Method 202 - Determination of Condensible Particulate Emissions from Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability.

1.1.1 This method applies to the determination of condensible particulate matter (CPM) emissions from stationary sources. It is intended to represent condensible matter as material that condenses after passing through a filter and as measured by this method (Note: The filter catch can be analyzed according to the appropriate method).

1.1.2 This method may be used in conjunction with Method 201 or 201A if the probes are glass-lined. Using Method 202 in conjunction with Method 201 or 201A, only the impinger train

configuration and analysis is addressed by this method. The sample train operation and front end recovery and analysis shall be conducted according to Method 201 or 201A.

1.1.3 This method may also be modified to measure material that condenses at other temperatures by specifying the filter and probe temperature. A heated Method 5 out-of-stack filter may be used instead of the in-stack filter to determine condensible emissions at wet sources.

1.2 Principle.

1.2.1 The CPM is collected in the impinger portion of a Method 17 (Appendix A, 40 CFR Part 60) type sampling train. The impinger contents are immediately purged after the run with nitrogen (N_2) to remove dissolved sulfur dioxide (SO_2) gases from the impinger contents. The impinger solution is then extracted with

methylene chloride $(MeCl_2)$. The organic and aqueous fractions are then taken to dryness and the residues weighed. The total of both fractions represents the CPM.

1.2.2 The potential for low collection efficiency exist at oil-fired boilers. To improve the collection efficiency at these type of sources, an additional filter placed between the second and third impinger is recommended.

2. PRECISION AND INTERFERENCE

2.1 Precision. The precision based on method development tests at an oil-fired boiler and a catalytic cracker were 11.7 and 4.8 percent, respectively.

2.2 Interference. Ammonia. In sources that use ammonia injection as a control technique for hydrogen chloride (HCl), the ammonia interferes by reacting with HCl in the gas stream to form ammonium chloride (NH₄Cl) which would be measured as CPM. The sample may be analyzed for chloride and the equivalent amount of NH₄Cl can be subtracted from the CPM weight. However, if NH₄Cl is to be counted as CPM, the inorganic fraction should be taken to near dryness (less than 1 ml liquid) in the oven and then allowed to air dry at ambient temperature to prevent any NH₄Cl from vaporizing.

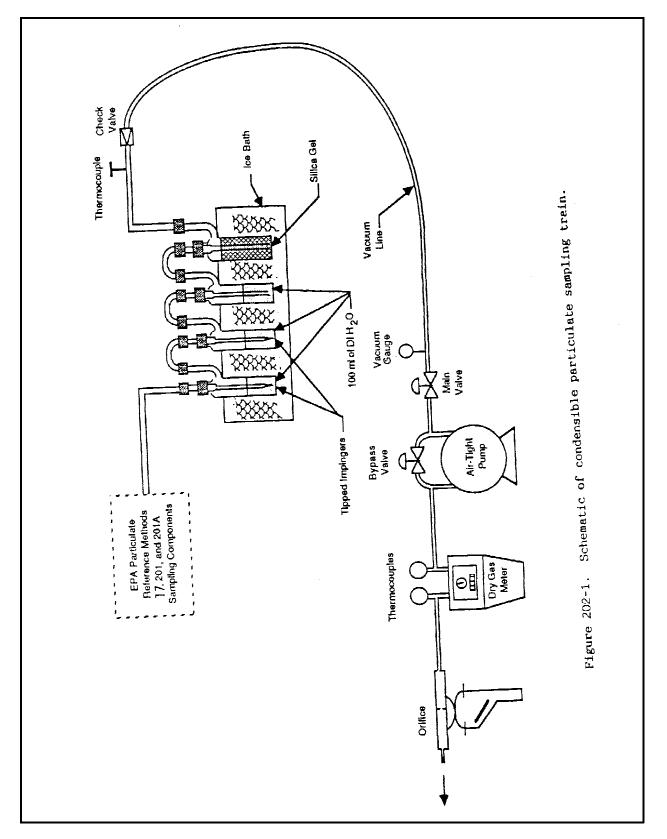
3. APPARATUS

3.1 Sampling Train. Same as in Method 17, Section 2.1, with the following exceptions noted below (see Figure 202-1). **Note:** Mention of trade names or specific products does not constitute endorsement by EPA.

