METHOD 111) DETERMINATION OF POLONIUM-210 EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in appendix A to 40 CFR Part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Application.

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Polonium	7440-08-6	Not specified

1.2 Applicability. This method is applicable for the determination of the polonium-210 content of particulate matter samples collected from stationary source exhaust stacks, and for the use of these data to calculate polonium-210 emissions from individual sources and from all affected sources at a facility.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method.

A particulate matter sample, collected according to Method 5, is analyzed for polonium-210 content: the polonium-210 in the sample is put in solution, deposited on a metal disc, and the radioactive disintegration rate measured. Polonium in acid solution spontaneously deposits on surfaces of metals that are more electropositive than polonium. This principle is routinely used in the radiochemical analysis of polonium-210. Data reduction procedures are provided, allowing the calculation of polonium-210 emissions from individual sources and from all affected sources at a facility, using data obtained from Methods 2 and 5 and from the analytical procedures herein.

3.0 Definitions. [Reserved]

4.0 Interferences. [Reserved]

5.0 Safety.

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test

method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Nitric Acid (HNO_3). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia,

or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

   5.2.4 Perchloric Acid ($HClO_4$). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing $HClO_4$ only in hoods specifically designed for $HClO_4$.

6.0 Equipment and Supplies.

   6.1 Alpha Spectrometry System. Consisting of a multichannel analyzer, biasing electronics, silicon surface barrier detector, vacuum pump and chamber.

   6.2 Constant Temperature Bath at 85 °C (185 °F).

   6.3 Polished Silver Discs. 3.8 cm diameter, 0.4 mm thick with a small hole near the edge.

   6.4 Glass Beakers. 400 ml, 150 ml.

   6.5 Hot Plate, Electric.

   6.6 Fume Hood.

   6.7 Teflon Beakers, 150 ml.

   6.8 Magnetic Stirrer.

   6.9 Stirring Bar.

6.10 Hooks. Plastic or glass, to suspend plating discs.

6.11 Internal Proportional Counter. For measuring alpha particles.

6.12 Nucleopore Filter Membranes. 25 mm diameter, 0.2 micrometer pore size or equivalent.

6.13 Planchets. Stainless steel, 32 mm diameter with 1.5 mm lip.

6.14 Transparent Plastic Tape. 2.5 cm wide with adhesive on both sides.

6.15 Epoxy Spray Enamel.

6.16 Suction Filter Apparatus. For 25 mm diameter filter.

6.17 Wash Bottles, 250 ml capacity.

6.18 Graduated Cylinder, plastic, 25 ml capacity.

6.19 Volumetric Flasks, 100 ml, 250 ml.

7.0 *Reagents and Standards.*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Ascorbic Acid.

7.2 Ammonium Hydroxide (NH$_4$OH), 15 M.

7.3 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91 (incorporated by reference - see § 61.18), Type 3. Use in all dilutions requiring water.

7.4 Ethanol (C$_2$H$_5$OH), 95 percent.

7.5 Hydrochloric Acid, 12 M.

7.6 Hydrochloric Acid, 1 M. Dilute 83 ml of the 12 M HCl to 1 liter with distilled water.

7.7 Hydrofluoric Acid, 29 M.

7.8 Hydrofluoric Acid, 3 M. Dilute 52 ml of the 29 M HF to 500 ml with distilled water. Use a plastic graduated cylinder and storage bottle.

7.9 Lanthanum Carrier, 0.1 mg La^{+3}/ml. Dissolve 0.078 gram lanthanum nitrate, La(NO$_3$)$_3$·6H$_2$O in 250 ml of 1 M HCl.

7.10 Nitric Acid, 16 M.

7.11 Perchloric Acid, 12 M.

7.12 Polonium-209 Solution.

7.13 Silver Cleaner. Any mild abrasive commercial silver cleaner.

7.14 Degreaser.

7.15 Standard Solution. Standardized solution of an alpha-emitting actinide element, such as plutonium-239 or americium-241.

