain deflector above the chimney is positioned high enough so that aerosol particulates passing beneath it are still above the glass tube inlet. Design of the sampling shelter may vary to suit individual needs.

(5) Pump – Use an air pump capable of drawing at least one-half cubic foot of air per minute through the tube and filter. (A Gast Model 0440-V2B pump with a by-pass control to regulate the air flow has been found to be satisfactory.)

(6) Dry gas meter – Use a meter which is accurate to at least 0.1 cubic foot. (The Sprague Model No. 175 and the Rockwell Model No. 175-S meters have been found to be satisfactory.)

(7) Flowmeter – A calibrated flowmeter can be used to determine air flow rates.

(8) Sodium bicarbonate (NaHCO_3) – 3% solution in distilled water containing a neutral wetting agent. 0.5% polyoxyethylene lauryl alcohol [Footnote](a) has been found to be satisfactory. Glycerin has also been used.

(9) Soda lime, 4–8 or 8–16 mesh.

(10) Drying tower.

PREPARATION OF APPARATUS.

Glass tubes. Clean all tubes before use with acid cleaning solution or other equivalent cleaner. An alternate method which has been found to be satisfactory is the use of hot detergent, followed by distilled water, methanolic potassium hydroxide (KOH) and finally distilled water.

Discard all tubes that cannot be cleaned.

For the final rinsing, attach all of the tubes in series with rubber tubing. Place an extra tube at the inlet and another at the outlet positions of the tube train, connect the train to distilled water and thoroughly rinse.

Drain the excess water from the tubes. Fill the inlet tube with 3% sodium bicarbonate. Force the solution through the rest of the tube train, thoroughly wetting the inside walls of each tube. Drain and blow out the excess solution. [Footnote](b)

[Beginning of original Page 5 of Appendix I]

Filter equipment. Wash and dry all parts of the filter membrane holder. Place the Whatman No. 32 paper or other membrane filter in the holder. Seal the holder by attaching a short length of rubber tubing (about 20 inches) to the inlet and outlet openings.

SAMPLE COLLECTION.

Procedure. At the sampling station, uncap the glass tube and place the tube in the chimney. Connect the tube to the pump inlet and the pump outlet to the meter with short pieces of rubber tubing. Start the pump and adjust the sampling rate to a maximum of 0.5 cubic feet per minute. At the end of the test period, remove the glass tube and replace the caps.

If the particulate matter in the air is to be collected, a filter holder is inserted between the glass absorption tube outlet and the pump inlet. All connections are again made with short pieces of rubber tubing and the glass tube is also butted against the metal filter holder inlet. At the end of the test period, remove the glass tube and filter holder and replace all caps.

Data recording. Include all information relating to the sampling, such as date, starting time, stopping time, sample flow rate, any unusual factors or conditions, temperature at the time of sampling, and barometric pressure at the time of sampling.

FORAGE SAMPLING. [References](2, 12)

Apparatus. (1) One quart glass jars, freezer bags or other inert container that can be used for sample storage. Paper bags may be used if forage leaf surface is dry.

(2) Sharp grass shears or knife.

Sample collection.

Procedure – Cut the forage with a sharp knife or shears about 2 inches above the ground to avoid contamination by soil particles. Collect about 200 grams of sample; cut it into 1/4" to 1/2" pieces and store it in an appropriate container.

Samples may be stored for up to 5 days before analysis, at refrigerator temperatures (5°C). Store the samples at 0°C or lower if they are to be kept for longer than 5 days.

Care must be taken to assure that the sample represents the intake of the animal using the forage. In general, the sample should include the main species of forage vegetation in about the same proportion as they grow in the field.

Do not take samples within 100 feet of any road unless it can be shown that road dust contamination is not a factor.

Data recording – The following information must be included as part of the sample identification:

- (1) Date of sample.
- (2) Time of day.
- (3) Location of sample.
- (4) Types and approximate proportions of vegetation in the sample.
- (5) Weather conditions.
- (6) Any abnormal factor such as heavy traffic, construction in the area, harvesting nearby, etc.
- (7) Original source of sample – is it stacked hay, baled hay, etc.
- (8) Name of person who took the sample.

FLUORIDE IN AMBIENT AIR AND FORAGE ANALYSIS METHODS.

WATER SOLUBLE FLUORINE COMPOUNDS – AMBIENT AIR.

[Beginning of original Page 6 of Appendix I]

DISCUSSION. The ion-selective electrode method [References](3, 4, 5) of analysis for fluoride ion has been found to be specific and rapid and is the method of choice for water soluble fluorides.

The water soluble fluorides include those collected from air by the sodium bicarbonate tube method and water soluble portions of the particulate matter collected on the filter.

The fluoride ion selective electrode is a specific ion sensor. The electrode is designed to be used with a standard calomel reference electrode and any modern pH meter having an expanded millivolt scale. The key element in the fluoride ion selective electrode is the doped single lanthanum fluoride crystal across which a potential is established by the presence of fluoride ions. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell may be represented by $\text{Ag}/\text{AgCl}, \text{Cl}^-(0.3), \text{F}^-(0.001\text{M})/\text{LaF}_3/\text{test solution}/\text{SCE}$. (SCE – Standard Calomel Electrode.)

The fluoride ion selective electrode can be used to measure the concentration of fluoride in aqueous

samples by the use of a calibration curve. The fluoride activity is dependent, however, upon the total ionic strength of the sample, and the electrode does not respond to fluorides which are bound or complexed. These difficulties are largely overcome by the addition of citrate ions to preferentially complex aluminum and the addition of a solution of high total ionic strength to decrease variations in sample ionic strength.

Polyvalent cations such as Si^{++++} , Al^{+++} will complex fluoride ion. The extent to which complexing takes place depends on the solution pH, the relative levels of the fluoride and the complexing species. The addition of citrate ion will preferentially complex concentrations less than 0.3 $\mu\text{g}/\text{liter}$ of aluminum and release the fluoride as the free ion. Also, in acid solution, hydrogen ion forms complexes with fluoride ion, but the complexing is negligible if the pH is adjusted to above pH 5. In alkaline solution the hydroxide ion also interferes with the electrode response to fluoride ion whenever the level of hydroxide ion is greater than one tenth the level of fluoride ion present. However, at pH 8 and below, the hydroxide concentration is 10^{-6} molar or less and no interference occurs with any measurable fluoride concentration.

APPARATUS AND REAGENTS. (1) Expanded scale pH meter of specific meter – No major adjustment of any of the instruments is normally required to use the electrodes in the concentration range 0.2 – 2.0 mg. fluoride per liter. For those instruments with zero at center scale (e.g. some Beckman & Leeds and Northrup meters), it is convenient to set the instrument by adjusting the calibration control so that the 1.0 mg. per liter standard reads at the center zero (100 mv) when the meter is in the expanded scale position. This cannot be done with some meters (e.g. Corning Model 12) which do not have a mv calibration control. If using a specific ion meter, follow the directions of the manufacturer in calibrating the instruments.

(2) Sleeve-type reference electrode – Orion #90-01-100, Beckman #40463, Corning #476012 or equivalent. Fibre-tip reference electrodes are often erratic in very dilute solutions and are not recommended.

(3) Fluoride electrode – Orion or equivalent – A combination fluoride electrode can be used.

(4) Magnetic stirrer – Teflon coated stirring bar.

(5) Stop watch or laboratory timer.

(6) Stock fluoride solution – Dissolve 0.2210 grams of anhydrous sodium fluoride (NaF), in distilled water and dilute to 1000 mls (1.00 ml = 0.100 mg F).

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(7) Standard fluoride solution – Dilute 100 ml stock fluoride solution to 1000 ml with distilled water (1.0 ml = 0.01 mg F). Store this reagent in a polyethylene bottle.

(8) Total ionic strength adjustment buffer (TISAB) – Place approximately 500 ml of distilled water in a one-liter beaker. Add 57 ml of glacial acetic acid, 58 grams of sodium chloride, and 0.30 grams of sodium citrate. Stir to dissolve. Place the beaker in a water bath for

cooling, insert a calibrated pH electrode and reference electrode into the solution and slowly add approximately 5 M sodium hydroxide (about 150 ml) until the pH is between 5.0 and 5.5 Cool to room temperature. Transfer to a one-liter volumetric flask and dilute with distilled water to one liter. If high aluminum (Al^{+++}) is a problem, the TISAB can be replaced by 0.1 M citric acid adjusted to pH 5.0 to 5.5 with sodium hydroxide.

Sample preparation

Sodium bicarbonate tube – Dissolve the sodium bicarbonate from the tube surfaces with 10 mls of the TISA buffer (refer to the reagent description section) and transfer to a 200 ml volumetric flask. Rinse the tube with water and add the rinsings to the flask. Dilute to 200 mls. Other dilution volumes may also be used.

Particulate filter – Remove the filter membrane from the holder and place in a 250 ml beaker. Rinse the holder from the inlet side and add the rinsings to the beaker. Add about 50 mls of water and stir for 5 minutes to dissolve any water soluble fluorides on the membrane. Filter through a Whatman No. 32 or equivalent filter paper into a 200 ml volumetric flask. Wash thoroughly and dilute to 200 ml. Other volumetric flasks for other volumes can be used. Save the filter containing the insoluble particulate for fluorine analysis as discussed in the "Analysis methods" section.

Analytical procedure – Prepare a series of standards by adding 0.2, 1.0, 5.0, 10.0, 15.0, and 20.0 ml of standard fluoride solution (1 ml = 0.01 mg. F) to a series of 100 ml volumetric flasks. Pipet 50 ml of TISAB solution into each flask and dilute to 0.1, 0.5, 1.0, 1.5, and 2.0 mg. F per liter, respectively. Other standard quantities can be used.

Pipet 50 ml. of sample into a 100 ml. volumetric flask, dilute to 100 mls. with TISAB and mix well. Adjust the temperature of all standards and samples to room temperature, which should preferably be between 23–27°C.

Transfer each standard and sample to a series of 150 ml. plastic beakers. Immerse the electrodes and measure the developed potential while stirring the test solution with a magnetic stirrer. (CAUTION: Stirring of the solution before immersion of the electrodes may entrap air around the crystal and produce erroneous readings or needle fluctuations.) The electrodes must remain in the solution at least three minutes before taking a final millivolt reading. If the sample contains 0.2 mg/liter of fluoride ion, or less, the electrodes must remain in the solution for 10 minutes. The electrodes must be rinsed with distilled water and carefully blotted dry between each reading.

When using an expanded scale pH meter, or specific ion meter, it is necessary to frequently recalibrate the electrode. Recalibration is done by checking the millivolt reading for the 1.0 mg F per liter standard and adjusting the calibration control until the meter reads as before. The calibration should be checked after reading each unknown and after reading each standard when preparing the standard curve.

Plot the millivolt values of the fluoride standards against concentration on 2-cycle semilogarithmic graph paper. Plot mg F per liter on the logarithmic axis, with

the lowest concentration at the bottom of the page. Using the millivolt reading for each unknown sample, determine the corresponding fluoride concentration from this standard curve.

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Calculations. Calculate gaseous fluorides as HF by volume at 25°C and 760 mm Hg pressure.

$$\frac{\text{HF, ppb by volume (25°C, 760 mm Hg)}}{= \frac{(A)(B)(D)(G)(2.21 \times 10^3)}{(C)(E)(F)}}$$

Calculate water soluble particulate fluoride as micrograms F/liter of air at 25°C [25°C] and 760 mm Hg pressure.

$$\frac{\text{F, } \mu\text{g/liter of air (25°C, 760 mm Hg)}}{= \frac{(A)(B)(D)(G)(2.55)}{(C)(E)(F)}}$$

A – mg F/liter, as measured

B – aliquot dilution volume, ml

C – aliquot volume, ml

D – sample dilution volume, ml

E – volume of air sampled, liters

F – barometric pressure at time of sampling, mm Hg

G – temperature, °K at time of sampling. °K=(°C + 273)

NOTE: The factor 2.21×10^3 includes F—>HF, mg HF—>ml HF, standard pressure, standard temperature (25°C) and volume adjustment factors.

