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FIELD TEST OF AMMONIA COLLECTION/ANALYSIS METHOD

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ABSTRACT

Addition of ammonia or urea to the combustion zone of a boiler has been shown to reduce the formation (and thus emissions) of oxides of nitrogen. However, under certain conditions, some of the ammonia will "slip" by and may be emitted to the atmosphere. Several states are interested in monitoring such ammonia "slip" emissions and other sources of ammonia. Industries are interested in using ammonia emissions data to guide them in optimizing the ammonia injection technology. However, no EPA-approved measurement method has been available.

This report gives information on results from a field test of a wet chemistry method for collection and analysis of ammonia at a coal-fired power plant. In the method, stack gases are sampled isokinetically, pulled through an in-stack filter, and bubbled through 0.1 N sulfuric acid impinger solution to trap the ammonia as ammonium ion. The ammonium ion is quantified by ion chromatography. From this analytical result and the measured total volume of the sample, the stack gas ammonia concentration can be calculated. The method was found to be acceptable per EPA Method 301 specifications if a correction factor is applied.

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INTRODUCTION

Addition of ammonia or urea to the combustion zone of a boiler has been shown to reduce the formation (and thus emissions) of oxides of nitrogen. However, under certain conditions, some of the ammonia will "slip" by and may be emitted to the atmosphere. Several states are interested in monitoring this ammonia "slip" and other ammonia emissions. Industries could use the ammonia emissions data to guide them in optimizing the ammonia injection technology. However, no EPA-approved measurement method has been available.

This report gives information on results from a field test of a wet chemistry method for collection and analysis of ammonia at a coal-fired power plant. In the method, stack gases are sampled isokinetically, pulled through an in-stack filter, and bubbled through 0.1 N sulfuric acid impinger solution to trap the ammonia as ammonium ion. The ammonium ion is quantified by ion chromatography. From these analytical results and the measured total volume of sample, the stack gas ammonia concentration can be calculated. The method was found to be acceptable per EPA Method 301 specifications if a correction factor is applied to the data.

LABORATORY STUDIES

A wet chemistry method, employing isokinetic sampling and using the Method 5 impinger train was chosen for study as the sampling and collection method. Ion chromatography was chosen as the analytical method.

Impinger Solution Studies

Initial work in the laboratory prior to the field tests was conducted to verify the collection efficiency of several types of acidic impinger solutions and evaluate the viability of ion chromatography as an analysis method for these solutions. Oxalic, hydrochloric, and sulfuric acid solutions all worked well. Sulfuric acid, 0.1 N solution, was chosen due to its excellent retention of ammonia and because it has been used in other stack sampling methods and is thus familiar to users. Studies were made at concentrations ranging from 1 to 5 ppmV ammonia. The sampling flow rate decided upon was 0.5 ft^3/min. The sampling time was generally 30 minutes to 1 hour. The impinger solutions were diluted to a sulfate concentration of ~0.04 N before analysis.

Sample Stability Studies

Refrigerated (~ 4 °C) and room temperature (~ 20 °C) 4 and 400 ppm by weight solutions of ammonium ion in 0.1 N acid were studied over a 20-day period. At either temperature, solutions were found to be stable and gave recoveries between 98 and 107 percent as compared to the initial value.

Effects of Moisture and Temperature

A laboratory ammonia generation system consisting of a source of clean air, a unit to supply water vapor, and a unit to inject dilute ammonia gas from a cylinder was assembled, tested, and verified to give reliable and reproducible concentrations of ammonia at concentrations from 1 to 5 ppmV. The Method 5 train (a Method 17 train without the in-stack filter) sampled from the ammonia generation system at a rate of ~0.5 ft^3/min at various probe and filter box temperatures and at various water vapor levels up to 10 percent. Near-quantitative recoveries of 1 ppmV ammonia were achieved at temperatures from 110 °C (230°F) to 175 °C (350 °F).

