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PROCEDURE FOR COLLECTION AND ANALYSIS OF AMMONIA IN STATIONARY SOURCES

Conditional Test Method (CTM-027)

This method has been validated at a coal-fired boiler at a power plant (call Rima Howell at (919) 541-0443 if you'd like a copy of the validation report) using the procedures in Test Method 301 (40 CFR Part 63, Appendix A). Use of this method at other sources is not recommended without proper validation.

1.0 SAMPLING EQUIPMENT AND SUPPLIES

1.1 Sampling Train

A Method 17 sampling train is required to collect the ammonia samples. This system is described in 40 CFR Part 60, Appendix A, and in the EPA *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III - Stationary Source Specific Methods*, Section 3.11, January, 1982 (EPA-600/4-77-027b). Figure 17-3 of 40 CFR 60, Appendix A, may be modified for use as a data sheet. Method 17 train components specified for collection and measurement of ammonia are as follows:

1.1.1 Probe Liner - Use borosilicate or quartz glass tubing, enclosed in a stainless steel sheath.

1.1.2 Probe Nozzle - Use a borosilicate or quartz glass nozzle. The design should have a sharp, tapered edge, and be formed in a button-hook or elbow configuration. Since isokinetic sampling is required, a range of interior diameter nozzles should be available to accommodate various stack flows.

1.1.3 Pitot Tube - Use a type S design, meeting the requirements of EPA Method 2 (40 CFR Part 60, Appendix A).

1.1.4 Differential Pressure Gauge - Use an inclined manometer or an equivalent device. Two are required, one to monitor stack pressure, and the other to monitor the orifice pressure differential.

1.1.5 In-Stack Filter Holder and Filter - A filter holder made of borosilicate glass or Teflon, a filter support (with a selection of gaskets such as silicone rubber, Teflon, or Viton, each capable of withstanding stack gas temperature), and a glass fiber filter are

required.

1.1.7 Impingers - Two Greenburg-Smith (G-S) impingers and two impingers with the tips removed are required. They are connected in series and all are immersed in an ice bath. The first G-S impinger assembly downstream of the filter holder is charged with 100 mL of 0.1N sulfuric acid (H_2SO_4) solution; the second G-S assembly also contains 100 mL of 0.1N sulfuric acid (H_2SO_4) solution; the third impinger has the tip removed and the container is either empty or contains 100 mL 0.1N H_2SO_4 (depending on the need to prevent breakthrough due to high ammonia concentrations and/or high flowrate requirement); and the fourth assembly, also with the impinger tip cut off, contains a pre-weighed amount (200 to 300 g) of indicating silica gel.

1.1.8 Metering System - The metering system is composed of a vacuum gauge, vacuum pump, thermometers accurate to ±3°C from 0 to 90°C (±6°F from 32 to 194°F) to measure gas temperatures entering and exiting the dry gas meter, a dry gas meter (accurate to 2 percent), and related tubing, fittings, and gauges. When used with a pitot tube, the metering system should allow verification that sampling is isokinetic and be adjustable to maintain isokinetic conditions.

1.2 Sample Recovery Apparatus

1.2.1 Wash Bottles - Two polyethylene wash bottles are needed. One contains deionized water for rinsing out droplets of impinger solution that adhere to impinger vessels and their connecting glassware after the solution has been poured into sample bottles. It is also used to rinse the interiors of the probe and the filter holder at the end of a sampling session. The second bottle contains reagent-grade acetone to rinse and speed the air drying of the water-rinsed components. NOTE: Do not add the acetone to the water rinses. Do not store acetone in plastic bottles; keep it in a glass container and transfer it to the plastic wash bottle when needed.

1.2.2 Graduated Cylinders - Glass or high-density polyethylene (HDPE) graduated cylinders to measure the volumes of the impinger solutions after a run to determine moisture content of stack or vent.

1.2.3 Sample Storage Containers - Clean HDPE bottles of 250 or 500-mL capacity are used to store the 0.1N H_2SO_4 impinger solutions and rinses for later ion chromatographic analysis. The spent silica gel is also stored in bottles for weighing. These bottles should have wide mouths and provide airtight seals.

1.3 Reagents and Other Supplies

1.3.1 Filters - Glass fiber filters without organic binders must be used. They should have a collection efficiency of at least 99.95 percent for 0.3-:m-diameter particles.