The factor 2.55 includes standard pressure, standard temperature (25°C) and weight – volume factors.

ppb – parts per billion.

FLUORIDE IN AMBIENT AIR AND FORAGE ANALYSIS METHODS.

FORAGE AND PARTICULATE MATTERS.

Sample preparation for distillation

Forage – Mix the sample thoroughly. Determine the moisture content by drying 10–20 grams (accurately weighed) at 80°C for 24 hours or until consecutive weighing shows no further weight loss.

Transfer the balance of the sample to a tared Inconel [Footnote](c) dish and weigh. Sprinkle 1.00 grams of low fluoride calcium oxide [Footnote](d) over the surface of the sample. Add distilled water until the sample is just covered and evaporate to dryness. Infrared lamps can be used to speed the evaporation and as an aid in charring the forage tissues.

Raise the temperature of the hotplate and continue heating until the sample is charred and partially ashed. Most of the ignition of the sample should occur at this stage.

Complete the ashing to a white or gray color at 550°–600°C in an electric furnace which is used only for the ignition of low fluoride materials. Transfer to a dessicator for cooling. Weigh the ash, pulverize, mix and store in a stoppered container.

Transfer approximately one gm of ash to a tared Inconel crucible and weigh accurately. Add about 5 gm of sodium hydroxide pellets, cover the crucible and fuse the contents for a few minutes over a gas burner. This treatment is necessary to assure a quantitative release of fluoride combined with silica in many varieties of vegetation. After cooling the melt, note its color. Blue–green color indicates the presence of manganese and treatment with hydrogen peroxide is required as described in the "procedure for single distillation, vegetation ash" section. Disintegrate the melt with hot water, washing down the lid and walls of the crucible. Proceed as described in the "isolation of fluoride" section.

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Particulate matter – Particulate matter collected during air sampling generally requires fusion with sodium hydroxide for conversion into a soluble form prior to the separation of fluoride by a Willard–Winter distillation. This treatment is also necessary for materials containing fluoride associated with aluminum, for materials high in silica and for many minerals.

Transfer the sample–bearing paper filter or membrane to an Inconel crucible or other resistant metal such as platinum or nickel, moisten with water and make alkaline to phenolphthalein with a known weight of low–fluoride calcium oxide. [Footnote](d) After evaporation to dryness, ignite the paper in a muffle furnace at a temperature of 550°–600°C until all carbonaceous matter has been oxidized. Control the combustion of filters of the cellulose ester membrane type by drenching with ethanolic sodium hydroxide and igniting with a small gas flame.

Fuse the residue from the ashing of the filter with 2 gm of sodium hydroxide. Dissolve the cold melt in a few ml of water, add a few drops of 30 percent hydrogen peroxide to oxidize sulfites and boil the solution to destroy excess peroxide. Proceed as described in the "isolation of fluoride" section.

ISOLATION OF FLUORIDE (Willard–Winter Distillation) [References](8, 10)

Principle of the method. The prepared sample is distilled from a strong acid such as sulfuric or perchloric, in the presence of a source of silica. Fluoride is steam–distilled as the fluosilicic acid under conditions permitting a minimum of volatilization and entrainment of the liberating acid.

Range and sensitivity. The Willard–Winter distillation method can accommodate quantities of fluoride ranging from 100 mg down to a few micrograms.

Interferences. Samples relatively free of interfering materials, and containing fluoride in forms from which it is easily liberated, may be subjected to a single distillation from perchloric acid at 135°C. Samples containing appreciable amounts of aluminum, boron, or silica require a higher temperature and larger volume of distillate for quantitative recovery. In this case a preliminary distillation from sulfuric acid at 165°C is used. Large amounts of chloride are separated by precipitation with silver perchlorate following the first distillation. Small amounts are held back in the second distillation from

perchloric acid by addition of silver perchlorate solution to the distilling flask.

Precision and accuracy. Recovery data for the Willard-Winter distillation, as given in the literature, are difficult to dissociate from inaccuracies inherent in various methods of sample preparation and final evaluation of fluoride. Recovery data from field samples are further complicated by variability of interfering substances and ranges of fluoride contained. In general, recoveries should be within ± 10 percent of the amount of fluoride present. Under favorable circumstances of sample composition and fluoride range, mean recoveries of approximately 99 percent with standard deviation of about 2.5 percent have been reported. Sodium fluoride standards must be distilled to determine the percent recovery under distillation conditions.

Apparatus and reagents.

(1) Steam generator – (Figure 1.A) A 2000 ml Florence flask made of heat-resistant glass. The flask is fitted with a stopper; have at least 3 holes for inserting 6 mm OD heat-resistant glass tubing. Through one of the glass tubes, bent at right angles, steam is introduced into the distilling flask. The second tube is a steam release tube (Figure 1, D) which controls the steam pressure. The small piece of rubber tubing which is slipped over the end of the steam release tube is clamped shut during sample distillation. The third tube is a safety tube. If desired, other tubes may be added to permit the steam generator to supply up to 3 distilling flasks. Any suitable heating device may be used.

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(2) Distilling flask – (Figure 1, B) A 250 ml modified Claisen flask made of heat resistant glass. The auxiliary neck of this flask is sealed and the outer end of the side tube is bent downward so that it may be attached to an upright condenser. The side tube is fitted with a one-hole rubber stopper to fit the condenser and the main neck with a two-hole stopper through which passes a thermometer and a 6-mm OD heat resistant glass inlet tube for admitting the steam. Any suitable heating device may be used.

(3) Liebig condenser – (Figure 1, C) Heat resistant glass, 300 mm jacket.

(4) Steam release tube – (Figure 1, D).

(5) Thermometer – (Figure 1, E) Partial immersion thermometer having a range of 0° to 200°C.

(6) Support plate – (Figure 1, F) Metal, ceramic, or hard asbestos board. The plate shall have a perfectly round 5-cm hole in which the distilling flask is placed as shown in Figure 1. The Claisen flask must fit well in the 5-cm hole so that the flask wall, above the liquid level, is not subjected to direct heat. Excessive heat on the wall of the flask causes the liberating acid to be distilled.

(7) Receiver – (Figure 1, G) 250 or 500 ml volumetric flask, or a 500 ml beaker.

(8) Safety tube – (Figure 1, H) A 6 mm OD heat-resistant glass tubing, 60 cm long, one end of which is 1 cm from the bottom of the steam generator flask.

(9) Rubber tubing – (Figure 1, I) For flask connections, made from natural rubber, lengths of rubber tubing shall be kept as short as possible.

(10) Soft glass beads – (Figure 1, J) 3 mm diameter, for use in the distilling flask to prevent superheating and to supply silica for the formation of fluosilicic acid during distillation.

(11) Porous pumice stones or boiling chips – (Figure 1, K).

(12) Pinchcock – (Figure 1, L) to control steam supply from the generator.

(13) Perchloric acid (70–72 percent by wt) – Concentrated perchloric acid (HClO₄). [Footnote e]

(14) Silver perchlorate solution (50 percent w/v) – Dissolve 100 gm of silver perchlorate (AgClO₄) in 100 ml of water.

(15) Sulfuric acid (96 percent by wt) – Concentrated sulfuric acid (H₂SO₄). [Footnote](e)

(16) Water – All references to water shall be understood to mean distilled or deionized water of reagent purity, free of F ion.

Procedure for forage ash, single distillation. Fill a steam generator about two-thirds full of water. Add a pellet of sodium hydroxide and a few drops of phenolphthalein indicator solution to insure that the water remains alkaline at all times. Add a piece of pumice to permit free boiling, and heat the water to boiling. Keep the steam release tube open at this time and place a pinchcock on the steam supply tubing.

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Transfer the disintegrated melt to a Claisen distilling flask containing five or six glass beads. Wash down the sides of the flask with water and bring the volume to 50 to 75 ml, the lesser volume being more desirable. Insert the rubber stopper that contains the thermometer and steam inlet tube in the main neck of the flask. Set the flask in the 5-cm diameter hole in the support plate and connect the outlet to a condenser.

Rinse the sides of the crucible in which the fusion was made with 50 ml of perchloric acid (70 to 72 per cent) [Footnote](f) and add 1 ml of silver perchlorate solution. Transfer the rinsings to the distilling flask by means of a small funnel attached to the steam inlet tube. Rinse the beaker or crucible with water and add the rinsings to the flask. If the sample contains manganese, add sufficient (2 to 10 drops) 3 percent hydrogen peroxide solution to the contents of the distilling flask to reduce manganese dioxide and permanganates. Mix the contents of the flask by gentle shaking and attach the flask to the steam generator. Place a 500 ml volumetric flask under the condenser to receive the distillate and begin heating the solution in the flask. Keep the pinchcock in place on the steam inlet tube until the contents of the distilling flask reach 135°C.

Remove the pinchcock on the steam inlet tube and place it on the steam release tube of the steam generator. Maintain the distillation temperature at 135° \pm 2°C. Swirl the contents of the distilling flask frequently to minimize deposition on the flask wall of any siliceous residues that might retain fluoride. After collecting 400–

500 ml of distillate during a period of about 1 1/2 to 2 hours, remove the pinchcock from the steam release tube and place it on the steam inlet tube. Disconnect the rubber tubing from the steam inlet tube, and discontinue heating. [Footnote](g)

Procedure for particulate matter, double distillation. Fill a steam generator, as directed under "procedure for single distillation." Transfer the sample solution to a Claisen flask and rinse the sides of the beaker or crucible which contained the sample with 50 ml of concentrated sulfuric acid. Transfer the rinsings to the distilling flask through a small funnel attached to the steam inlet tube. Mix the contents of the flask by swirling. Rinse, remove the funnel, and connect the distilling flask to the steam generator. Place a 400 ml beaker under the condenser and begin heating the distilling flask and steam generator. Keep the pinchcock in place on the steam inlet tube until the contents of the distilling flask reach $165^{\circ} \pm 5^{\circ}\text{C}$. Swirl the contents of the flask as required to prevent accumulation of insoluble material on the walls of the flask above the liquid level. Collect about 375 ml of distillate during a period of about 1 1/2 to 2 hours.

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Add sodium hydroxide solution (10 g/liter) to the distillate until alkaline to phenolphthalein indicator. Evaporate the distillate to 10–15 ml by heating below the boiling point.

The concentrated distillate is redistilled from perchloric acid as directed under "procedure for single distillation." Small quantities of chloride are fixed in the distilling flask by the addition of 1 ml of silver perchlorate solution. A 250 ml quantity of distillate is collected in a volumetric flask.

DETERMINATION OF FLUORIDE, FORAGE DISTILLATE.

Principle of the method. Reaction of fluoride with the metal ion part of a Zirconium–SPADNS dye complex results in fading of the absorbance of the solution.

Sensitivity and range. The Zirconium–SPADNS reagent obeys Beer's law over the range of 0.02 μg to 1.40 μg fluoride/ml with a detection limit of about 0.02 $\mu\text{g}/\text{ml}$.

In common with other spectrophotometric methods, this one is temperature sensitive and absorbances must be read within $\pm 2^{\circ}\text{C}$ of the temperature at which the calibration curve was established.

Interferences. Moderate variations in acidity of sample solutions will not interfere with the Zirconium–SPADNS reagent.

Many ions interfere with this reagent, but those most likely to be encountered are aluminum, iron, phosphate and sulfate. If these are present above the trace level, their effects must be eliminated.