Verification of Spiking Cylinder Ammonia Concentration

Because ammonia is a reactive gas, the quantitative delivery of the gas from the spiking cylinder to the point of attachment to the Method 17 train spike port was verified in the laboratory. The Scott Specialty Gas cylinder (143 ppmV certified value) was connected to the same mass flow controller system that would be used at the field site. The system was first flushed with gas at a high flow rate. The flow rate was then set to ~0.07 L/min and the output of the mass flow controller was bubbled for 40 minutes through 0.1 N sulfuric acid contained in a series of three midget impingers. Analysis of the impinger solutions with an ammonia sensing electrode showed 94.4 percent recovery of the predicted concentration. These results were within the limits of the cylinder manufacturer's stated accuracy.

FIELD STUDIES

Sampling Location

A coal-fired power plant which uses the urea-injection technology for NO_x control was agreed upon as a suitable test site. Plant personnel, who were very helpful and cooperative, mentioned that particulate matter would be present at various points in the process. This particulate matter would likely contain ammonium salts and furthermore could absorb or desorb ammonia gas. This knowledge should be taken into consideration during sampling. After conferring with EPA, it was decided to modify the proposed sampling method by placing an in-stack filter at the entrance to the probe rather than placing the filter downstream of the probe in the Method 5 filter box. This change made the stack sampling procedure like that of EPA Method 17. The purpose of the in-stack filter was to remove particles at the earliest point in the sampling stream and keep them at stack temperature rather than allow them to enter the filter box and be subjected to higher temperatures than present in the stack or vent.

Presurvey Study

A presurvey study was conducted at the power plant. Three locations were suggested. One was immediately downstream of the boiler firebox in an area that was very hot. The second was further downstream of the boiler at a point where some of the particles had been removed mechanically but prior to the sulfur dioxide scrubber and the baghouse. The third location was a point on the stack itself. Plant personnel believed that emissions collected at the third point would have little or no ammonia present since the sulfur dioxide scrubber and the baghouse that precede this point are effective ammonia scrubbers. The second point was chosen for sampling because it was convenient and ammonia was expected to be present.

Presurvey tests showed that ammonia was indeed present at the second location at concentrations of approximately 12 to 14 ppmV. Particulate matter was also present and some difficulties were encountered with the use of the in-stack filters. An ammonia-specific electrode was used to make on-site checks of the ammonia concentrations. Ion chromatography analysis of the solutions occurred a few days later and the results agreed within ± 10 percent with the values obtained with the ammonia-specific electrode.

During the time interval between the presurvey and the full method testing, the collection method was further studied, a quadtrain sampling system was built, and new in-stack filters were acquired for use.

Method Tests

A Site-Specific Test Plan was prepared for use during the method testing phase. All tests of the method were made at the location noted above. Samples were collected in quadruplicate using a quadtrain assembly. Instructions given in EPA Method 301

concerning sample spiking were followed. A total of nine runs were made over a four-day period. Of these, six were considered valid. The contents of the impingers were analyzed on-site using an ammonia-specific electrode so that the spiking level for the next run could be decided based on the results of the prior run. However, this strategy was only partially successful since the plant operation varied depending on the electrical demand of the customers. Thus, the particulate loading and ammonia concentration were not as uniform as had been hoped. These variations, in turn, required changes in sample collection duration and affected the ability to accurately predict spike gas concentrations.

SECTION 2
CONCLUSIONS AND RECOMMENDATIONS

Laboratory and field experiments were carried out to validate a collection and analysis method for ammonia emitted from stationary sources. The method, based on isokinetic sampling according to EPA Method 17 and ion chromatography analysis of ammonium, is presented in Appendix A of this report.

Laboratory experiments demonstrated that 0.1 N sulfuric acid impinger solution was very efficient in collecting ammonia in air at concentrations of 1 ppm and higher, at flow rates of approximately 0.5 ft^3/min. Samples were shown to be stable for greater than 20 days when stored at room temperature or when refrigerated at 4 °C. Laboratory experiments also determined the optimum temperature that would prevent ammonia in a moist sample from being retained in the glass sampling probe or on the fiberglass particulate filter was between 110 °C and 175 °C.