8.0 Sample Collection, Preservation, Transport, and

Storage. [Reserved]

9.0 Quality Control

9.1 General Requirement.

9.1.1 All analysts using this method are required to demonstrate their ability to use the method and to define their respective accuracy and precision criteria.

9.2 Miscellaneous Quality Control Measures.

Section	Quality Control Measure	Effect
10.1	Standardization of alpha spectrometry system	Ensure precision of sample analyses
10.3	Standardization of internal proportional counter	Ensure precise sizing of sample aliquot
11.1, 11.2	Determination of procedure background and instrument background	Minimize background effects
11.3	Audit sample analysis	Evaluate analyst's technique

10.0 Calibration and Standardization.

10.1 Standardization of Alpha Spectrometry System.

10.1.1 Add a quantity of the actinide standard solution to a 100 ml volumetric flask so that the final concentration when diluted to a volume of 100 ml will be approximately 1 pCi/ml.

10.1.2 Add 10 ml of 16 M HNO_3 and dilute to 100 ml with water.

10.1.3   Add 20 ml of 1 M HCl to each of six 150 ml beakers. Add 1.0 ml of lanthanum carrier, 0.1 mg lanthanum per ml, to the acid solution in each beaker.

10.1.4   Add 1.0 ml of the 1 pCi/ml working solution (from Section 10.1.1) to each beaker. Add 5.0 ml of 3 M HF to each beaker.

10.1.5   Cover beakers and allow solutions to stand for a minimum of 30 minutes. Filter the contents of each beaker through a separate filter membrane using the suction filter apparatus. After each filtration, wash the filter membrane with 10 ml of distilled water and 5 ml of ethanol, and allow the filter membrane to air dry on the filter apparatus.

10.1.6   Carefully remove the filter membrane and mount it, filtration side up, with double-side tape on the inner surface of a planchet. Place planchet in an alpha spectrometry system and count each planchet for 1000 minutes.

10.1.7   Calculate the counting efficiency of the detector for each aliquot of the 1 pCi/ml actinide working solution using Eq. 111-1 in Section 12.2.

10.1.8   Determine the average counting efficiency of the detector, E_c, by calculating the average of the six determinations.

10.2 Preparation of Standardized Solution of Polonium-209.

10.2.1 Add a quantity of the Po-209 solution to a 100 ml volumetric flask so that the final concentration when diluted to a 100 ml volume will be approximately 1 pCi/ml.

10.2.2 Follow the procedures outlined in Sections 10.1.2 through 10.1.6, except substitute 1.0 ml of polonium-209 tracer solution (Section 10.2.1) and 3.0 ml of 15 M ammonium hydroxide for the 1 pCi/ml actinide working solution and the 3 M HF, respectively.

10.2.3 Calculate the activity of each aliquot of the polonium-209 tracer solution using Eq. 111-2 in Section 12.3.

10.2.4 Determine the average activity of the polonium-209 tracer solution, F, by averaging the results of the six determinations.

10.3 Standardization of Internal Proportional Counter

10.3.1 Add a quantity of the actinide standard solution to a 100 ml volumetric flask so that the final concentration when diluted to a 100 ml volume will be approximately 100 pCi/ml.

10.3.2 Follow the procedures outlined in Sections 10.1.2 through 10.1.6, except substitute the 100 pCi/ml

actinide working solution for the 1 pCi/ml solution, place
the planchet in an internal proportional counter (instead of
an alpha spectrometry system), and count for 100 minutes
(instead of 1000 minutes).

10.3.3 Calculate the counting efficiency of the
internal proportional counter for each aliquot of the 100
pCi/ml actinide working solution using Eq. 111-3 in 12.4.

10.3.4 Determine the average counting efficiency of
the internal proportional counter, E_I, by averaging the
results of the six determinations.

11.0 Analytical Procedure.

NOTE: Perform duplicate analyses of all samples,
including background counts, quality assurance audit
samples, and Method 5 samples. Duplicate measurements are
considered acceptable when the difference between them is
less than two standard deviations as described in EPA
600/4-77-001 or subsequent revisions.