In vegetation analysis, ashing and distillation by the Willard–Winter technique generally assure a sample solution sufficiently free of interfering ions for direct colorimetric evaluation. Traces of free chlorine in the distillate, if present, must be reduced with hydroxylamine hydrochloride.

Precision and accuracy. Because of the wide variability in composition of samples, and in methods and conditions of sampling, no general statements of precision and accuracy for field samples can be given. Precision studies of pure sodium fluoride standards indicate that, within the concentration ranges for which the reagents follow Beer's law, a standard deviation of ± 0.015 – 0.020 μg of fluoride/ml can be expected.

Apparatus and reagents. (1) Spectrophotometer – An instrument is required which is capable of accepting sample cells of 1 cm to 2.5 cm optical path, and which is adjustable throughout the visible wavelength region. Each spectrophotometer sample cell is given an identification mark and calibrated by reading a portion of the reagent blank solution at the designated wave-length. The determined cell correction is subsequently applied to all absorbance readings made with that cell.

(2) Sodium fluoride stock solution (1 ml=1.0 mg F) – Dissolve 2.2105 gm of 100 percent sodium fluoride (NaF) or the equivalent weight of reagent grade sodium fluoride, in water and dilute to 1 liter. Store in a polyethylene bottle.

(3) Sodium fluoride working standard solution (1 ml=10 μg F) Dilute 5.0 ml of the stock solution to 500 ml. Store in a polyethylene bottle.

(4) SPADNS stock solution 4, 5–dihydroxy–3 [p–sulfophenyl]azo] 2, 7–naphthalene disulfonic acid trisodium salt. Dissolve 0.985 gm SPADNS dye in water and dilute to 500 ml.

(5) SPADNS reference solution – Add 10 ml SPADNS stock solution to 100 ml of water. Dilute 7 ml concentrated hydrochloric acid to 10 ml and add to the diluted SPADNS solution. This solution is stable and may be reused indefinitely.

(6) Zirconium solution – Dissolve 0.133 gm of zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) in 25 ml of water, add 350 ml of concentrated hydrochloric acid, and dilute to 500 ml with water.

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(7) Zirconium–SPADNS reagent – Mix equal volumes of the SPADNS and the zirconium solutions. Cool to room temperature before use. This reagent may be stored in a polyethylene bottle for about six months at room temperature.

Procedure. Dilute a suitable aliquot of the sample solution to 25 ml and add 5.0 ml of Zirconium–SPADNS reagent. Mix and allow to stand for 30 minutes to establish temperature equilibrium before transferring the solution to a spectrophotometer cell (cells of 1 cm to 2.5 cm optical path may be used). Measure the absorbance at 570 m μ with the spectrophotometer adjusted to read zero absorbance with the SPADNS reference solution.

Prepare a standard series containing from zero to 35 μg of fluoride by pipetting aliquots of the standard sodium fluoride solution (10 μg F per ml) into 25 ml volumetric flasks. Add 5 ml of Zirconium–SPADNS reagent to each flask, dilute to 25 ml and mix well. Allow the standards to stand 30 minutes to reach temperature equilibrium. Measure absorbances at 570 millimicrons

after adjusting the spectrophotometer to read zero absorbance with the SPADNS reference solution. Prepare a calibration curve relating fluoride concentration in micrograms to absorbance values at the selected working temperature.

Calculation. Calculate forage fluoride as parts per million by weight, oven dry basis.

$$\text{ppm F dry forage} = \frac{(\mu\text{g F in total distillate}) \times (\text{Weight total ash, gms})}{(\text{Weight distilled ash, gms}) \times (\text{Weight dry forage, gms})}$$

DETERMINATION OF FLUORIDE, PARTICULATE MATTER DISTILLATE.

Principle of the method. In the direct titration of fluoride with standard thorium nitrate solution, the sample solution of distillate containing sodium alizarin-sulfonate is buffered at pH 3.0. Upon addition of thorium nitrate, insoluble thorium fluoride is formed. When the endpoint is reached, and all fluoride has reacted, the addition of another increment of thorium nitrate causes the formation of a pink "lake."

In the back titration procedure, the pink "lake" is first formed by addition of sodium alizarin-sulfonate and a slight excess of thorium nitrate to the sample. Equal amounts of dye and thorium solution are added to a fluoride-free reference. The reference solution is then titrated with standard sodium fluoride solution until a color match is achieved with the unknown sample.

Range and sensitivity. The direct titration procedure can accommodate 10 to 0.05 mg fluoride in the total sample. The back titration modifications can measure 50 to about 5 μg fluoride in the total sample. With photometric endpoint detection, direct titration can also be used for the lower ranges.

Interferences. Ions capable of forming insoluble or undissociated compounds with fluorine or with thorium interfere with these titrimetric methods and must be separated. Among the more common of the interfering cations are Al^{+3} , Ba^{+2} , Ca^{+2} , Fe^{+3} , Th^{+4} , TiO_2^{+2} , VO^{+2} , and Zr^{+4} . The principal interfering anions are PO_4^{-3} and SO_4^{-2} . However, any material which constitutes an appreciable change in total ionic strength of the sample solution will affect the endpoint color as well as stoichiometry of the reaction. Thus, excessive acidity in the distillate from a Willard-Winter distillation, as from the liberating acid of chloride content of the sample, will interfere. This effect may be reduced by careful control of temperature and rate of admission of steam, and by separation of chloride.

Sulfide and sulfite interferences are prevented by preliminary oxidation with 30 percent hydrogen peroxide in boiling solution, as described in the "Sample Preparation" section. Interference by free chlorine is eliminated by addition of hydroxylamine hydrochloride solution.

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Apparatus and reagents. (1) Fluorescent lamp - To provide illumination for titrating.

(2) Microburet - Having 5 ml capacity, 0.01 ml divisions, and a reservoir holding about 50 ml.

(3) Nessler tubes - Matches set of 50 ml, tall-form tubes with shadowless bottoms. Tubes may be fitted with either ground glass or rubber stoppers. The set should be checked for optical similarity as follows: Add 40 ml of water, 1 ml of sodium alizarin-sulfonate solution, and 2 ml of 0.05 N hydrochloric acid to the tubes. Add thorium nitrate solution from a buret until the color of the solution just changes to pink. Close the top of the tube and invert several times. Add the same quantity of thorium nitrate solution to the remaining tubes. Fill all the tubes to the 50 ml mark with water and mix. Compare the colors and reject any tubes showing differences in shade or intensity.

(4) Nessler tubes - Matched set of 100 ml, tall-form tubes with shadowless bottoms. The set should be checked for optical similarity, using the same technique as with the 50 ml tubes, except that the quantities of reagents shall be doubled.

(5) Nessler tube rack or comparator.

(6) Photometric titrator (optional) - A Beckman Model B Spectrophotometer equipped with an Alcoa Research Laboratories' titration attachment⁽¹¹⁾ or equivalent. Light from the monochromator passes through a 20.3 cm (8-inch) sample cell to the blue-sensitive phototube mounted at the outboard end of the cell housing. A magnetic stirrer is attached under the cell compartment. The tip of a semi-microburet passes through the cell housing and is immersed in the solution to be titrated. A ball-and-socket joint connects the tip to the buret, facilitating removal of the sample cell. The titration cell is 5.1 cm (2 inches) wide, 7.6 cm (3 inches) deep, and 20.3 cm (8 inches) long.

(7) Buffer-indicator solution - Dissolve 0.40 gm of sodium alizarin-sulfonate in about 200 ml of water. Weigh 47.25 gm of monochloroacetic acid into a 600 ml beaker and dissolve in 200 ml of water. Combine the two solutions with stirring. Dissolve 10 gm of sodium hydroxide pellets in 50 ml of water, cool to approximately 15° to 20°C, and add to the above solution slowly with stirring. Filter and dilute to 500 ml. Prepare fresh weekly.

(8) Chloroacetate buffer solution - Dissolve 9.45 gm of monochloroacetic acid and 2.0 gm of sodium hydroxide (NaOH) in 100 ml of water. This solution is stable for more than two weeks if stored under refrigeration.

(9) Hydrochloric acid, standard solution (0.05N) - Dilute 4.28 ml of hydrochloric acid (HCl, sp gr 1.19) to 1 liter. The normality of this solution should be exactly equal to that of the 0.05 N sodium hydroxide (NaOH) solution.

(10) Hydroxylamine hydrochloride solution - 1 gm of $\text{NH}_2\text{OH} \cdot \text{HCl}$ /100 ml of water.

(11) Phenolphthalein indicator solution (0.5 g/liter) - Dissolve 0.5 gm of phenolphthalein in 60 ml of ethyl alcohol and dilute to 1 liter with water.

(12) Sodium alizarin-sulfonate solution (0.80 g/liter)
– Dissolve 0.40 gm of sodium alizarin-sulfonate in 1000 ml water. [Footnote h]

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(13) Sodium alizarin-sulfonate solution (0.01 g/liter)
– Dissolve 0.01 gm of sodium alizarin-sulfonate in 1000 ml of water.

(14) Sodium fluoride, 100 percent.

(15) Sodium fluoride, standard solution (1.00 ml=1.00 mg F) – Dissolve 2.2105 gm of sodium fluoride (NaF, 100 percent) in water, dilute to 1 liter in a volumetric flask and mix. Store in a polyethylene bottle.

(16) Sodium fluoride, standard solution (1 ml=0.01 mg F) – Dilute 10 ml of NaF solution (1.00 ml=1.00 mg F) to 1 liter with water in a volumetric flask, mix, and store in a polyethylene bottle.

Procedure.

Procedure for direct titration, high concentrations (10 to 0.05 mg F in the total sample).

Pipet an aliquot of the distillate into a 400 ml beaker and dilute to 100 ml. Add 1 ml of sodium alizarin-sulfonate solution (0.80 g/liter), and then sodium hydroxide solution (10 g/liter) dropwise until a pink color is obtained. Discharge the pink color by adding 0.05 N hydrochloric acid dropwise. Add 1 ml of chloroacetate buffer solution dropwise, and titrate with thorium nitrate solution (1 ml=1.9 mg F) to a faint, persistent pink endpoint. Determine a blank obtained by carrying the same amount of all reagents through the entire procedure, including ashing and distillation.

Procedure for back titration, medium concentration (0.05 to 0.01 mg F in the total sample).

Transfer 50 ml of the distillate into a 50 ml Nessler tube, add 1 ml of sodium alizarin-sulfonate solution (0.01 g/liter) and sufficient 0.05 N sodium hydroxide solution to produce a pink color. Note precisely the volume of 0.05 N sodium hydroxide solution required for neutralization. Then discard the titrated solution. If more than 4 ml of 0.05 N sodium hydroxide solution is required, make the remaining distillate alkaline, evaporate to 10 to 15 ml, and transfer it to a distilling flask. Repeat the distillation, precautions being taken to reduce the amount of perchloric acid distilled over.

Transfer another 50-ml portion of distillate into a 50 ml Nessler tube (sample tube) and add 1 ml of sodium alizarin-sulfonate solution (0.01 g/liter). Adjust the acidity with 0.05 N hydrochloric acid until the equivalent of exactly 2 ml of acid is present; that is, 2 ml minus the number of ml of 0.05 N sodium hydroxide solution required for neutralization as described. If between 2 ml and 4 ml of 0.05 N sodium hydroxide solution were required for neutralization, omit the addition of hydrochloric acid to the distillate. Add thorium nitrate solution (0.25 g/liter) from a microburet until a faint pink color appears. Note the volume of thorium nitrate solution required, and save the Nessler tube for comparison with the standard.