Analysis of impinger solutions by ion chromatography was demonstrated to be accurate within 10 percent of expectations and precise if sulfate concentrations in the sample matrix and in the calibration solutions were both matched at ~ 0.04 N.

A field validation study of the method was conducted at a coal-fired power plant that uses the urea injection process to control NO_x emissions. Six sets of valid samples were taken over a four-day period. EPA Method 301 procedures were used to evaluate the precision and accuracy (bias) of the method.

CONCLUSIONS

The following conclusions regarding the performance of the method can be drawn.

Interference to analysis. No other peaks appeared in the vicinity of the ammonium peak in the ion chromatograph. The presence of small amounts of particulate matter in the samples and the occurrence of ammonium concentrations below 0.3 μg/mL of impinger solution are believed to adversely affect the precision and accuracy of the analysis procedure.

Precision evaluation. Tests of the method yielded a relative standard deviation (RSD) for the pooled spiked and unspiked samples of 19.2 percent. Thus, the method meets the Method 301 precision criteria that the RSD for both spiked and unspiked samples be less than 50 percent.

Accuracy (bias) evaluation. The sampling bias for the method was found to be 0.68 μg/L (0.96 ppmV) which is 15 percent of the mean theoretical spiked sample value of 4.57 μg/L. The t-statistic for bias was calculated and gave a result of 3.13. This t-statistic was compared to the critical value at the 95 percent confidence interval and n-2 degrees of freedom (i.e., 10) , which is 2.23. The bias of the method is thus statistically significant and the calculated correction factor (0.87) should be applied.

RECOMMENDATIONS

It is recommended that the method be employed for collection and analysis of ammonia from stationary sources. Special care must be taken when particulate matter is present so that it does not break through the filter and enter the sampling probe and/or impingers. This happened in several instances in the field validation of the method. The precision of sampling and recovery of spiked samples were affected by the presence of these particles.

SECTION 3
PROCEDURES

SAMPLE COLLECTION AND ANALYSIS

Procedures for collection and analysis of ammonia using the EPA Method 17 train and ion chromatography are given in Appendix A to this report. The reader should also consult the Code of Federal Regulations, Section 40, Part 60, Appendix A, Method 17.

DATA ASSESSMENT

EPA Method 301 provides procedures by which one can determine if a proposed test method meets Agency requirements when no validated method exists for comparison. Method 301 includes procedures for determining and documenting the systematic error (bias) and precision of measured concentrations from a given source. Three sampling approaches are described in Method 301; isotopic spiking, comparison against a validated test method, and analyte spiking. Isotopic spiking is only suited for methods that are capable of identifying different isotopic masses of analytes (e.g. mass spectrometry and neutron activation analysis). Comparison against a validated test method requires that a validated test method exist for the compounds of interest; however, no such method exists for ammonia. Thus, analyte spiking is the only approach available in Method 301 for validating the ammonia collection/analysis method.

The analyte spiking approach requires that at least four trains collect samples simultaneously from a single pollutant source. Half (i.e., two) of the sampling trains are spiked with a known additional amount of the pollutant. A minimum of six sampling runs are required, each using quadruplicate trains.

Systematic Error (Bias)

Bias. The bias (B) is calculated from the measured sampling train response and the calculated spike level as:

$$B = S_m - M_m - CS \quad (1)$$

where S_m = mean measured spiked value,
M_M = mean measured unspiked value, and
CS = calculated spike value.

Since our calculated spike values were slightly different for each spiked sample train and run, the bias (B_{ij}) was calculated separately for each train (I) and run (j) as:

$$B_{ij} = S_{ij} - M_j - CS_{ij} \quad (2)$$

where S_{ij} = measured spiked value for train i on run j,
M_j = average of measured unspiked values for run j, and
CS_{ij} = calculated spike value for train i on run j.