3.1.1 The probe extension shall be glass-lined or Teflon.

3.1.2 Both the first and second impingers shall be of the Greenburg-Smith design with the standard tip.

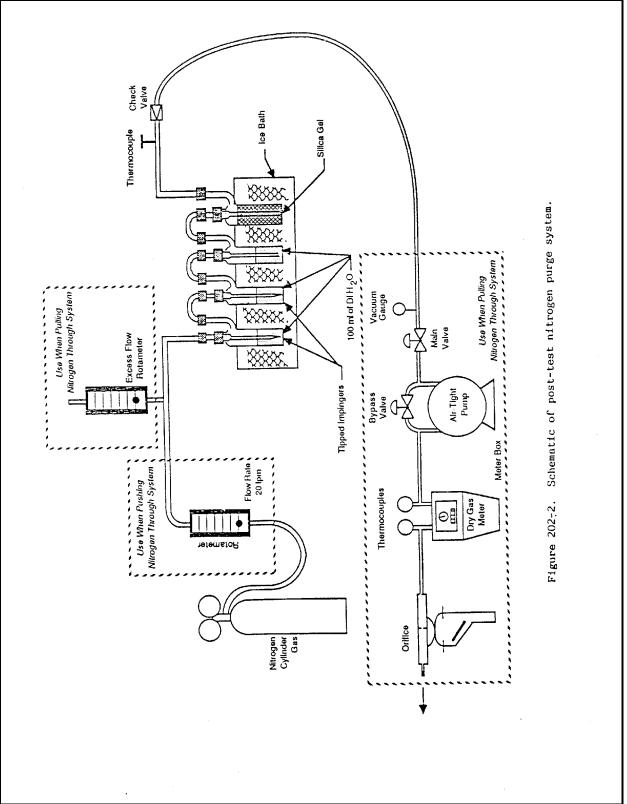
3.1.3 All sampling train glassware shall be cleaned prior to the test with soap and tap water, water, and rinsed using tap water, water, acetone, and finally, MeCl₂. It is important to completely remove all silicone grease from areas that will be exposed to the MeCl₂ during sample recovery.



3.2 Sample Recovery. Same as in Method 17, Section 2.2, with the following additions:

3.2.1 N₂ Purge Line. Inert tubing and fittings capable of delivering 0 to 28 liters/min of N₂ gas to the impinger train from a standard gas cylinder (see Figure 202-2). Standard 0.95 cm (3/8-inch) plastic tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve may be used.

3.2.2 Rotameter. Capable of measuring gas flow at 20 liters/min.



3.3 Analysis. The following equipment is necessary in addition to that listed in Method 17, Section 2.3:

3.3.1 Separatory Funnel. Glass, 1-liter.

3.3.2 Weighing Tins. 350-ml.

3.3.3 Drying Equipment. Hot plate and oven with temperature control.

3.3.4 Pipets. 5-ml.

3.3.5 Ion Chromatograph. Same as in Method 5F, Section 2.1.6.

4. REAGENTS

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

4.1 Sampling. Same as in Method 17, Section 3.1, with the addition of deionized distilled water to conform to the American Society for Testing and Materials Specification D 1193-74, Type II and the omittance of Section 3.1.4.

4.2 Sample Recovery. Same as in Method 17, Section 3.2, with the following additions:

4.2.1 N_2 Gas. Zero grade N_2 gas at delivery pressures high enough to provide a flow of 20 liters/min for 1 hour through the sampling train.

4.2.2 Methylene Chloride, ACS grade. Blanks shall be run prior to use and only methylene chloride with low blank values (0.001 percent) shall be used.

4.2.3 Water. Same as in Section 4.1.

4.3 Analysis. Same as in Method 17, Section 3.3, with the following additions:

4.3.1 Methylene Chloride. Same as Section 4.2.2.

4.3.2 Ammonium Hydroxide. Concentrated (14.8 M) NH₄OH.

4.3.3 Water. Same as in Section 4.1.

4.3.4 Phenolphthalein. The pH indicator solution, 0.05 percent in 50 percent alcohol.

5. PROCEDURE

5.1 Sampling. Same as in Method 17, Section 4.1, with the following exceptions:

5.1.1 Place 100 ml of water in the first three impingers.

5.1.2 The use of silicone grease in train assembly is not recommended because it is very soluble in $MeCl_2$ which may result in sample contamination. Teflon tape or similar means may be used to provide leak-free connections between glassware.

5.2 Sample Recovery. Same as in Method 17, Section 4.2 with the addition of a post-test N_2 purge and specific changes in handling of individual samples as described below.