Pour 50 ml of water into a 50-ml Nessler tube (standard tube) and add 1 ml of sodium alizarin-sulfonate solution (0.01 g/liter). If neutralization of the

sample required 2 ml or less of 0.05 N sodium hydroxide solution, pipet exactly 2 ml of 0.05 N hydrochloric acid into the standard tube. If the 50 ml aliquot of the distillate required more than 2 ml of 0.05 N sodium hydroxide solution for neutralization, no further acidification of the distillate is necessary, but add to the standard tube a quantity of acid equivalent to that found in the sample distillate.

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From a microburet add sodium fluoride solution (1 ml = 0.01 mg F) equivalent to about 80 percent of the fluoride present in the sample aliquot, as indicated by the thorium nitrate solution required. Mix thoroughly, add the same volume of thorium nitrate solution as that required for titration of the sample aliquot, and again mix thoroughly. The color in the standard tube will be deeper than that in the sample tube.

From the microburet, continue to add sodium fluoride solution (1 ml=0.01 mg F) to the standard tube until its color matches that of the sample tube. (If the colors cannot be matched, repeat the distillation.) Equalize the volumes in the sample and standard tubes by adding water. After the addition of water, mix thoroughly, then allow all bubbles to escape before making the final color comparison. Check the end point by adding 1 or 2 drops of sodium fluoride solution (1 ml=0.01 mg F) to the standard tube. If the colors were originally matched, the color in the standard tube will be distinctly lighter in shade than in the sample tube.

Determine a blank by carrying the same amount of all reagents through the entire procedure including ashing and distillation. With proper attention to details, blanks of 5 μ g of fluoride, or less, can be obtained.

Procedure for back titration, low concentrations (less than 0.01 mg F in the total sample).

Distill successive 85 to 90 ml portions of distillate directly into three or four 100 ml Nessler tubes. Take care to keep the amount of perchloric acid distilling over as small as possible, because the entire distillate is titrated and there is no aliquot available for a separate acidity determination. Analyze each of the distillate portions in the 100 ml Nessler tubes separately as follows:

Add 2 ml of sodium alizarin-sulfonate solution (0.01 g/liter) and neutralize the acid by adding 0.05 N sodium hydroxide solution until a pink color is produced. Add 4 ml of 0.05 N hydrochloric acid and sufficient thorium nitrate solution (0.25 g/liter) to provide a faint pink color. Compare the treated distillate portion with a standard of equal total volume containing 2 ml of sodium alizarin-sulfonate solution (0.01 g/liter), 4 ml of hydrochloric acid and the same volume of thorium nitrate solution (0.25 g/liter) as is required to produce the pink color in the sample tube. Add sodium fluoride solution to the standard tube until the color matches that of the sample tube. The sum of all significant amounts of fluoride found in each successive portion of distillate is the total amount of fluoride in the sample.

Procedure for photometric titration. Transfer the distillate to a 20.3 cm (8-inch) titration cell and add 5 ml

of hydroxylamine hydrochloride solution. Adjust, if necessary, to pH 3.6 with 0.05 N perchloric acid, and then add 5 ml of buffer-indicator solution. [Footnote](i)

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Place the cell in the titrating attachment, immerse the buret tip, and start the stirring motor. Close the titrator lid, set the wave length to 525 mu, and the sensitivity knob to the proper position (usually 1). Close the shutter and adjust the slit width to give a transmittance reading of 100.

Titrate with standard thorium nitrate (0.01 N solution) to a transmittance reading of 75 percent. Record the volume to the nearest 0.005 ml.

Deduct a blank obtained by carrying the same amount of all reagents through the entire procedure, including ashing and distillation. Determine the amount of fluoride present from a calibration curve.

Standardization of thorium nitrate solutions.

Thorium nitrate, standard stock solution (1 ml=1.9 mg F).

Weigh 0.100 gm of sodium fluoride into a distilling flask and collect 250 ml of distillate as previously described. Titrate 50 ml of the distillate (20 mg of NaF) with the solution being standardized. Carry a blank through the same procedure. Calculate the strength of the thorium nitrate solution in terms of mg of fluoride ion/ml of solution as follows:

$$\text{Fluoride ion, mg/ml} = \frac{(20 \text{ mg NaF}) (C)}{A - B}$$

Where:

A = ml of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ solution required for titration of the fluoride.

B = ml of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ solution required for titration of the blank.

C = factor for NaF to F = 0.4524

Thorium nitrate solution, 0.01 N (1 ml=0.19 mg F) - Photometric Titration Solution. Pipet aliquots of standard sodium fluoride solution covering the range 10 to 1000 μg of fluoride into 500 ml volumetric flasks and dilute to volume. Transfer to a 20.3 cm titration cell, add 5 ml of hydroxylamine hydrochloride solution, and adjust to pH 3.6 with 0.05 N perchloric acid. Add 5 ml of buffer-indicator solution and titrate as described in the "procedure for photometric titration" section.

Calculation. Calculate particulate fluoride [Footnote](j) as milligrams per cubic meter at 25°C and 760 mm Hg pressure:

$$\text{Particulate fluoride [Footnote j] milligrams F/m}^3 = \frac{(A-B) (C) (D) (E) (F)}{(G) (P) (V)}$$

A — ml titrating solution [Footnote](k) used to titrate sample aliquot.

B — ml titrating solution used to titrate reagent blank.

C — fluoride equivalent of titrating solution as mg F/ml solution.

D — ml total distillate collected. [Footnote](l)

E — $(1000 \text{ liters/meter}^3) (760 \text{ mm Hg}) \div (273+25)^\circ = 2550$.

F — 273 + sampling temperature in °C.

G — ml distillate titrated. [Footnote](k)

P — barometer pressure at time of sampling, mm Hg.

V — volume of atmosphere sampled.

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FOOTNOTES

(Collected Notes)

(a) Brij-35, Atlas Chemical Co., Wilmington, Delaware.

(b) Excess sodium bicarbonate solution is undesirable as it breaks loose from tube wall when dry and is included as particulate material on the filter.

(c) Inconel dishes can be obtained from Precision Metal Spinning Co., 9825 Dixie Highway, Clarkston, Mich. Platinum, nickel or other dishes nonreactive to fluoride can be used.

(d) Available on special order from G. Frederick Smith Chemical Co., P.O. Box 23344, Columbus, Ohio 43223.

(e) Acid giving excessively high fluoride blanks requires preboiling at 135°C, with admission of steam, prior to the addition of samples.

(f) Caution. When using perchloric acid, the usual precautions should be taken. Hot concentrated perchloric acid may react explosively with reducing substances, such as organic matter. Therefore, it is wise to see that any organic matter in the sample is destroyed in the ashing process prior to distillation. Precautions for the use of perchloric acid are available in "Chemical Safety Data Sheet SD-11, Perchloric Acid Solution," published by the Manufacturing Chemists' Association of the United States.

(g) Caution. The distilling flasks should be cleaned using only a brush and distilled water. Repeated use of alkaline cleaning solution produces an etched surface that is difficult to clean and tends to retain fluoride.

(h) In the literature, this reagent is also known as alizarin Red S, alizarin Red, alizarin-S, alizarin carmine, alizarin, sodium alizarin-sulfonate, sodium alizarin monosulfonate, monosodium alizarin-sulfonate, and 3-alizarin-sulfonic acid sodium salt. The dye is identified by Color Index No. 58005.

(i) The addition of buffer-indicator solution should adjust the pH to 3.0. For amounts of fluoride ordinarily encountered, the pH of the distillate should be 3.5 to 3.7 if the distillation is properly controlled. The addition of buffer-indicator solution will maintain a pH of 3.0 under these conditions. For extreme cases, where acidity of the distillate is less than pH 3.5, 0.05 N sodium hydroxide may be used to raise the pH to the proper level. However, it has been found to be the rule that distillations properly conducted will have a pH greater than 3.5. The use of sodium hydroxide for neutralization

produces a slight change in the factor due to the sodium perchlorate formed.

(j) Designate whether this is total particulate or water insoluble particulate.

(k) The term "titrating solution" refers to either the $\text{Th}(\text{NO}_3)_4$ solution used in accordance with the "procedure for direct titration," or the NaF solution (1 ml=0.01 mg F) used in "procedure for back titration."

(l) The volume or total distillate collected normally is 250 ml. However, if any other volume of total distillate is collected, this volume shall be substituted for 250. The volume of the distillate titrated normally is 50 ml but may vary as described in "procedure for back titration, low concentrations." If this procedure applies, for each portion of distillate titrated, the value of G is equal to the value of D.

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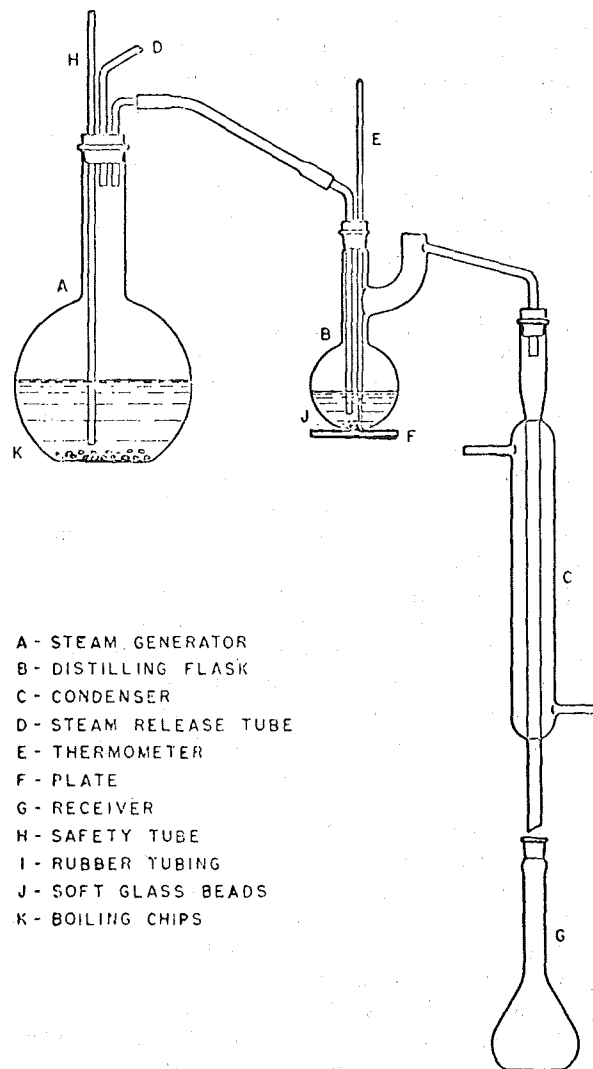
(12) Recommended Criteria for Taking Forage Samples to Determine Fluoride Levels, Proposed Aluminum Association Procedure (Oct. 13) 1969.

(13) Inter-society Committee on Methods for Ambient Air Sampling and Analysis; Tentative Method of Analysis for Fluoride Content of the Atmosphere and

Plant Tissue (Semiautomated Method), Health Laboratory Sciences 6:84-101, 1969.

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Figure 1 - Apparatus for distillation of fluoride.



- A - STEAM GENERATOR
- B - DISTILLING FLASK
- C - CONDENSER
- D - STEAM RELEASE TUBE
- E - THERMOMETER
- F - PLATE
- G - RECEIVER
- H - SAFETY TUBE
- I - RUBBER TUBING
- J - SOFT GLASS BEADS
- K - BOILING CHIPS

[Order 15, Appendix I (codified as WAC 18-48-900), filed 5/28/70.]

Chapter 18-56 WAC SULFUR OXIDE STANDARDS

WAC	
18-56-010	Preamble.
18-56-020	Definitions.
18-56-030	Air quality standards.
18-56-040	Air quality objective.
18-56-050	Method of measurement.
18-56-060	Data reporting.
18-56-990	Appendix I—Sampling and analysis for sulfur dioxide in ambient air.