The overall bias (B) was then calculated as the average of the bias over all runs (j) and spiked trains (I), i.e.:

$$B = \frac{\sum_{i=1}^{2} \sum_{j=1}^{6} B_{ij}}{12} \quad (3)$$

Significance of Bias. The statistical significance of the bias is evaluated using the Student's t statistic, which is calculated as:

$$t = \frac{|B|}{\sqrt{\frac{s_u^2 + s_s^2}{12}}} \qquad (4)$$

where B = Bias (Equation 3) and
s_u , s_s = standard deviation of the unspiked and spiked samples, respectively (Equations 6 and 7).

The bias is significantly non-zero if the t value calculated by equation 4 is greater than the critical value of Student's t for 95 percent confidence and n - 2 degrees of freedom (i.e., t = 2.228 at 10 degrees of freedom).

Correction Factor

A method with statistically significant bias may be acceptable under the provisions of EPA Method 301 if the bias level is sufficiently low, in this case within 30 percent. If this is so, the results would be multiplied by a factor to correct for the bias. A method correction factor is to be used if and only if the bias is significantly non-zero.

If the bias is not significant, then no correction factor is to be calculated. Otherwise, the correction factor (CF) is calculated as:

$$CF = \frac{1}{1 + \frac{B}{CS}} \qquad (5)$$

where B = Bias (Equation 3) and
CS = calculated spike level (averaged over all spiked samples).

The correction factor must be between 0.7 and 1.3 for a method to be acceptable.

Precision

Unspiked Samples. The standard deviation of the unspiked values (SD_u) is calculated as:

$$SD_u = \sqrt{\frac{\sum_{j=1}^{n} d_j^2}{2n}} \qquad (6)$$

where d_j = difference between unspiked trains for the j^{th} run and
n = number of sampling runs.

Spiked Samples. The standard deviation of the spiked values (SD_s) is calculated as:

$$SD_s = \sqrt{\frac{\sum_{j=1}^{n} d_j^2}{2n}} \qquad (7)$$

where s_j = difference between spiked trains and
n = number of sampling runs.

Pooled Standard Deviation. If the standard deviations of the spiked and unspiked samples are not significantly different, they may be pooled to obtain an overall method standard deviation. The significance of the difference in the spiked and unspiked standard deviations is evaluated by calculating the F ratio statistic as:

$$F = \frac{s_u^2}{s_s^2} \qquad (8)$$

where s_u and s_s are the standard deviations of the unspiked and spiked samples, respectively (Equations 6 and 7). If the calculated F ratio is within the limits for a 95 percent confidence level at 5 degrees of freedom (i.e., 0.139 to 7.146), then the pooled standard deviation (SD_{pooled}) may be calculated as:

$$SD_{pooled} = \sqrt{\frac{s_s^2 + s_u^2}{2}} \qquad (9)$$

where s_u = standard deviation of the unspiked samples (Equation 6) and
s_s = standard deviation of the spiked samples (Equation 7).

Relative Standard Deviation. The relative standard deviation (RSD) is calculated as:

$$RSD = \frac{s}{S_m} \qquad (10)$$

where s = standard deviation (pooled if possible),
S_m = mean of unspiked samples (mean of spiked samples if s is for spiked samples).

The method and data are acceptable if the RSD is less than or equal to 50 percent.

SECTION 4
RESULTS AND DISCUSSION

Results from the field validation test samples, collected from the power plant vent on the dates July 18 through 21, 1995, are given in Table 1. For each sample, the table lists the sample's number, the sampling date and clock time of sampling, the volume of sample collected, the measured ammonia concentration in μg/L of dry gas, the calculated and theoretical amounts of ammonia spiked from the compressed gas cylinder, the ppmV concentration of ammonia in the vent gas, and the percent recovery of the spike gas. Footnotes to the table explain the methods of calculation.

By way of explanation, number 1-A describes the sample from quadruplicate run number 1 with an individual sample train designation of A. In each run there were four sample train designations: A, B, C, and D.