11.1 Determination of Procedure Background.
Background counts used in all equations are determined by
performing the specific analysis required using the
analytical reagents only. All procedure background counts
and sample counts for the internal proportional counter
should utilize a counting time of 100 minutes; for the alpha

spectrometry system, 1000 minutes. These background counts should be performed no less frequently than once per 10 sample analyses.

11.2 Determination of Instrument Background. Instrument backgrounds of the internal proportional counter and the alpha spectrometry system should be determined on a weekly basis. Instrument background should not exceed procedure background. If this occurs, it may be due to a malfunction or contamination, and should be corrected before use.

11.3 Quality Assurance Audit Samples. An externally prepared performance evaluation sample shall be analyzed no less frequently than once per 10 sample analyses, and the results reported with the test results.

11.4 Sample Preparation. Treat the Method 5 samples [*i.e.,* the glass fiber filter (Container No. 1) and the acetone rinse (Container No. 2)] as follows:

11.4.1 Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a 150-ml Teflon beaker.

11.4.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount

of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Transfer the contents to a 400-ml glass beaker. Add polonium-209 tracer solution to the glass beaker in an amount approximately equal to the amount of polonium-210 expected in the total particulate sample. Record the activity of the tracer solution added. Add 16 M nitric acid to the beaker to digest and loosen the residue.

11.4.3 Transfer the contents of the glass beaker to the Teflon beaker containing the glass fiber filter. Rinse the glass beaker with 16 M HNO_3. If necessary, reduce the volume in the beaker by evaporation until all of the nitric acid HNO_3 from the glass beaker has been transferred to the Teflon beaker.

11.4.4 Add 30 ml of 29 M HF to the Teflon beaker and evaporate to near dryness on a hot plate in a properly operating hood.

NOTE: Do not allow the residue to go to dryness and overheat; this will result in loss of polonium.

11.4.5 Repeat step 11.4.4 until the filter is dissolved.

11.4.6 Add 100 ml of 16 M HNO_3 to the residue in the Teflon beaker and evaporate to near dryness.

NOTE: Do not allow the residue to go to dryness.

11.4.7 Add 50 ml of 16 M HNO_3 and 10 ml of 12 M perchloric acid to the Teflon beaker and heat until dense fumes of perchloric acid are evolved.

11.4.8 Repeat steps 11.4.4 to 11.4.7 as necessary until sample is completely dissolved.

11.4.9 Add 10 ml of 12 M HCl to the Teflon beaker and evaporate to dryness. Repeat additions and evaporations several times.

11.4.10 Transfer the sample to a 250-ml volumetric flask and dilute to volume with 3 M HCl.

11.5 Sample Screening. To avoid contamination of the alpha spectrometry system, check each sample as follows:

11.5.1 Add 20 ml of 1 M HCl, 1 ml of the lanthanum carrier solution (0.1 mg La/ml), a 1 ml aliquot of the sample solution from Section 11.4.10, and 3 ml of 15 M ammonium hydroxide to a 250-ml beaker in the order listed. Allow this solution to stand for a minimum of 30 minutes.

11.5.2 Filter the solution through a filter membrane using the suction filter apparatus. Wash the filter membrane with 10 ml of water and 5 ml of ethanol, and allow the filter membrane to air dry on the filter apparatus.

11.5.3 Carefully remove the filter membrane and mount it, filtration side up, with double-side tape on the inner surface of a planchet. Place the planchet in an internal proportional counter, and count for 100 minutes.

11.5.4 Calculate the activity of the sample using Eq. 111-4 in Section 12.5.

11.5.5 Determine the aliquot volume of the sample solution from Section 11.4.10 to be analyzed for polonium-210 , such that the aliquot contains an activity between 1 and 4 picocuries. Use Eq. 111-5 in Section 12.6.

11.6 Preparation of Silver Disc for Spontaneous Electrodeposition.

11.6.1 Clean both sides of the polished silver disc with silver cleaner and with degreaser.

11.6.2 Place disc on absorbent paper and spray one side with epoxy spray enamel. This should be carried out in a well-ventilated area, with the disc lying flat to keep paint on one side only. Allow paint to dry for 24 hours before using disc for deposition.