1.3.2 Silica Gel - Indicator type, mesh size 6-16.

1.3.3 Water - Deionized water that has been blank-checked for ammonium ion and other constituents of interest. The conductivity should be 5 :S/cm or lower.

1.3.4 0.1N Sulfuric Acid Solution - Obtain by purchase of reagent grade 0.1N acid or by volumetric dilution of higher concentrations of reagent grade acid by pouring the acid into deionized water.

1.3.5 Other Supplies - Stopwatch, pocket barometer, plastic cooler to store sample bottles, polyethylene bags and labels for storage and labeling of sample bottles, and crushed ice are needed. Plastic gloves and/or plastic forceps are needed to handle the filters.

2.0 ASSEMBLY OF EQUIPMENT FOR SOURCE SAMPLING

2.1 Sample Train Assembly

Figure 17-1 (40 CFR Part 60, Appendix A) illustrates the arrangement of equipment at the source location. The calibration of the heater settings and the sample metering system should be completed in the laboratory before transferring the equipment to the field.

2.1.1 Filter Holder and Probe - Place a glass fiber filter on the filter support of the filter holder. Use plastic gloves or plastic forceps to handle the filter. Avoid contact with the hands. Assemble the filter holder and attach it to the end of the probe. Attach the probe nozzle to the entrance of the filter holder. Insert the probe, with nozzle attached, into a port of the source vent or stack.

2.1.2 Impinger Train - Prepare the four impingers as follows. First G-S impinger: 100 mL of 0.1N sulfuric acid. Second G-S impinger: 100 mL of 0.1N sulfuric acid. Third impinger: empty or contains 100 mL 0.1N H_2SO_4 (depending on the need to prevent

breakthrough due to high ammonia concentrations and/or high flowrate requirement). Fourth impinger: a known, preweighed amount (200-300 g) of indicating silica gel, 6-16 mesh. Connect the first impinger to the exit of the glassware union joined to the probe liner exit. Connect the four impingers to each other. Connect the fourth impinger to the inlet of the sample meter system. Add crushed ice and cold water to the container that holds all impingers. Immerse the impingers to a point at least 10 cm above the level of the impinger liquid level. Allow the impingers to cool for 10 minutes before beginning to sample.

3.0 OPERATION OF AMMONIA SAMPLING TRAIN

3.1 Sampling Procedure

Follow the isokinetic sampling procedure outlined in Section 4.1, Method 17.

3.2 Set Temperatures

Determine the temperature of the stack gas. Preheat the in-stack filter, the probe and the heated area just prior to the entrance to the first impinger to a temperature at or slightly above the stack gas temperature.

3.3 Activate the Sample Train

Leak-check the sample train following the procedures in Section 4.1.4 of Method 17. Record the start point reading of the dry gas meter.

During the sampling period, make several readings of the thermometers at the inlet and outlet wells of the dry gas meter. Record and average these readings. Periodically check the volume of liquid in the first impinger. Very moist stack gas samples could cause the impinger to overflow. If this is about to happen, discontinue sampling and record the time and volume sampled.

At the end of the sampling period, turn off the sampling system. Record the final volume indicated by the dry gas meter. Calculate the total volume sampled.

3.4 Remove and Package Samples

Remove the glass fiber filter and store it in a labeled and pre-weighed petri dish; put the dish in a plastic bag. Save the filter should it be needed for later extraction and analysis. NOTE: Analysis of filter catch is not required for the purposes of this

method. After cleaning and drying the filter holder, install a new filter.

Determine the volume of liquid in each of impingers 1, 2, and 3 by pouring their contents into individual clean graduated cylinders. Record the volume on the data sheet. Pour the contents of each graduated cylinder into individual 250- or 500-mL HDPE bottle. Next, use the deionized water wash bottle to rinse out all interior surfaces of impingers 1, 2, and 3 and the corresponding graduated cylinders. Add the rinse water to the respective bottles for impingers 1, 2, and 3. Rinse the glassware between the filter holder and the first impinger. This rinse may be stored in a small HDPE bottle for separate analysis or it may be combined with the liquid from impinger 1. Limit the volume of rinse water so that the total volume of each impinger plus its rinses is no more than 230 mL. This will allow 20 mL of rinse water to be used in the laboratory to transfer the sample to a 250-mL volumetric flask. In general, do not rinse glassware with acetone to dry it. If acetone must be used to dry the glassware, do not combine the acetone rinse with any sample. Discard the acetone rinses in a proper manner.