WAC 18-56-010 Preamble. In the interest of the people of the state of Washington, it is the objective of the state department of ecology to obtain and maintain the cleanest air possible, consistent with the highest and best practicable control technology.

In areas where existing concentrations of sulfur oxides are lower than concentrations allowed by the standards enumerated below, degradation of the atmosphere should be minimized. The highest and best practicable control technology should be applied to all sources, unless it is determined by the responsible air pollution control agency that application of lesser technology is justified. Air quality standards should not be construed to encourage degradation of existing air quality. [Order 72-7, § 18-56-010, filed 1/24/72, 2/2/72; Order 13, § 18-56-010, filed 5/18/70.]

WAC 18-56-020 Definitions. (1) Air quality objective — The concentration and exposure time of a contaminant or multiple contaminants in the ambient air below which, according to available knowledge, undesirable effects will not occur.

(2) Air quality standard — An established concentration, exposure time and frequency of occurrence of a contaminant or multiple contaminants in the ambient air which shall not be exceeded.

(3) Primary air mass station (PAMS-SO₂) — A type of station designed to measure contamination in an air mass and representing a relatively broad area. The sampling site shall be representative of the general area concerned. The probe inlet shall be a minimum of fifteen feet and a maximum of one hundred fifty feet above ground level. Actual elevation should vary to prevent adverse exposure conditions caused by surrounding buildings and terrain. The probe inlet shall be placed ten to twenty feet above a supporting rooftop.

(4) Primary ground level monitoring station (PGLMS-SO₂) — Stations designed to provide information on contaminant concentrations near the ground and provide data valid for the immediate area only. The probe inlet shall be six to fifteen feet above ground level with an optimum height of ten feet. The probe inlet shall not be less than two feet from any building or wall. The sampling site shall be representative of the immediate area.

(5) Special stations (SS-SO₂) — Any station that does not meet the criteria or purpose of the standard stations are defined as special stations. [Order 72-7, § 18-56-020, filed 1/24/72, 2/2/72; Order 13, § 18-56-020, filed 5/18/70.]

WAC 18-56-030 Air quality standards. Sulfur oxide in the ambient air, measured as sulfur dioxide at a primary air mass station, a primary ground level monitoring station, or a special station, shall not exceed the following concentrations averaged over the specified time periods:

(1) Four-tenths parts per million by volume average for any one hour not to be exceeded more than once per year.

(2) Twenty-five one-hundredths parts per million by volume average for any one hour not to be exceeded more than two times in any consecutive seven days.

(3) One-tenth parts per million by volume average for any one day (twenty-four hours), not to be exceeded more than once per year.

(4) Two one-hundredths parts per million by volume average for any one year (annual arithmetic mean). [Order 72-7, § 18-56-030, filed 1/24/72, 2/2/72; Order 13, § 18-56-030, filed 5/18/70.]

WAC 18-56-040 Air quality objective. In recognition of the need for continuing improvement of the quality of the air resource, it is the intent of the department of ecology to work toward the achievement of the following objective for sulfur oxides: The sulfur oxide concentration measured as sulfur dioxide at a primary air mass station, primary ground level monitoring station, or special station shall not exceed 0.3 parts per million average for five minutes. [Order 72-7, § 18-56-040, filed 1/24/72, 2/2/72; Order 13, § 18-56-040, filed 5/18/70.]

WAC 18-56-050 Method of measurement. For determining compliance with this regulation, sulfur oxides shall be measured as sulfur dioxide by acidified peroxide reagent conductivity, coulometric, or colorimetric techniques approved by, and on file with, the department of ecology. Other continuous and manual methods equivalent in sensitivity, accuracy, reproducibility, and selectivity to the approved methods may be used after approval by the department of ecology. [Order 72-7, § 18-56-050, filed 1/24/72, 2/2/72; Order 13, § 18-56-050, filed 5/18/70.]

WAC 18-56-060 Data reporting. Local and regional air pollution control agencies sampling for sulfur oxides shall notify the department of ecology of all violations of this regulation. The notification shall be submitted quarterly. Summaries shall provide the following information:

(1) Location of sampler.

(2) Type of station — air mass, ground level, or special station.

(3) Time span involved (including specific hours, days, and year).

(4) Actual concentrations recorded that exceeded the standard.

(5) The department of ecology shall notify the regional or local agencies of results of samples exceeding the standards within the agency jurisdiction on a quarterly basis. This notification shall include:

(a) Location.

(b) Time span.

(c) Standard exceeded.

(d) Concentrations recorded. [Order 72-7, § 18-56-060, filed 1/24/72, 2/2/72; Order 13, § 18-56-060, filed 5/18/70.]

WAC 18-56-990 Appendix I--Sampling and analysis for sulfur dioxide in ambient air.

[Footnotes and bibliographic references noted in the text of the following appendix are found at the end of the appendix but before the illustrations.]

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Part 1

**SULFUR DIOXIDE IN AMBIENT AIR
MANUAL SAMPLING AND ANALYSIS PROCEDURES**

DISCUSSION

These procedures are adapted with modification from the "intersociety committee methods for ambient air sampling and analysis, tentative method of analysis for sulfur dioxide content of the atmosphere (colorimetric) 42401-01-69T," as published in Health Laboratory Science, 6, 228-236 (1968). Variation B of the reference method is used.

PRINCIPLE OF THE METHOD

Sulfur dioxide is absorbed from a measured air sample by aspirating the air through a solution of potassium tetrachloromercurate. This reacts to form a dichlorosulfitomercurate complex which is resistant to oxidation. [References 1, 2] Ethylenediaminetetraacetic acid, disodium salt (EDTA) is added to this solution to complex heavy metals that can interfere with the formation of the dichlorosulfitomercurate. [References 3, 4] After the absorption is completed, ozone in the solution is allowed to decay. [Reference 4] The solution is treated first with sulfamic acid to destroy the nitrite anion formed from absorbed oxides of nitrogen. [Reference 5] It is treated next with solutions of formaldehyde and purified acid-bleached pararosaniline containing phosphoric acid for pH control. Pararosaniline, formaldehyde, and bisulfite anion react to form the intensely colored pararosaniline methyl sulfonic acid, which behaves as a two-color pH indicator. The final solution is adjusted to pH 1.2 ± 0.1 by the addition of 3M phosphoric acid to the pararosaniline reagent. The wave length of maximum absorbance under these conditions is 575 millimicrons and the compound has a molar extinction of 37.0×10^3 . [Reference 4]

Atmospheric sulfur dioxide concentrations of interest usually range from a few pphm to several ppm. Higher concentrations (5 to 500 ppm), used in special studies, must be analyzed by using smaller gas samples. A rapid redox reaction occurs between Hg (11) and the sulfite ion, if concentrations of this ion exceed 500 $\mu\text{g/ml}$. [Reference 6]

Collection efficiency falls off rapidly below 0.01 ppm and varies with the geometry of the absorber, the size of the gas bubbles, and the contact time with the solution. [Reference 7, 8, 9]

RANGE AND SENSITIVITY

The lower limit of detection of sulfur dioxide in 10 ml of TCM is 0.3 μl (based on twice the standard deviation), and represents a concentration of 0.01 ppm SO₂ in an air sample of 30 liters. Extrapolation to lower values cannot be made by taking larger volumes of air (e.g. 100 liters at 0.003 ppm).

Beer's law is followed through the working range of 0.1 - 1.0 absorbance units (0 - 35 μg SO₂ in 25 ml final solution).

INTERFERENCES

Interferences are eliminated by sulfamic acid for oxides of nitrogen, [References 4, 5] by time delay for ozone, [Reference 4] and by EDTA and phosphoric acid for heavy metals. [References 3, 4] With this procedure, at least 60 μg of Fe (111), 10 μg of Mn (11), and 10 μg

of Cr (111) in 10 ml of absorbing reagent can be tolerated. No significant interference was found with 10 μ g of Cu (11) and 22 μ g V (V).

PRECISION AND ACCURACY

86 The precision at the 95 percent confidence level is 4.6 percent. [Reference 4]

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APPARATUS AND REAGENTS

APPARATUS

Absorber – A midget impinger should be used. The orifice of the impinger must not be more than 1/4 inch from the bottom of the absorber. The absorber is filled to the 10 ml mark with absorbing solution and a gas flow rate between 0.2 – 1.0 liter/min. is used. Bubble fracturing must occur as the bubbles strike the bottom. Two impingers are used in series to check for absorption efficiency. There should be no carry-over into the second impinger.

Air volume measurement – The air flow measuring device must be capable of measuring the air flow within \pm 2 percent. A wet or dry gasmeter or a calibrated rotometer is satisfactory. Calibrated hypodermic needles may be used as critical orifices if the pump is capable of maintaining greater than 0.5 atmosphere pressure differential across the needle. [Reference 11] When using a critical orifice, the incoming air must be free of particulate matter.

Spectrophotometer or colorimeter – The instrument must be suitable for measurement of color at 575 millimicrons. The wave length calibration of the instrument must be verified.

REAGENTS. All chemicals must meet the ACS specifications for reagent chemicals.

Distilled water – Distilled water must conform to the ASTM D1193 standard for nonreferee reagent water. It must be free from oxidants.

Absorbing reagent – 0.04M Potassium Tetrachloromercurate (TCM), (K_2HgCl_4) – Dissolve 10.86 g mercuric chloride (CAUTION: Highly poisonous. If it comes in contact with skin, flush off with water immediately), 5.96 g of potassium chloride and 0.066g of EDTA disodium salt in water and dilute to 1 liter in a volumetric flask. The absorbing reagent is normally stable for 6 months, but should be discarded if a precipitate forms.

Sulfamic acid – 0.6 percent – Dissolve 0.6 g of sulfamic acid in 100 ml of distilled water. Prepare fresh daily.

1-Butanol – Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Check by shaking 20 ml of 1-butanol with 5 ml of 20 percent KI. If a yellow color appears in the alcohol phase, redistill the 1-butanol from silver oxide.

Buffer stock solution (pH 4.69) – Dissolve 13.61 g of sodium acetate trihydrate in distilled water in a 100 ml volumetric flask. Add 5.7 ml of glacial acetic acid and dilute to volume.

1.0 N Hydrochloric acid – Dilute 86 ml of 11.6 HCl (36 percent) HCl to 1 liter with distilled water.

Purified pararosaniline, 0.2 percent stock solution – It is recommended that the "Harleco #64327 purified 99%

pararosaniline hydrochloride solution" [Footnote a] be used as the 0.2 percent stock solution.

If a purified 99% pararosaniline dye* [See footnote [a].] is used, dissolve 0.200 g in 100 mls of 1 N HCl.

If an impure dye is used, it must be purified as follows:

Equilibrate 100 mls 1-butanol and 100 mls 1N HCl by mixing in a 500 ml separatory funnel. Dissolve 0.1 g of pararosaniline hydrochloride (PRA) in 50 ml of the equilibrated acid and let stand for several minutes. Transfer the acid dye solution to a 125 ml separatory funnel containing 50 ml of the equilibrated 1-butanol and extract. The violet impurity will transfer to the organic phase. Transfer the lower (aqueous) phase into another separatory funnel, add 20 ml of equilibrated 1-butanol and extract again. Repeat the extraction three more times with 10 ml portions of equilibrated 1-butanol. This should remove all of the violet impurity. (If the 1-butanol phase is still violet after 5 extractions, discard the lot of dye.) After the final extraction, filter the aqueous phase through a cotton plug into a 50-ml volumetric flask and dilute to volume with 1 N HCl. This stock solution will be yellowish red.

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Dye specifications – When assayed as described below, the maximum absorbance must be at 540 millimicrons, and the calculated purity must be greater than 95 percent.

When used as described in the analytical procedure, the reagent blank must not exceed 0.050 absorbance units using a 1 cm cell.

Assay procedure – The pararosaniline stock solution need be assayed only once for each lot of dye.