The operational data from the sampling trains were monitored during sample collection. On several occasions the particulate collected from the vent built up to such an extent on the in-stack filters that the sampling train's ability to maintain isokinetic flow was nearly exceeded. In such cases the planned sampling time was shortened and the spiking gas was turned off early. Data from samples 3, 7, and 9 were not used in the Method 301 computations. Samples 3 and 9 were invalidated due to filter overloading which demanded the sampling pumps be shut off after a very short sampling period; sample 7 was invalidated due to an apparent error in metering gas from the spiking cylinder to the quadtrain.

TABLE 1. AMMONIA METHOD FIELD TEST RESULTS

Sample No. (sampling date and time)	Volume Sampled[a] (spike volume), L	Measured NH_3, µg/L[b]	Calculated NH_3 spiked, µg/L[c] (calculated/ theoretical)	NH_3, ppmV, vent gas[d]	Percent recovery of spike[e]
7-18-95 (1451-1531)					
1-A	466.3	3.235	-	4.6	-
1-B	429.5 (39.1)	12.918	10.09/9.22	-	109.4
1-C	441.1	2.421	-	3.4	-
1-D	425.1 (38.8)	14.374	11.546/9.24	-	125.0
7-19-95 (0812-0852)					
2-A	409.7 (14.7)	4.534	3.697/3.630	-	101.8
2-B	435.2	0.933	-	1.3	-
2-C	426.2 (15.0)	5.184	4.347/3.556	-	122.2
2-D	435.1	0.742	-	1.0	-
7-19-95 (1645-1700)					
4-A	165.2 (7.1)	4.856	4.522/4.352	-	103.9
4-B	173.5	0.328	-	0.5	-
4-C	165.7 (6.8)	4.848	4.514/4.131	-	109.3
4-D	170.0	0.341	-	0.5	-
7-19-95 (1959-2039)					
5-A	517.6	0.903	-	1.3	-
5-B	363.5 (16.6)	6.393	5.707/4.620	-	123.5
5-C	455.4	0.469	-	0.7	-
5-D	366.6 (16.8)	6.441	5.755/4.629	-	124.3

TABLE 1. AMMONIA METHOD FIELD TEST RESULTS (Continued)

Sample No. (sampling date and time)	Volume Sampled[a] (spike volume), L	Measured NH_3, µg/L[b]	Calculated NH_3 spiked, µg/L[c] (calculated/ theoretical)	NH_3, ppmV, vent gas[d]	Percent recovery of spike[e]
7-20-95 (1152-1222)					
6-A	231.5 (6.8)	12.649	5.099.2.952	1.3	-
6-B	234	7.136	-	-	123.5
6-C	232.3 (6.4)	11.764	4.214/2.777	0.7	-
6-D	232.5	7.964	-	-	124.3
7-21-95 0846-0916)					
8-A	210.7	5.018	-	7.1	-
8-B	214.1 (6.1)	5.910	1.549/2.875	-	53.9
8-C	225.9	3.705	-	5.3	-
8-D	213.0 (6.0)	6.327	1.966/2.870	-	68.5

[a] All volumes corrected to 20 deg. C, 1 atmosphere pressure. Spiked sample volumes corrected by subtracting volume of spiking gas from total volume.

[b] Analytical values determined in the laboratory approx. 10 days after sample collection. Expressed as µg NH_3/L of dry stack gas.

[c] Calculated ammonia spiked, µg/L = [(measured concen., µg/L, spiked sample) - (avg. meas. concen. µg/L, unspiked samples)]
Example for spiked sample 1-B: [(12.918) - (3.235 + 2.421)/2] = 10.09 µg/L
Theoretical ammonia spiked, µg/L = $\frac{\text{(cylinder concentration, ppm)(spiking volume, L)}(10^{-6}\ \text{g/µg})(17.03\ \text{g/mole})}{\text{(24.04 L/mole)(volume sampled, L)}}$

Example for spiked sample 1-B: $\frac{(143\ \text{ppm})(39.1\ \text{L})(10^{-6}\ \text{g/µg})(17.03\ \text{g/mole})}{(24.04\ \text{L/mole})(429.5\ \text{L})} = 9.22\ \text{µg/L}$

[d] ppmV NH_3 in stack gas = (µg NH_3/L of dry gas measured) x (1.41250734)
Example for unspiked sample 1-A: (3.235 µg/L) x (1.41250734 µL/µg) = 4.569 ppmV

[e] Percent recovery of spike = (calculated spike)/(theoretical spike) x 100

The vent gas ammonia concentrations ranged from 0.5 to 11.2 ppmV and averaged 3.9 ppmV. The power plant's operating conditions varied in response to load requirements during the time frame of the sampling tests.