5.2.1 Post-test N₂ Purge for Sources Emitting SO₂. (Note: This step is recommended, but is optional. When little or no SO_2 is present in the gas stream, i.e., the pH of the impinger solution is greater than 4.5, purging has been found to be unnecessary.) As soon as possible after the post-test leak check, detach the probe and filter from the impinger train. Leave the ice in the impinger box to prevent removal of moisture during the purge. If necessary, add more ice during the purge to maintain the gas temperature below 20°C. With no flow of gas through the clean purge line and fittings, attach it to the input of the impinger train (see Figure 202-2). To avoid over- or under-pressurizing the impinger array, slowly commence the N_2 gas flow through the line while simultaneously opening the meter box pump valve(s). Adjust the pump bypass and N_2 delivery rates to obtain the following conditions: (1) 20 liters/min or $)H_{e}$ and (2) an overflow rate through the rotameter of less than 2 liters/min. Condition (2) guarantees that the N_2 delivery system is operating at greater than ambient pressure and prevents that possibility of passing ambient air (rather than N_2) through the impingers. Continue the purge under these conditions for

1 hour, checking the rotameter and)H value(s) periodically. After 1 hour, simultaneously turn off the delivery and pumping systems.

5.2.2 Sample Handling.

5.2.2.1 <u>Container Nos. 1, 2, and 3</u>. If filter catch is to be determined, as detailed in Method 17, Section 4.2.

5.2.2.2 <u>Container No. 4</u> (Impinger Contents). Measure the liquid in the first three impingers to within 1 ml using a clean graduated cylinder or by weighing it to within 0.5 g using a balance. Record the volume or weight of liquid present to be used to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid into a clean sample bottle (glass or plastic); rinse each impinger and the connecting glassware, including probe extension, twice with water, recover the rinse water, and add it to the same sample bottle. Mark the liquid level on the bottle.

5.2.2.3 <u>Container No. 5</u> (MeCl₂ Rinse). Follow the water rinses of each impinger and the connecting glassware, including the probe extension with two rinses of MeCl₂; save the rinse products in a clean, glass sample jar. Mark the liquid level on the jar.

5.2.2.4 <u>Container No. 6</u> (Water Blank). Once during each field test, place 500 ml of water in a separate sample container.

5.2.2.5 <u>Container No. 7</u> (MeCl₂ Blank). Once during each field test, place in a separate glass sample jar a volume of $MeCl_2$ approximately equivalent to the volume used to conduct the $MeCl_2$ rinse of the impingers.

5.3 Analysis. Record the data required on a sheet such as the one shown in Figure 202-3. Handle each sample container as follows:

5.3.1 <u>Container Nos. 1, 2, and 3</u>. If filter catch is analyzed, as detailed in Method 17, Section 4.3.

5.3.2 <u>Container Nos. 4 and 5</u>. Note the level of liquid in the containers and confirm on the analytical data 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. Measure the liquid in Container No. 4 either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Remove a 5-ml aliquot and set aside for later ion chromatographic (IC) analysis of sulfates. (**Note:** Do not use this aliquot to determine chlorides since the HCl will be evaporated during the first drying step; Section 8.2 details a procedure for this analysis.)

5.3.2.1 Extraction. Separate the organic fraction of the sample by adding the contents of Container No. 5 (MeCl₂) to the contents of Container No. 4 in a 1000-ml separatory funnel. After mixing, allow the aqueous and organic phases to fully separate, and drain off most of the organic/MeCl₂ phase. Then add 75 ml of MeCl₂ to the funnel, mix well, and drain off the lower organic phase. Repeat with another 75 ml of MeCl₂. This extraction should yield about 250 ml of organic extract. Each time, leave a small amount of the organic/MeCl₂ phase in the separatory funnel ensuring that no water is collected in the organic phase. Place the organic extract in a tared 350-ml weighing tin.

5.3.2.2 Organic Fraction Weight Determination (Organic Phase from Container Nos. 4 and 5). Evaporate the organic extract at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the organic fraction for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg.