Tighten the cap securely and place each bottle in a plastic bag and record a sample number and identifying information on the bag with an indelible marker or securely affix a prepared label. Labels can be made up in advance. Place the sample bottles in an ice cooler. Once in the laboratory, store the bottles in a refrigerator at 4°C (39°F) and analyze the samples by ion chromatography within 2 weeks after collection. Store the filters, in their petri dishes, in a cool, dry location. A summary of the workup and packaging procedures suggested for the method is given in Table A-1.

3.5 Conduct Additional Runs

Conduct 2 additional runs in order to complete 3 runs for each test site. Follow the procedures described in Sections 3.1, 3.2, 3.3 and 3.4.

When a sampling session at a testing location is complete, disassemble and clean the interiors of the nozzle, the probe liner, the filter holder, the filter support, the impingers, and all supporting glassware.

3.6 Quality Control and Quality Assurance

Designate a sample of the 0.1N sulfuric acid impinger solution as the field blank by placing it in an impinger vessel for an hour but collect no sample. Package the field blank as described for samples. Analyze the collection solution for ammonium to ensure that the background due to onsite handling and exposure is negligible

compared to the ammonium content of samples.

4.0 ANALYSIS OF AMMONIA, AS AMMONIUM ION, BY ION CHROMATOGRAPHY

4.1 Sample Preparation

Analyze samples within 2 weeks after their collection in the field. Keep samples refrigerated (not frozen) at 4°C (39°F) and allowed them to slowly warm to laboratory temperature before analysis.

Table A-1. List of Samples from Method 17 Train for Ammonia

Component	Workup Procedure	Packaging
In-stack filter (47 mm glass fiber)(Optional)	Remove filter from holder with tweezers; place in pre-labeled, pre-weighed plastic Petri dish (Optional)	50 mm plastic Petri dish.
In-stack filter housing (front half)(Optional)	Brush adhering particles into Petri dish with artist's brush. Clean with water; wipe dry with lab tissue.	Same as above.
In-stack filter housing (back half) and union connecting it to probe liner	Visually examine for particles. There should be none. Note this. Rinse with three, 10-mL portions of 0.1N H_2SO_4 from squeeze bottle; rinse into plastic funnel atop 250 mL poly. bottle. Rinse filter housing, union, and funnel 3 times with water; discard rinses. Dry housing and funnel with lab tissue.	250 mL poly. bottle.
Glass probe liner and glassware connecting it to Impinger # 1.	Visually examine for particles. There should be none. Note this. Rinse interiors with three, 10-mL portions of 0.1N H_2SO_4 into plastic funnel atop same 250 mL poly. bottle used above. Rinse probe liner and glassware 3 times with water; discard rinses.	Same bottle as above.

Impinger # 1 (stem and body). Impinger liquid. Repeat this procedure for Impinger # 2 and Impinger # 3.	Pour impinger solution into clean, dry graduated poly. cylinder and record volume. Then pour solution into a 250 mL poly. bottle. Rinse each impinger stem, impinger body, and graduated cylinder with three, 5-mL portions of water and transfer these rinses to the 250 mL bottle. Drain water from each impinger stem and body. Shake graduated cylinder and plastic funnel until near dryness.	Use a separate 250 mL poly. bottle for each impinger.
Impinger # 4. Silica gel.	Weigh tared impinger body plus used silica gel to determine weight gain. Transfer silica gel to a 250 mL poly. bottle via funnel. Scrape out any remaining particles with a metal spatula. Remove dust from ground glass surfaces with lab tissue.	250 mL poly. bottle.