PRECISION EVALUATION

Results of the Method 301 statistical analysis of precision are shown in Table 2. Tests of the method yielded a pooled relative standard deviation (RSD) of 19.2 percent. Thus, the method meets the Method 301 precision criteria that the RSD be less than 50 percent.

ACCURACY EVALUATION

The ammonia collection/analysis method gave an average recovery of 112.2 percent. Table 2 also presents accuracy assessment information for the method. The sampling bias for the method was found to be 0.68 μg/L (0.96 ppmV) which is 15 percent of the mean theoretical spiked sample value of 4.57 μg/L (6.43 ppmV). The t-statistic for bias was calculated and gave a result of 3.13. This t-statistic was compared to the critical value at the 95 percent confidence interval and n-2 degrees of freedom (10), which is 2.23. The bias of the method was statistically significant and thus the calculated correction factor (0.87) should be applied.

TABLE 2. PRECISION AND ACCURACY OF AMMONIA METHOD[a]

STATISTIC	RESULT
Standard deviation of spiked samples, SD_S	0.540 µg/L
Standard deviation of unspiked samples, SD_U	0.524 µg/L
Pooled Standard Deviation	0.532 µg/L
Relative Pooled Standard Deviation	0.1924
Sampling bias	0.679
t value for bias	3.13[a]
Correction factor	0.87[b]

[a] Critical value for ten degrees of freedom at 95 % confidence interval = 2.23.

[b] Correction factor is applicable based on these results.

APPENDIX A

PROCEDURE FOR COLLECTION AND ANALYSIS OF AMMONIA USING EPA METHOD 17 AND ION CHROMATOGRAPHY ANALYSIS

DRAFT - 1/16/96

Method 206 - PROCEDURE FOR COLLECTION AND ANALYSIS OF AMMONIA IN STATIONARY SOURCES

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. This probe liner must be capable of being heated from 120 (248°F) to 170 ± 15°C (338 ± 59°F).

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.

1.1.6 Filter Heating System - The system must be able to achieve and control air temperatures from 120°C (248°F) to 170°C ± 15°C (338 ± 59°F) around the filter holder.

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 99.995 percent for 0.3-μm-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 μS/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 A-1 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. Position the inlet of the nozzle near the center of the stack or at the point of average flow for the vent or stack. Keep the inlet at least 25 cm from the side of the stack. Insert the pitot tube and place it in a location adjacent to the in-stack filter but not too close to the probe nozzle inlet. The in-stack filter/probe assembly and the pitot tube may be bound together and inserted simultaneously into the stack or vent. Follow the spacing recommendations given in Section 2.1 of Method 17. Connect the pitot tube to a differential pressure gauge (inclined manometer).

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. If acidic gases are known to be present and the stack temperature exceeds 110 °C (230°F), raise the temperature of the probe and heated area to 175 °C (350°F) to minimize the reaction of acidic gases and ammonia in the area between the filter and the entrance of the first impinger.

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.