5.3.2.3 Inorganic Fraction Weight Determination. [Note:

If NH₄Cl is to be counted as CPM, the inorganic fraction should be taken to near dryness (less than 1 ml liquid) in the oven and then allow to air dry at ambient temperature. If multiple acid emissions are suspected, the ammonia titration procedure in Section 8.1 may be perferred.] Using a hot plate, or equivalent, evaporate the aqueous phase to approximately 50 ml; then, evaporate to dryness in a 105°C oven. Redissolve the residue in 100 ml of water. Add five drops of phenolphthalein to this solution; then, add concentrated (14.8 M) NH₄OH until the

sample turns pink. Any excess NH_4OH will be evaporated during the drying step. Evaporate the sample to dryness in a $105^{\circ}C$ oven, desiccate the sample for 24 hours, weigh to a constant weight, and record the results to the nearest 0.1 mg. (Note: The addition of NH_4OH is recommended, but is optional when little or no SO_2 is present in the gas stream, i.e., when the pH of the impinger solution is greater than 4.5, the addition of NH_4OH is not necessary.)

5.3.2.4 Analysis of Sulfate by IC to Determine Ammonium Ion (NH_4^+) Retained in the Sample. (Note: If NH_4OH is not added, omit this step.) Determine the amount of sulfate in the aliquot taken from Container No. 4 earlier as described in Method 5F (Appendix A, 40 CFR Part 60). Based on the IC SO_4^{-2} analysis of the aliquot, calculate the correction factor to subtract the NH_4^+ retained in the sample and to add the combined water removed by the acid-base reaction (see Section 7.2).

5.3.3 Analysis of Water and $MeCl_2$ Blanks (Container Nos. 6 and 7). Analyze these sample blanks as described above in Sections 5.3.2.3 and 5.3.2.2, respectively.

5.3.4 Analysis of Acetone Blank (Container No. 8). Same as in Method 17, Section 4.3.

6. CALIBRATION

Same as in Method 17, Section 5, except for the following:

6.1 IC Calibration. Same as Method 5F, Section 5.

6.2 Audit Procedure. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit sample. If this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are

made with both enforcement agencies.

6.3 Audit Samples. Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing:

Source Test Audit Coordinator (MD-77B) Quality Assurance Division Atmospheric Research and Exposure Assessment Laboratory U.S. Environmental Protection Agency Research Triangle Park, NC 27711

or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis. **6.4 Audit Results.** Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the appropriate enforcement agency.

7. CALCULATIONS

Same as in Method 17, Section 6, with the following additions:

7.1 Nomenclature. Same as in Method 17, Section 6.1 with the following additions.

- C_{cpm} = Concentration of the CPM in the stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
- C_{S04} = Concentration of SO_4^{-2} in the sample, mg/ml.
 - m_b = Sum of the mass of the water and MeCl₂ blanks, mg.
 - m_c = Mass of the NH₄⁺ added to sample to form ammonium sulfate, mg.

 m_i = Mass of inorganic CPM matter, mg. m_o = Mass of organic CPM, mg. m_r = Mass of dried sample from inorganic fraction, mg. V_b = Volume of aliquot taken for IC analysis, ml. V_{ic} = Volume of impinger contents sample, ml.

7.2 Correction for NH_4^+ and H_4O . Calculate the correction factor to subtract the NH_4^+ retained in the sample based on the IC SO_4^{-2} and if desired, add the combined water removed by the acid-base reaction.

$$m_{c} = K C_{SO_{2}} V_{ic}$$
 Eq. 202-1

Where:

K = -0.0208, when correcting for $\rm NH_4^+$ and $\rm H_2O.$

- = 0.354, when only correcting for NH_4^+ .
- 7.3 Mass of Inorganic CPM.

$$m_i = m_r \frac{V_{ic}}{V_{ic} - V_b} - m_c$$
 Eq. 202-2

7.4 Concentration of CPM.

$$C_{cpm} = \frac{m_{o} + m_{i} - m_{b}}{VM_{std}}$$
 Eq. 202-3

8. ALTERNATIVE PROCEDURES

8.1 Determination of NH₄⁺ Retained in Sample by Titration.
8.1.1 An alternative procedure to determine the amount of NH₄⁺ added to the inorganic fraction by titration may be used. After dissolving the inorganic residue in 100 ml of water, titrate the solution with 0.1 N NH₄OH to a pH of 7.0, as indicated by a pH meter. The 0.1 N NH₄OH is made as follows: Add 7 ml of concentrated (14.8 M) NH₄OH to 1 liter of water. Standardize against standardized 0.1 N H₂SO₄ and calculate the exact normality using a procedure parallel to that described in Section 5.5 of Method 6 (Appendix A, 40 CFR Part 60). Alternatively, purchase 0.1 N NH₄OH that has been standardized against a National Institute of Standards and Technology reference material.