11.7 Sample Analysis.

11.7.1 Add the aliquot of sample solution from Section 11.4.10 to be analyzed for polonium-210, the volume of which was determined in Section 11.5.5, to a suitable

200-ml container to be placed in a constant temperature bath.

   NOTE: Aliquot volume may require a larger container.

   11.7.2 If necessary, bring the volume to 100 ml with 1 M HCl. If the aliquot volume exceeds 100 ml, use total aliquot.

   11.7.3 Add 200 mg of ascorbic acid and heat solution to 85 °C (185 °F) in a constant temperature bath.

   11.7.4 Suspend a silver disc in the heated solution using a glass or plastic rod with a hook inserted through the hole in the disc. The disc should be totally immersed in the solution, and the solution must be stirred constantly, at all times during the plating operation. Maintain the disc in solution for 3 hours.

   11.7.5 Remove the silver disc, rinse with deionized distilled water, and allow to air dry at room temperature.

   11.7.6 Place the disc, with deposition side (unpainted side) up, on a planchet and secure with double-side plastic tape. Place the planchet with disc in alpha spectrometry system and count for 1000 minutes.

12.0 Data Analysis and Calculations.

   12.1 Nomenclature.

A = picocuries of polonium-210 in the Method 5 sample (from Section 12.8).

A_A = picocuries of actinide added.

A_L = volume of sample aliquot used, in ml (specified in Section 11.5.1 as 1 ml).

A_S = aliquot to be analyzed, in ml.

B_B = procedure background counts measured in polonium-209 spectral region.

B_T = polonium-209 tracer counts in sample.

C_T = total counts in polonium-210 spectral region.

D = decay correction for time "t" (in days) from sample collection to sample counting, given by: $D=e^{-0.005t}$

E_C = average counting efficiency of detector (from Section 10.1.8), as counts per disintegration.

E_{Ci} = counting efficiency of the detector for aliquot i of the actinide working solution, counts per disintegration.

E_I = average counting efficiency of the internal proportional counter, as determined in Section 10.3.4, counts per disintegration.

E_{Ii} = counting efficiency of the internal proportional counter for aliquot i of the 100 pCi/ml actinide working solution, counts per disintegration.

E_Y = the fraction of polonium-209 recovered on the planchet (from Section 12.7).

F = average activity of polonium-209 in sample (from Section 10.2.4), in pCi.

F_i = activity of aliquot i of the polonium-209 tracer solution, in pCi.

L = dilution factor (unitless). This is the volume of sample solution prepared (specified as 250 ml in Section 11.1.10) divided by the volume of the aliquot of sample solution analyzed for polonium-210 (from Section 11.7.1).

M_i = phosphorous rock processing rate of the source being tested, during run i, Mg/hr.

M_k = phosphate rock processed annually by source k, in Mg/yr.

n = number of calciners at the elemental phosphorus plant.

P = total activity of sample solution from Section 11.4.10, in pCi (see Eq. 111-4).

Q_{sd} = volumetric flow rate of effluent stream, as determined by Method 2, in dscm/hr.

S = annual polonium-210 emissions from the entire facility, in curies/yr.

$V_{m(std)}$ = volume of air sample, as determined by Method 5, in dscm.

X_k = emission rate from source k, from Section 12.10, in curies/Mg.

10^{-12} = curies per picocurie.

2.22 = disintegrations per minute per picocurie.

250 = volume of solution from Section 11.4.10, in ml.

12.2 Counting Efficiency. Calculate the counting efficiency of the detector for each aliquot of the 1 pCi/ml actinide working solution using Eq. 111-1.

$$E_{Ci} = \frac{C_S - C_B}{2.22\ A_A\ T} \qquad \textbf{Eq. 111-1}$$

where:

C_B = background counts in same peak area as C_S.

C_S = gross counts in actinide peak.

$T \quad = \quad$ counting time in minutes, specified in Section 10.1.6 as 1000 minutes.