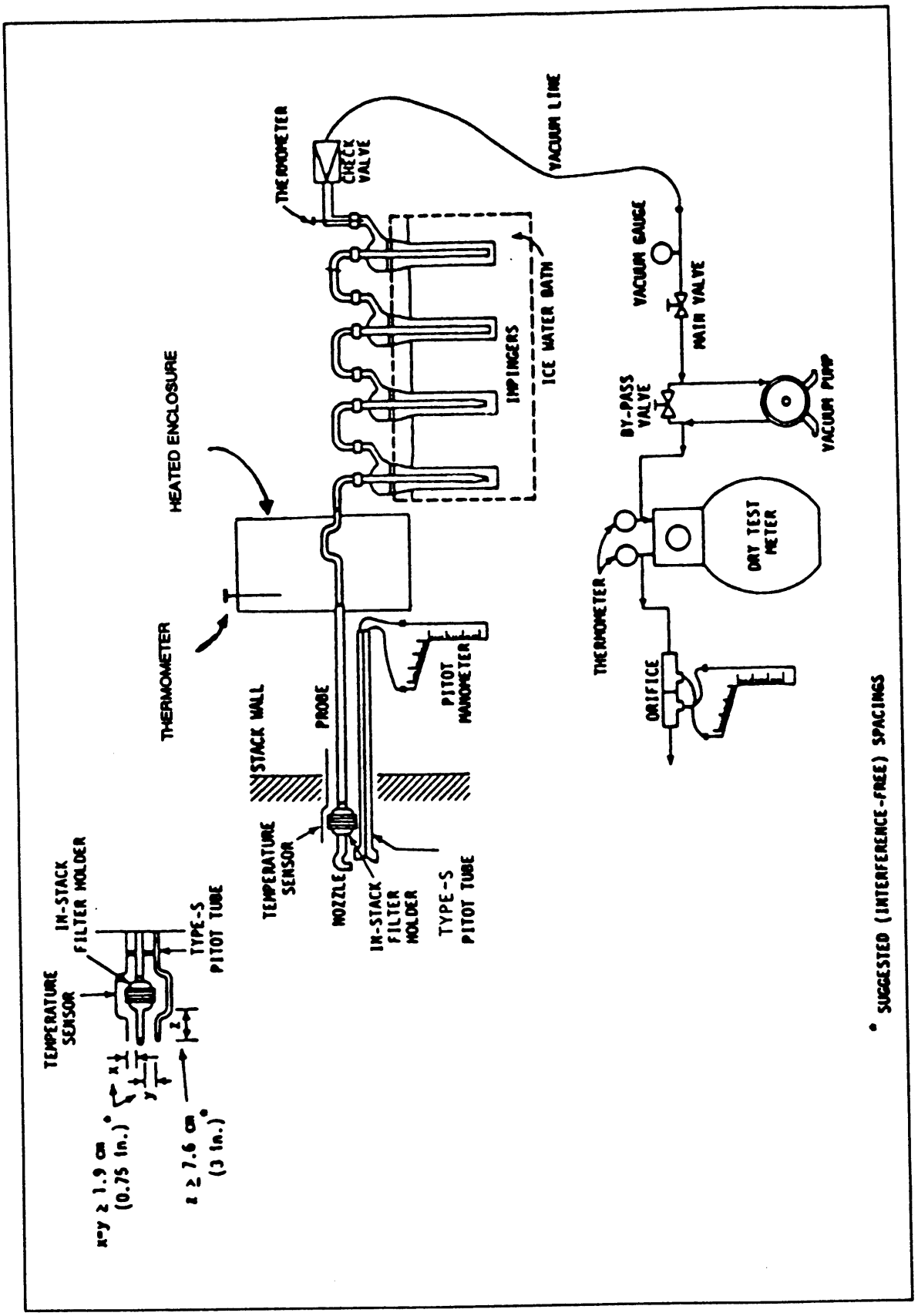

Figure A-1. Illustration of Method sampling train assembly.

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 interior of the glass sampling probe (and the glass connecting the probe to the first impinger) with deionized water. 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 glass fiber filter as the field blank. Take it to the site and install it in a filter holder for an hour but collect no sample. 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)	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)	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 Rinses of Filter Holder, Probe, and Connecting Glassware - These components are rinsed with 0.1N H_2SO_4 to preserve ammonia as ammonium ion. Dilute aliquots with water so the final H_2SO_4 concentration is ~ 0.04N. This ensures a reproducible response in the ion chromatographic analysis. If the final dilution volume is other than 250 mL, a new conversion factor (see Equation 2) must be applied.

4.1.3 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 µL.

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 µg 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.

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

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
ΔH	=	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.

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

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:

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