 ${\bf 8.1.2}$ Calculate the concentration of ${\rm SO_4^{-2}}$ in the sample using the following equation.

$$C_{SO_4} = \frac{48.03 V_t N}{100}$$
 Eq. 202-4

Where:

N = Normality of the NH₄OH, mg/ml. V_t = Volume of NH₄OH titrant, ml. 48.03 = mg/meq.

100 = Volume of solution, ml.

8.1.3 Calculate the CPM as described in Section 7.

8.2 Analysis of Chlorides by IC. At the conclusion of the final weighing as described in Section 5.3.2.3, redissolve the inorganic fraction in 100 ml of water. Analyze an aliquot of the redissolved sample for chlorides by IC using techniques similar to those described in Method 5F for sulfates. Previous drying of the sample should have removed all HCl. Therefore, the remaining chlorides measured by IC can be assumed to be NH_4Cl , and this weight can be subtracted from the weight determined for CPM.

8.3 Air Purge to Remove SO_2 from Impinger Contents. As an alternative to the post-test N_2 purge described in Section 5.2.1, the tester may opt to conduct the post-test purge with air at 20 liter/min. Note: The use of an air purge is not as effective as a N_2 purge.

8.4 Chloroform-ether Extraction. As an alternative to the methylene chloride extraction described in Section 5.3.2.1, the tester may opt to conduct a chloroform-ether extraction. **Note:** The chloroform-ether was not as effective as the MeCl₂ in removing the organics, but it was found to be an acceptable organic extractant. Chloroform and diethlyether of ACS grade, with low blank values (0.001 percent), shall be used. Analysis of the chloroform and diethlyether blanks shall be conducted according to Section 5.3.3 for MeCl₂.

8.4.1 Add the contents of Container No. 4 to a 1000-ml separatory funnel. Then add 75 ml of chloroform to the funnel, mix well, and drain off the lower organic phase. Repeat two more times with 75 ml of chloroform. Then perform three extractions with 75 ml of diethylether. This extraction should yield approximately 450 ml of organic extraction. Each time, leave a small amount of the organic/MeCl₂ phase in the separatory funnel ensuring that no water is collected in the organic phase.

8.4.2 Add the contents of Container No. 5 to the organic extraction.

Place approximately 300 ml of the organic extract in a tared 350-ml weighing tin while storing the remaining organic extract in a sample container. As the organic extract evaporates, add the remaining extract to the weighing tin.

8.4.3 Determine the weight of the organic phase as described in Section 5.3.2.2.

8.5 Improving Collection Efficiency. If low impinger collection efficiency is suspected, the following procedure may be used.

8.5.1 Place an out-of-stack filter as described in Method 8 between the second and third impingers.

8.5.2 Recover and analyze the filter according to Method 17, Section 4.2. Include the filter holder as part of the connecting glassware and handle as described in Sections 5.2.2.2 and 5.2.2.3.

8.5.3 Calculate the Concentration of CPM as follows:

$$C_{cpm} = \frac{m_{o} + m_{i} + m_{f} - m_{b}}{VM_{std}}$$
 Eq. 202-5

where:

 $\rm m_{f}$ = Ammout of CPM collected on out-of-stack filter, mg.

8.6 Wet Source Testing. When testing at a wet source, use a heated outof-stack filter as described in Method 5.

9. BIBLIOGRAPHY

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6. Commonwealth of Pennsylvania, Department of Environmental Resources. Chapter 139, Sampling and Testing (Title 25, Rules and Regulations, Part I, Department of Environmental Resources, Subpart C, Protection of Natural Resources, Article III, Air Resources). January 8, 1960.

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Moisture Determination

Volume or weight of liquid in impingers_____ ml or g Weight of moisture in silica gel_____ g

Sample Preparation (Container No. 4)

Amount of liquid lost during transport	ml
Final volume	ml
pH of sample prior to analysis	
Addition of NH4OH required?	
Sample extracted 2X with 75 ml MeCl ₂ ?	

For Titration of Sulfate

Normality	of NH₄OH	Ν
Volume of	sample titrated	_ ml
Volume of	titrant	_ ml

Sample Analysis

Container	We	ight of	Condensi	ble	Parti	culate,	mg
number	Final	Weight	Tare	Wei	.ght	Weight	Gain
4 (Inorgani 4 & 5 (Organ	,						
			Total				

				IULAI	
			Less	Blank	
Weight	of	Condensible	Partic	culate	

Figure 202-3. Analytical data sheet