Dilute 1 ml of the stock solution to 100 ml with distilled water in a 100 ml volumetric flask. Transfer a 5 ml aliquot to a 50 ml volumetric flask. Add 5 ml of buffer stock solution and dilute the mixture to 50 ml with distilled water. After 1 hour, determine the absorbance at 540 millimicrons. Determine the concentration of PRA by the formula:

$$5 \text{ PRA} = \frac{(\text{Absorbance})(K)}{(\text{grams PRA})}$$

K equals 21.3 (Mean value after extensive purification of dye) for a 1 cm cell and a 0.04 mm slit width in a Beckman DU spectrophotometer. The K factor must be determined for other instruments.

Pararosaniline reagent – Add 20 ml of pararosaniline stock solution to a 250 ml volumetric flask. Add an additional 0.2 ml of stock solution for each percent the stock assays below 100 percent. Add 200 ml of 3M H_3PO_4 and dilute to 250 ml with distilled water. This reagent is stable for at least nine months.

Formaldehyde – 0.2 percent – Dilute 5 ml of 40 percent formaldehyde to 1 liter with distilled water. Prepare fresh daily.

STANDARDIZATION REAGENTS

Stock iodine solution (0.1 N) – Place 12.7 g of iodine in a 250 ml beaker. Add 40 g of potassium iodide and 25

mls of water. Stir until dissolved and dilute to 1 liter with distilled water.

Dilute iodine solution (0.01 N) – Dilute 50 mls of the stock iodine solution to 500 mls with distilled water.

Starch indicator solution – Mix 0.4 g of soluble starch and 0.002 g of mercuric iodide (preservative) with water to form a slurry and add slowly to 200 ml of boiling water. Continue boiling until clear. Cool the solution and transfer to stoppered bottle.

Standard 0.1 N sodium thiosulfate solution – Dissolve 25 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and 0.1 g of sodium carbonate (Na_2CO_3) in 1 liter of freshly boiled, cooled distilled water. Allow the solution to stand for one day before standardizing. Accurately weigh about 1.5 g of potassium iodate, primary standard grade, dried at 180°C. Dissolve in water and dilute to 500 mls in a volumetric flask. To standardize the sodium thiosulfate solution, pipette 50 ml of the iodate solution into a 500 ml iodine flask. Add 2 g of potassium iodide and 10 ml of a 1:10 dilution of concentrated hydrochloric acid. Stopper the flask. Wait 5 minutes and titrate to a pale yellow color with the thiosulfate solution. Add 5 ml of starch indicator solution and continue the titration until the blue color disappears.

$$\text{Normality of thiosulfate} = \frac{\text{Wt. (grams KIO}_3) \times 10^3 \times 0.1}{\text{ml of titer} \times 35.67}$$

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Standard 0.01 N sodium thiosulfate solution – Dilute 25 mls of the standard 0.1 N sodium thiosulfate solution to 250 mls with distilled water. This solution must be prepared fresh daily.

Standard sulfite solution – Dissolve 0.400 g of sodium sulfite (Na_2SO_3) in 500 ml of distilled water. This solution is equivalent to between 320 and 400 μg of SO_2 per ml. To standardize, pipette accurately 50 ml of the 0.01 N iodine into each of two 500 ml iodine flasks. To flask A (blank) add 25 ml of distilled water, and to flask B (sample) pipette 25 ml of the standard sulfite solution. Stopper the flasks and allow to react for 5 minutes. Titrate each flask in turn to a pale yellow color with standard 0.01 N sodium thiosulfate. Add 5 ml of starch solution and complete the titration. Calculate the concentration of sulfur dioxide in the standard solution as follows:

$$\text{SO}_2, \mu\text{g/ml} = \frac{(A-B) N K}{V}$$

Where:

- A = number of ml for blank
- B = number of ml for sample
- N = normality of thiosulfate solution
- K = 32,000 (micro equivalent weight for SO_2)
- V = mls sample volume

Dilute sulfite solution – Immediately after standardization, pipette accurately 2 mls* [See footnote [b].] of the standard sulfite solution into a 100 ml volumetric flask and dilute (to volume) with 0.04 M TCM. This

solution is stable for a maximum of three days at room temperature and one week under refrigeration.

PREPARATION OF STANDARD CURVE

With sodium sulfite – Accurately pipette graduated amounts of the dilute sulfite solution (such as: 0,1,2,3, and 5 ml) into a series of 25 ml volumetric flasks. Add sufficient 0.04 TCM to each flask to bring the volume to 10 ml. Then add the sulfamic acid, formaldehyde and pararosaniline reagents and distilled water as described in the analysis procedure. For greatest precision, a constant temperature bath is preferred. The temperature of calibration and analysis should be the same. A standard curve should be prepared for each analysis.

The absorbances of the solutions are plotted (as ordinates) against the equivalent values of SO_2 . A linear relationship is obtained. The intercept with the vertical axis of the line best fitting the points is usually within 0.005 unit of the reagent blank (zero standard) absorbance value. At least one control sample is included with each series of determinations to insure the reliability of the standard curve.

With SO_2 permeation tube – Permeation tubes (a) [See footnote [c].] that contain liquid sulfur dioxide can be used. The permeation characteristics of permeation tubes are furnished by the manufacturer, and may vary with manufacturers and batches of tubes. The permeation characteristics may also vary as the tube ages. Therefore, each tube must be calibrated periodically to verify its permeation rate. This calibration can be made gravimetrically or volumetrically [References 12, 15] and the tube can then be used to prepare standard concentrations of sulfur dioxide in air. Wet chemical analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of sulfur dioxide.

[Beginning of original Page 7 of Appendix I]

Standard concentrations of sulfur dioxide in air can be prepared by using one of the systems shown in Figures 1, 2, 3 and 4, or the equivalent.

The equipment shown in these systems consists of a watercooled condenser, constant-temperature water bath maintained at any temperature between 20°C–30°C (measured to $\pm 0.1^\circ\text{C}$), cylinders containing pure dry nitrogen or pure dry air, appropriate pressure regulators, needle valves and flow meters for the nitrogen and dry air diluent gas streams. The diluent gases are brought to temperature by passage through at least 6 feet of copper coil immersed in a water bath. Insert a calibrated permeation tube into the permeation chamber which is maintained at the desired temperature by circulating water from the constant-temperature bath (a) [See footnote [d].] Pass a stream of dry air or nitrogen over the tube at a known rate. The gas stream is diluted to the desired sulfur dioxide concentration by the addition of clean, dry air (b) [See footnote [e].] The flow rate of the air can be varied from 0.2 to 15 liters per minute depending upon the system used. The flow rate of the

sampling system determines the lower limit for the flow rate of the diluent gas, and both must be measured to an accuracy of 1 to 2 percent. The sulfur dioxide concentration can also be varied by changing the temperature and/or tubes in the permeation tube chamber.

Example of the preparation of a standardization curve

The systems are designed to provide an accurate measure of sulfur dioxide in the 0.01 to 0.5 ppm range, but they can be modified to meet special needs.

For this example the volume of air passed through the absorption bubbler will be held constant at 30 liters and the SO₂ concentration will be varied in the air stream.

The concentration of SO₂ in the air sample is computed as follows:

$$C = \frac{Pr \times M}{R \times r}$$

Where:

- C = Concentration of SO₂ in ppm
- Pr = Permeation rate in μg/min
- M = Reciprocal of vapor density, 0.382 μl/μg
- R = Flow rate of diluent air, liter/min.

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Data for a typical calibration curve are listed in Table 1.

TABLE 1 TYPICAL CALIBRATION DATA

Concentra- tions of SO ₂ ppm.	Amount of SO ₂ in μl for 30 liters	Absorbance of Sample
0.005	0.15	0.01
0.01	0.30	0.02
0.05	1.50	0.12
0.10	3.00	0.23
0.20	6.00	0.47
0.30	9.00	0.70
0.40	12.00	0.94

For long-term sampling, the conditions can be adjusted to collect 300 liters of sample in a larger volume of absorbing reagent. An aliquot representing 0.1 of the volume can then be taken for the analysis and the remainder of the procedure is the same as described in the analysis section of this method.

CALCULATIONS. Compute the concentration of sulfur dioxide in the sample by the following formula:

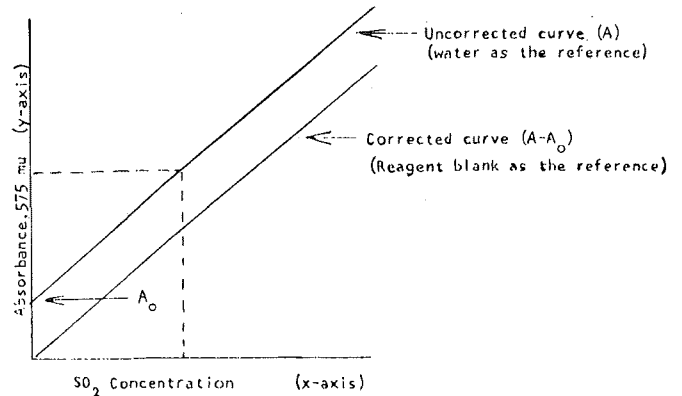
$$\text{ppm} = \frac{(A-A_0) B (0.382)}{V}$$

Where:

- A is the sample absorbance.
- A₀ is the point at which the curve crosses the y-axis.
- Refer to curve example below.
- B is the calibration factor, μg/absorbance unit. 0.382
- is the volume (μl) of 1 μg SO₂ at 25°C, 760 mm Hg.
- V is the sample volume in liters corrected to 25°C and 760 mm Hg (PV = nRT).

The micrograms of SO₂ in the sample can also be taken directly from curve A and substituted for (A-A₀)B in the above formula.

Example of a Standard Curve.



[Beginning of original Page 9 of Appendix I]

NOTE: A₀ is the point at which the curve crosses the y-axis. The reagent blank absorbance should be within 0.005 units of the absorbance at this point and usually is the same as A₀.

SAMPLING AND ANALYSIS PROCEDURE

Collection of sample – Place 10 ml of 0.04 M TCM absorbing solution in the absorber. Two absorbers are connected in series to check for complete absorption. Connect the sampling probe upstream of the absorber with glass, stainless steel, or teflon. Rigid tubing may be joined with butted joints under polyethylene tubing. A trap and calibrated air flow meter, and/or a gas meter equipped with thermometer and manometer are placed between the probe and the pump. Instead of the flowmeter or gas meter, a hypodermic needle in parallel with a manometer can be used as a critical orifice if the pump can maintain a differential pressure of at least 0.5 atmosphere across the needle. The duration and rate of air flow selected depend on the concentration of sulfur dioxide being measured. For best results, rates and sampling time should be chosen to absorb 0.5 to 3.0 μg (0.2 to 1.3 μl at 760 mm Hg, 25°C) of sulfur dioxide per ml of absorbing solution. Shield the absorbing reagent

from direct sunlight during and after sampling by covering the absorber with a suitable wrapping, such as aluminum foil, to prevent deterioration. Samples should not be stored for more than a few hours. However, if the sample must be stored before analysis, keep it refrigerated at 5°–10°C. If a precipitate is observed, remove it by centrifugation.

Analysis – After collection, transfer the sample quantitatively to a 25 ml volumetric flask. Use about 5 ml of distilled water for rinsing. Wait 20 minutes before adding color developing reagents to allow any ozone to decompose. For each set of determinations, prepare a reagent blank by adding 10 ml of the unexposed absorbing reagent to a 25 ml volumetric flask. Add 1 ml of 0.6 percent sulfamic acid to each flask and allow it to react for 10 minutes to destroy the nitrite ion formed from absorbed oxides of nitrogen. With volumetric pipettes, add 2.0 mls of the 0.2 percent formaldehyde, then 5.0 ml of the pararosaniline reagent.

Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with distilled water. At 30 minutes after adding color developing reagent determine the absorbances of the sample and of the blank at 575 millimicrons. Use distilled water (not the reagent blank) as the reference. Do not allow the colored solution to stand in the colorimeter cell; otherwise, a film of dye may be deposited on the glass surfaces.

If the absorbance of the sample solution falls between 1.0 and 2.0, the sample can be diluted 1:1 with the reagent blank and the absorbance immediately determined again. Solutions with higher absorbances can be diluted up to six-fold with the reagent blank in order to obtain on-scale readings within 10 percent of the true absorbance value.

The SO₂ content of the sample is determined by comparison with a standard curve showing SO₂ concentration vs. absorbance. The accuracy of the curve must be verified for at least one point every four hours during any sequence of manual sampling and analysis. The accuracy of the curve must be verified each time fresh absorbing reagent or pararosaniline reagent is used and whenever the temperature during color development varies more than ± 2°C from the temperature at which the standard curve was prepared.

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Part 2

SULFUR DIOXIDE IN AMBIENT AIR CONTINUOUS MONITORING

DISCUSSION

The acid-peroxide electro conductivity method shall be used for the continuous monitoring of sulfur dioxide in ambient air. The interference from other pollutants in the atmosphere should be determined for the particular area in which sampling is planned. Instrument manufacturers' specifications should list the magnitude of interference by specific gases. [References 16, 17]

This method is used for the continuous automatic sampling, analyzing, and recording of SO₂ concentrations in outside ambient air in the concentration range

from 0.01 to 2 ppm. The upper limit may vary from 1 to 5 ppm, depending upon reagent flow and airflow rates and on electronic amplification. Air is continuously admitted to the absorber where the SO₂ in the airstream is absorbed and oxidized by a liquid absorbent. The electrical conductivity of the resulting solution is continuously measured and recorded, and the readings obtained are proportional to the concentration of SO₂ in the sampled air.

REAGENTS

All chemicals used must be ACS analytical reagent grade.

The distilled water must conform to the ASTM D1193 standard for nonreferee reagent water.

Absorbing solution – Prepare a distilled water solution containing 3×10^{-3} molar hydrogen peroxide (H₂O₂) and 5×10^{-5} normal sulfur acid (H₂SO₄). Two milligrams per liter of Dovicide B (2,4,5, trichlorophenate) or the equivalent are added to prevent algae growth. A nonionic wetting agent is added to aid in the wetting of the reaction chamber of the monitoring instrument.

Before use, the solution must be analyzed to verify the reagent strength. The pH must be 4.2–4.8. The hydrogen peroxide concentration must be at least 3×10^{-3} molar. A suggested analytical method for peroxide is a potassium permanganate titration in strongly acid solution.

Absorbing solution preparation – Transfer 19 liters of distilled water to a suitable container such as a 5 gallon plastic bottle. Add 10.0 mls of 0.1 normal sulfuric acid, 4.2 mls of 30 percent hydrogen peroxide, 8.0 mls of Kodak 200B nonionic wetting agent and 10 mls of a 0.36 percent Dovicide B solution. Mix thoroughly and analyze for reagent strength. Other volumes can be prepared by adjusting the reagent quantities proportionally.

Reagent specificity – The acid in this particular reagent is for the purpose of maintaining the described pH and thus limiting interferences from acid gases. The acidified hydrogen peroxide absorbing reagent of pH 4.2–4.8 limits CO₂, H₂S, and oxides of nitrogen interference as well as accelerating the absorption of SO₂. The SO₂ is removed from the reaction zone by the peroxide oxidation to sulfate. This process also produces two hydrogen ions per molecule of SO₂ absorbed, which adds significantly to the reagent conductance. The oxidation step is specific to SO₂, and the overall electro conductivity response to SO₂ is many times greater than that of the nitrogen oxides, CO₂, and H₂S. [Reference 16]

APPARATUS (Figure 5)

Sampling probe – The sampling probe can be made of pyrex glass, 316 stainless steel or teflon. The intake end is equipped with a rain loop, and a loose glass wool filter is added to remove large particulate matter. This filter is positioned indoors, and, if necessary, inside the thermostatically controlled cabinet to prevent condensation of water vapor. The air sampling line, including the probe, should be kept as short as possible and still meet station requirements.

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Absorber – A venturi scrubber or any reagent-air-contacting system capable of an absorbing efficiency of at least 98 percent for all SO₂ concentrations is acceptable.

Air flow equipment – Use a flowmeter, needle valve, or other device capable of regulating flows with an accuracy of ± 2 percent. A suitable device is recommended to continuously record the air flow rate on the conductivity recorder chart or shut off data input completely should error exceed ± 2 percent of normal air flow.

Absorbing reagent flow – Use a metering pump, flowmeter, or other device capable of measuring flows with an accuracy of ± 2 percent.

Pumps and metering devices – Air pumps and liquid metering devices must be variable and capable of the continuous accuracy described in air and reagent flow.

Instrument temperature control –

(1) Thermostatically controlled cabinet – The reagent feed lines, absorption column and conductivity cells shall be enclosed in an insulated compartment, with thermostatically maintained temperature control to $\pm 1^\circ\text{F}$.

(2) Unheated cabinet – Instruments not equipped with temperature controlled cabinets must have conductivity cells incorporating thermistor compensation for temperature variation. The area in which the sampler is located must be free from large temperature changes.

Conductivity electrodes – Two pairs of platinum dip electrodes are most commonly used. One pair measures the conductivity of the unreacted reagent and the other pair measures the conductivity of the reacted reagent.

Conductivity recorder – Any instrument capable of recording the differential output of the conductivity cells in the SO₂ concentration range of zero to 2 ppm with an accuracy of ± 1 percent of full scale is acceptable. The recorder should use chart paper of sufficient grid accuracy to determine a 24-hour average concentration of 0.05 ppm SO₂, on the 0–1 ppm full scale range.

Reagent reservoir – Any inert container with sufficient volume to contain up to one week's supply of reagent can be used. The reagent must be protected from air pollutants by attaching soda lime and charcoal filters or the equivalent to the air inlet line.

Electronic check – A means of checking by electrical impedance is recommended for all SO₂ analyzers. Checks of 25 percent and 75 percent are acceptable. Insertion of such a device may be manual or automatic. This shall be used only to check accuracy of the electronics and is not a substitute for dynamic calibration.

Zero reference – A zero reference shall be made at least twice weekly. This will be accomplished by diversion of the normal sample stream through a filter capable of removing all traces of sulfur dioxide. This zero reference shall be stable to $\pm .005$ ppm for thirty minutes. Air and liquid flow rates shall indicate no greater than ± 2 percent change during such a check period.

INSTRUMENT CALIBRATION PROCEDURES

Static calibration method – The instrument should be statistically calibrated with sulfuric acid solutions of known composition corresponding to atmospheric SO₂

concentrations covering the range of the instrument. For a 0–2 ppm instrument, calibration solutions corresponding to 0.5, 1.0, 1.5, and 2.0 ppm SO₂ are prepared by the addition of calculated amounts of dilute H₂SO₄ to the absorbing reagent. This method does not take into consideration absorption column efficiency and other factors; therefore, it cannot be used as a substitute for dynamic calibration but shall be done semiannually in conjunction with the dynamic calibration.

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Establish instrument zero by introducing the unexposed absorbing reagent in both the reference and sample conductivity cells. Calibration solutions are then substituted for the absorbing reagent in the sample conductivity cell. After normal operating temperatures and liquid flow rates have been established for each reference point, compare and record the instrument reading with the calibration solution equivalent SO₂ concentration. Adjust the instrument by means of the span control to indicate the correct concentration. Sulfur dioxide free air is now introduced directly into the system, as in normal operation. Air, free of sulfur dioxide, can be obtained by passing it through activated charcoal and soda lime. Adjust the instrument again, if necessary. A minimum of four reference points shall be recorded.

Do not adjust the span of temperature controlled instruments until the cabinet temperature has remained constant for at least 15 minutes.

Dynamic calibration method – The dynamic calibration methods take into account the collection efficiency of the absorbing column under standard flow conditions and shall be performed semiannually along with static calibrations. Contact column changes will require dynamic and static recalibration. Conductivity cell replacement or replatinization requires only the static calibration reference.

Standard air-SO₂ mixtures may be prepared in a compressed gas cylinder, an inert collapsible plastic bag or a temperature controlled permeation tube chamber. The gas mixtures from these containers are introduced directly into the monitoring instrument for calibration purposes.

Standard SO₂-air dilutions can be obtained commercially in compressed gas cylinders. (Most states have regulations regarding unlicensed pressurization of steel vessels.)

Collapsible inert plastic bags can be used by introducing a measured amount of SO₂ with a gas syringe. A measured amount of filtered air or nitrogen is then added to give the desired concentration.

The temperature controlled permeation chamber is the preferred method of obtaining standard SO₂-air dilutions. This method is discussed in full under "preparation of standard curve" in the "manual sampling and analysis procedures" section.

The standard air-SO₂ mixture can be introduced simultaneously into the analyzer and the manual absorber. The instrument record is then adjusted to read SO₂ concentrations as determined by the manual method. A typical dynamic calibration system is shown in Figure 4.

CALIBRATION PROCEDURE

A complete examination of the monitoring instrument must be made to verify that it is in optimum operating condition before calibration. This examination must include:

- (1) The cleanliness of glass parts – all must be clean.
- (2) Verification of air and liquid flow meter calibration information.
- (3) An electrical impedance check – used fixed resistance to assure that the instrument meets the manufacturer's specification.

[Beginning of original Page 13 of Appendix I]

(4) Checks of electronic tubes – replace those that have been used for six months or more.

(5) The recorder – verify that it gives a linear response and has had routine maintenance.

(6) All mechanical parts – verify that they are operating smoothly.

(7) Sample lines – replace if they are leaking, not clean or appear that they may fail because of age or other factors.

(8) Instrument maintenance – verify that the instrument has been maintained in accordance with the manufacturer's specification.

(9) Zero reference – the zero reference must be held for at least 30 minutes before calibration.

(10) The absorbing solution – it must show a pH of 4.2–4.8 and an H_2O_2 concentration of 3×10^{-3} molar. When it is installed in the instrument, all air bubbles that may collect in the reagent feed line must be removed.

(11) Instrument temperature – the temperature equilibrium must be $\pm 1^\circ\text{F}$.

(12) Air and liquid flow – both must be in equilibrium before calibration is started.

The calibration of the monitoring instrument with standard air-SO₂ mixtures must include the following:

(1) The chart reading must agree with ± 1 percent of the standard atmosphere concentration as determined by the manual sampling and analysis section of this method.

(2) A minimum of four reference points in the regions of 10, 25, 50, and 100 percent of the full chart scale must be determined to plot an instrument response curve.

(3) The instrument response to a standard air-SO₂ mixture must be maintained for a minimum of 15 minutes at each reference point.

INSTRUMENT PERFORMANCE SPECIFICATIONS

(1) Instruments shall be capable of operation with a full scale range of 0–1 ppm with an adjustment for higher ranges if required.

(2) **Zero reproducibility** of ± 1 percent full-scale deflection over a 24-hour period.

(3) **Linearity** – for any sample and range, the analyzer shall give a recorded response which is within ± 2 percent of full scale of a linear response to that sample. Reproducibility shall be ± 2 percent of full scale for successive identical samples.

(4) **Span drift** – the distance between the recorded zero point on any range shall not drift by more than ± 1 percent of full scale in 24 hours.

(5) **Effect of zero and span adjustments** – a 5 percent manual adjustment of zero shall not change the span (the difference between zero point and span point) of the instrument by more than 1 percent of full scale. A 5 percent manual adjustment of span shall not change the zero point more than 1 percent of full scale. Attenuation from one range to another shall not cause the recorded zero point to move by more than 1 percent of full scale.