12.3   Polonium-209 Tracer Solution Activity. Calculate the activity of each aliquot of the polonium-209 tracer solution using Eq. 111-2.

$$F_i = \frac{C_S - C_B}{2.22 \; E_{Ci} \; T} \qquad \textbf{Eq. 111-2}$$

where:

$C_B \quad = \quad$ background counts in the 4.88 MeV region of spectrum the in the counting time T.

$C_S \quad = \quad$ gross counts of polonium-209 in the 4.88 MeV region of the spectrum in the counting time T.

$T \quad = \quad$ counting time, specified in Section 10.1.6 as 1000 minutes.

12.4   Control Efficiency of Internal Proportional Counter.   Calculate the counting efficiency of the internal proportional counter for each aliquot of the 100 pCi/ml actinide working solution using Eq. 111-3.

$$E_{Ii} = \frac{C_S - C_B}{2.22 \; A_A \; T} \qquad \textbf{Eq. 111-3}$$

where:

C_B = gross counts of procedure background.

C_S = gross counts of standard.

T = counting time in minutes, specified in Section 10.3.2 as 100 minutes.

12.5 Calculate the activity of the sample using Eq. 111-4.

$$P = \frac{250 \ (C_S - C_B)}{2.22 \ \overline{E_I} \ A_L \ T}$$ **Eq. 111-4**

where:

C_B = total counts of procedure background. (See Section 11.1).

C_S = total counts of screening sample.

T = counting time for sample and background (which must be equal), in minutes (specified in Section 11.5.3 as 100 minutes).

12.6 Aliquot Volume. Determine the aliquot volume of the sample solution from Section 11.4.10 to be analyzed for polonium-210 , such that the aliquot contains an activity between 1 and 4 picocuries using Eq. 111-5.

$$A_S = \frac{250 \ (\text{desired picocuries in aliquot})}{P}$$ **Eq.111-5**

12.7 Polonium-209 Recovery. Calculate the fraction of polonium-209 recovered on the planchet, E_Y, using Eq. 111-6.

$$E_Y = \frac{B_T - B_B}{2.22\ \overline{F}\ \overline{E_C}\ T} \qquad \textbf{Eq. 111-6}$$

where:

T   =   counting time, specified in Section 11.1 as 1000 minutes.

12.8 Polonium-210 Activity. Calculate the activity of polonium-210 in the Method 5 sample (including glass fiber filter and acetone rinse) using Eq. 111-7.

$$A = \frac{(C_T - C_B)\ L}{2.22\ E_Y\ \overline{E_C}\ T\ D} \qquad \textbf{Eq. 111-7}$$

where:

C_B =   procedure background counts in polonium-210 spectral region.

T   =   counting time, specified in Section 11.1 as 1000 minutes for all alpha spectrometry sample and background counts.

12.9 Emission Rate from Each Stack.

12.9.1 For each test run, i, on a stack, calculate the measured polonium-210 emission rate, R_{Si}, using Eq. 111-8.

$$R_{Si} = \frac{(10^{-12}) \, A \, Q_{sd}}{V_{m(std)} \, M_i}$$

Eq. 111-8

12.9.2 Determine the average polonium-210 emission rate from the stack, R_S, by taking the sum of the measured emission rates for all runs, and dividing by the number of runs performed.

12.9.3 Repeat steps 12.9.1 and 12.9.2 for each stack of each calciner.

12.10 Emission Rate from Each Source. Determine the total polonium-210 emission rate, X_k, from each source, k, by taking the sum of the average emission rates from all stacks to which the source exhausts.

12.11 Annual Polonium-210 Emission Rate from Entire Facility. Determine the annual elemental phosphorus plant emissions of polonium-210, S, using Eq. 111-9.

$$S = \frac{\sum_{k=1}^{n} (X_k \, M_k)}{n}$$

Eq. 111-9

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References.

1. Blanchard, R.L. "Rapid Determination of Lead-210 and Polonium-210 in Environmental Samples by Deposition on Nickel." Anal. Chem., <u>38</u>:189, pp. 189-192. February 1966.

17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]