4.1.1 Impinger Solutions - Pour the solutions from impingers 1 and 2 (and possibly 3) from their HDPE sampling bottles into separate 250-mL volumetric flasks. Rinse out the interior walls of the bottles several times with approximately 10-mL portions of deionized water. Add each rinse to the applicable 250-mL volumetric flask until the total volume reaches the mark. Do not prepare the solution in impinger 3 for analysis unless analysis of the contents of impingers 1 and 2 indicates breakthrough of ammonia has occurred (the general rule for whether breakthrough has occured is when the concentration of impinger 2 is greater than 10 percent of the concentration of impinger 1). This process of rinsing and diluting takes the 0.1N H_2SO_4 impinger solution to an approximately 0.04N H_2SO_4 solution, making it compatible with the 0.04N H_2SO_4 solutions used for setup and calibration of the ion chromatograph.

4.1.2 Silica Gel - Determine the weight of the used silica gel and compare this to its initial, unexposed weight. Record the net weight of water absorbed by the silica gel.

4.2 Sample Analysis

An ion chromatograph equipped with a conductivity detector is used for ammonium ion separation and quantitation.

4.2.1 Ion Chromatography Conditions - The conditions found to be suitable for analysis of a sample containing 1 ppmV ammonium in 0.4N sulfuric acid collection media are (Mention of trade names in this case does not constitute endorsement by the Agency; model names and numbers are mentioned in order to provide guidance to the user):

Instrument: Dionex Model 2120i	
Separator Column: Dionex HPIC-CS1	
Suppressor Column:	Dionex Cation Micromembrane
Eluent: 0.005 N hydrochloric acid	
Eluent flow rate: 2.3 mL/min	
Regenerant:	0.1 M tetrabutylammonium hydroxide
Sample loop volume:	100 :L.

4.2.2 Calibration - Prepare a calibration curve each analysis day using at least six standards that bracket the expected range of sample concentrations. This is usually from 0.1 to 10.0 :g of NH_4^+ per mL of sample. If an electronic integrator is available, use the signal's peak area for calibration and data reduction rather than the peak height. Calibration standards are prepared in 0.04N H_2SO_4, the same concentration of acid as in the diluted samples.

4.2.3 Quality Control and Quality Assurance - Aqueous samples containing known amounts of ammonium ion are available from the U.S. Environmental Protection Agency (EPA), National Institute of Standards and Technology (NIST), and other sources. Use these for quality assurance audits of the analytical process. Conduct quality control checks by periodically analyzing a solution that has an ammonium ion concentration in the range of the calibration standards but that has been prepared independently using a different bottle of ammonium salt than that used to prepare the calibration standards. Make periodic blank checks of reagents.

4.3 Calculations

4.3.1 Determine the total volume of dry gas sampled by subtracting the initial reading of the dry gas meter (DGM) from its final reading. Correct this sample volume to standard conditions (20 °C,

760 mm Hg or 68 °F, 29.92 in. Hg) using the following equation.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m} \right) \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right] \quad (1)$$

where

$V_{m(std)}$	=	Volume of gas sample measured by the DGM, corrected to standard conditions
V_m	=	Volume of gas sample as measured by DGM
Y	=	DGM calibration factor
T_{std}	=	Standard absolute temperature, 293 K
T_m	=	Absolute average DGM temperature, K
P_{bar}	=	Barometric pressure at the sampling site, mm Hg
P_{std}	=	Standard absolute pressure, 760 mm Hg
)H	=	Average pressure differential across the orifice meter, mm H_2O
13.6	=	Specific gravity of mercury.

Express $V_{m(std)}$ in liters. One cubic ft. = 28.316 L.

4.3.2 Determine the concentration of ammonium ion (NH_4^+) in the diluted impinger solution by application of the ion chromatography (IC) calibration equation. Express this in milligrams NH_4^+ per liter of solution.

4.3.3 Calculate the volume of ammonia gas present in the sample.

$$V_a = \frac{(N)(0.25)(24.04)}{(1000)(18)} \quad (2)$$

where

V_a	=	Volume of ammonia gas in the sample of gas taken from the source
N	=	Sum of concentrations of ammonium ion, mg/L, in all impinger solutions (and in the probe rinse, if applicable)

0.25 = Conversion factor, assuming sample in impinger was diluted to 0.25 L (250 mL)
24.04 = Liters of ideal gas per mole of substance
1/1000 = Factor to convert mg/L to g/L
18 = Formula weight of ammonium ion.

4.3.4 Calculate the ppmV of ammonia present in the stack gas sample:

$$C_{NH_3} = \frac{V_a, L}{V_{m(std)}, L} \times 10^6. \qquad (3)$$