(6) **Warm-up time** – the analyzer shall be operating within specifications within one hour after connection to a source of power.

(7) **Noise level** – shall not exceed 1 percent of any operating range (peak to peak).

(8) **Effect of temperature and voltage** – the analyzer shall maintain all specifications while operating within a surrounding air temperature of 30°–120°F and subjected to line voltage variations of 95–125 volts AC.

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(9) **Speed of response** – an analyzer shall indicate 90 percent of the final reading one minute after the concentration at the instrument inlet has been changed.

(10) **Interference** – shall be specified by gas, related range of concentration in the atmosphere, and percent of span interference for a sulfur dioxide range 0–2.0 ppm.

FOOTNOTES

(Collected notes)

- [a] *Available from Harleco. Hartman-Leddon Company, Philadelphia, Pennsylvania, 19143.
- [b] *If a cell path length of 1-inch is used for absorbance measurement of the developed color, dilute 1 ml of the standard sulfite solution to 100 mls with 0.04 M TCM.
- [c] (a) Available from Metronics, Inc., 3201 Porter Drive, Palo Alto, California, 94304, and Polyscience Corporation, 909 Pitner Avenue, Evanston, Illinois, 26202.
- [d] (a) The tube must be temperature equilibrated in the permeation chamber for at least four hours and preferably overnight.
- [e] (b) Clean dry air may also be prepared by passing ambient air from a relatively uncontaminated outside source through absorption tubes packed with activated carbon and soda-lime followed in series by an efficient fibre glass filter.

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Permeation tube schematic for laboratory use

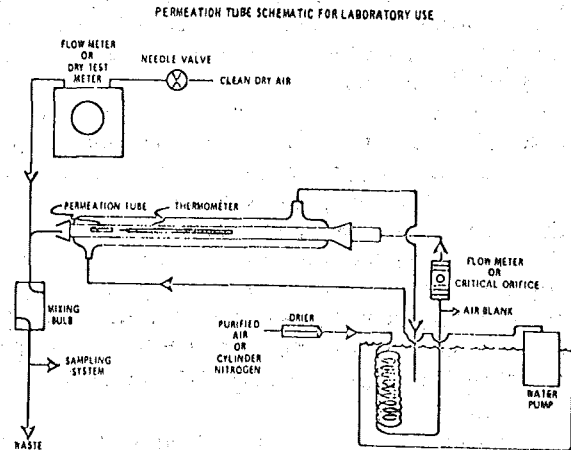


Figure 1—Gas dilution system for preparation of standard concentrations of sulfur dioxide for laboratory use by the permeation tube method.

Permeation tube schemata for field use

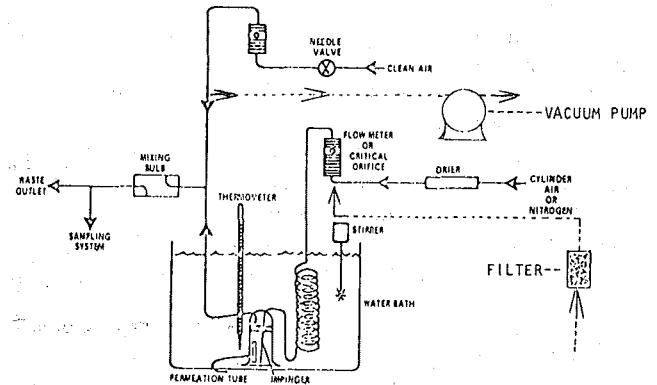


Figure 2—Gas dilution system for preparation of standard concentrations of sulfur dioxide for field use by the permeation tube method.

Dotted lines — Optional vacuum system

Filter — Low pressure soda lime/activated charcoal

[Beginning of original Page 16 of Appendix I]
Calibrated permeation tube gas condensing apparatus

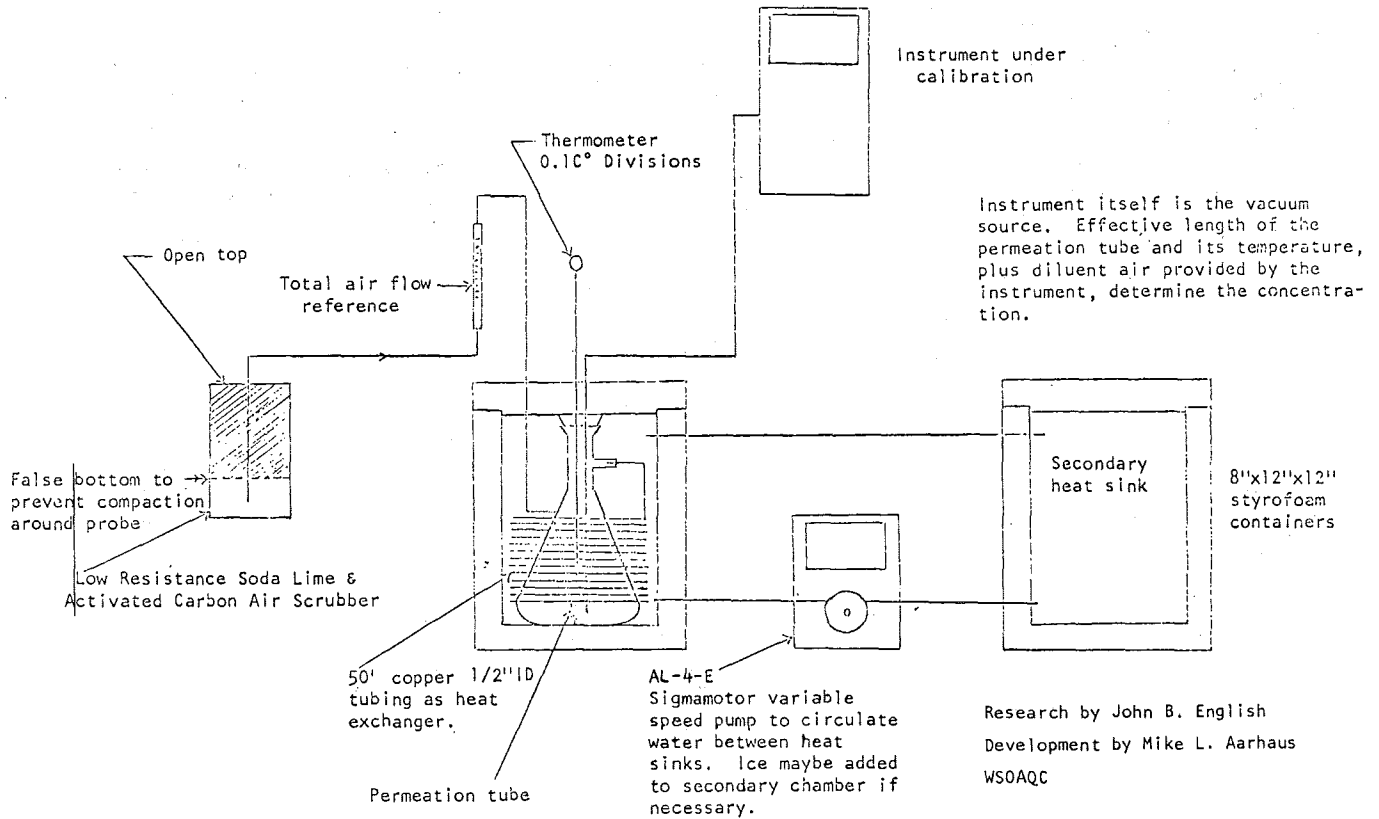
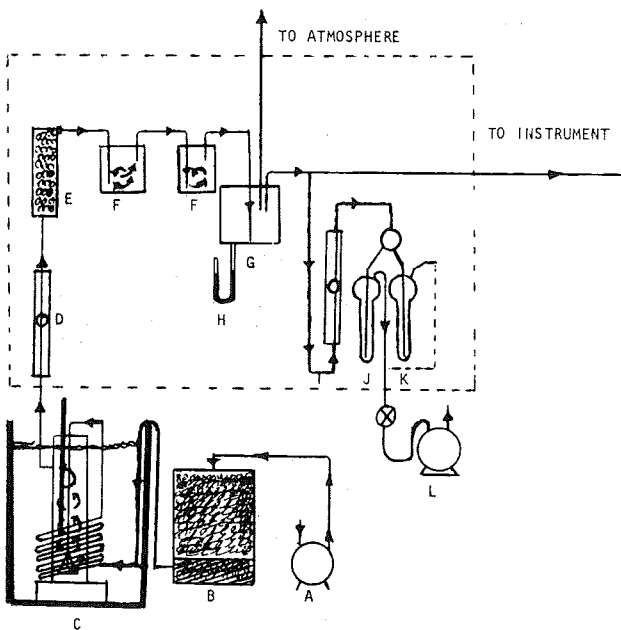


Figure 3

NOTE: The method is limited to total flow sampling procedure because of the inadequate gas mixing characteristics of the system.

[Beginning of original Page 17 of Appendix I]



- A. Pump – providing flow through scrubber. Temperature, bath, and calibration panel.
- B. Chemical scrubber – 8-12 mesh soda lime or equivalent (top) glass wool particulate filter (bottom) providing dry SO₂ free air
- C. Circulating water bath controlled to 0.1°C. Permeation chamber (Greenburg-Smith Impinger) thermometer inside 50' coiled copper tubing inline with gas stream from scrubber to impinger to temperature condition gas sample.
- D. Variable area flowmeter (total volume flow reference)
- E. Glass column packed with helices (teflon or glass) for initial mixing (optional)
- F. Mixing chambers
- G. Sampling chamber (vented to atmosphere)
- H. Manometer (1/4" water column positive pressure)
- I. Variable area rate meter for impinger flow reference
- J. Ballast impinger to maintain dynamic flow to impinger system though wet chemistry sample is not being taken.
- K. Sample impinger (vacuum source transferred from one impinger to another)
- L. Vacuum pump

Figure 4—Dynamic gas dispensing system.

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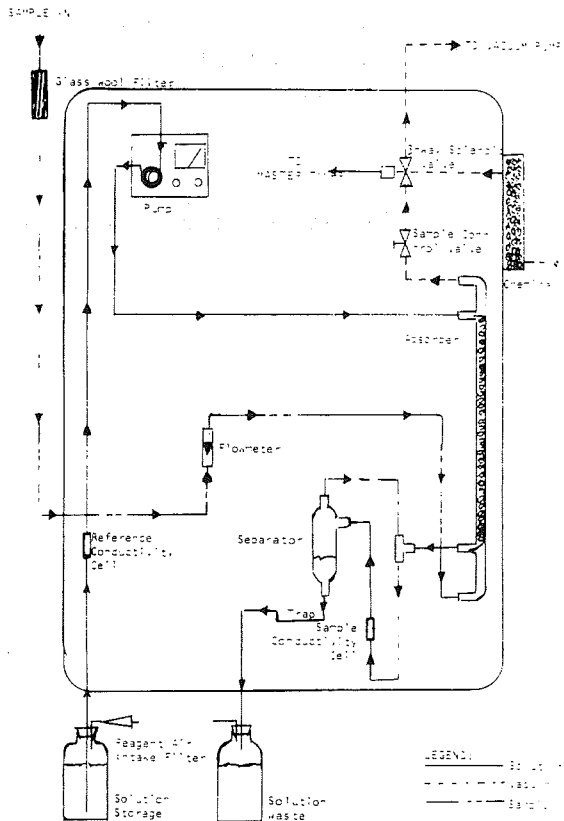


Figure 5—General flow diagram for sulfur dioxide analyzer

[Order 13, Appendix 1—Part 1 and 2 (codified as WAC 18-56-990), filed 5/18/70.]