Standard Operating Procedure for Coating and Extracting Compact Parallel-Plate Denuders for Ammonia Determination

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

Prepared by: Steven J. Walters Date: 3/2/2010

Prepared by: Constance Fowler Date: 3/2/10

Reviewed by: James B. Flanagan Date: 3/2/10

Approved by: R. K. M. Jayanty Date: 3/2/10

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1.0 Purpose and Applicability

This document outlines procedures for coating a denuder with phosphorous acid and extracting the denuder for the collection and quantifying of gas-phase basic species in the ambient air, primarily ammonia. This standard operating procedure (SOP) applies to coating and extracting glass parallel-plate denuders of the type that could be used by the MetOne SASS chemical speciation sampler. The procedures may also be used, with some modifications, to process other types of denuders, such as glass annular denuders. Other uses of the parallel plate denuder, not covered in this SOP, involve coating the surfaces with basic substances (e.g., sodium carbonate) for use in capture and quantifying acidic gases (e.g., nitric acid vapor, sulfur dioxide) present in ambient air.

2.0 Safety Precautions

2.1 Always wear clean, dry, laboratory grade gloves when handling any components involved in these procedures and corrosive chemicals. Disposable nitrile gloves provide adequate protection against accidental hand contact with small quantities of most laboratory chemicals.

2.2 Always wear protective eyewear when conducting the laboratory procedures specified in this SOP.

2.3 Read, understand, and follow the Material Safety Data Sheets (MSDSs) for all chemicals involved in this procedure. Several chemicals are corrosive or should not contact the skin for other reasons.

2.3 Always keep open chemical containers in properly operating fume hoods and wear adequate protective clothing, as outlined in the MSDSs.

2.5 Always label secondary containers used in this procedure.

2.6 Disposal of waste materials should be in accordance with the appropriate MSDS.

3.0 Equipment and Materials

3.1 Laboratory nitrile gloves, appropriately sized. VWR Brand Cat. No. 40101.

3.2 Phosphorous acid, 99%. 100-200 g. Aldrich, Cat. No. 215112.

3.3 Citric acid, monohydrate. 500 g. J.T. Baker Brand, Cat. No. 0118-01

3.4 Methanol, 4 liters, reagent grade. VWR Brand Cat. No. VW4300-3.

3.5 Volumetric flask, 250 mL, Pyrex Class A. VWR Brand Cat. No. 29610-182.

3.6 Glove box or cabinet; heavy clear flexible plastic film. Fulcrum Inc., Model GC-2 with two chambers and four air valve assemblies.

3.7 Laboratory deionized/reverse osmosis water.

3.8 Source of ammonia-free nitrogen gas or clean air to purge glove box.

3.9 Sample bottles, narrow-mouth, high-density polyethylene, 15 mL capacity, VWR Brand Cat. No. 160570-007.

3.10 Graduated cylinders, 10 and 50 mL capacity, VWR Brand Cat. No. 24711-295 or equivalent.

3.11 Pyrex rectangular glass baking dishes, various sizes. (could be a local purchase).

3.12 Plastic powder funnels, sized to fit inside neck of volumetric flasks and sample bottles.

3.13 Antistatic, polystyrene, 3.4 oz. weigh boats. VWR Cat. No. 89106-766

3.14 Wristwatch or small electronic timer.

3.15 Denuder drying manifold or assembly as given in Section 6.3.6. (Must be custom-designed for the laboratory; at this time there are no commercially available drying manifolds. See References 1 and 2.).

3.16 Thermo Scientific Finnpipette, 1-10 mL auto-pipette and pipette tips. Cat. No. EW-25013-24

3.17 BD Falcon lidded, sterile, 47 mm, disposable petri slides. WR Cat. No. 25373-085.

3.18 BD Falcon 16mL, round-bottom, capped, sterile, polystyrene test tubes. VWR Cat. No. 60819-422 (use as filter storage and extraction container).

3.19 Various laboratory supplies (fine-tipped plastic and/or stainless steel tweezers, beakers, watch glasses, plastic rinse bottles containing deionized water and methanol, laboratory tissue wipes, marking pen, labels, etc.). These items may be selected from general laboratory stock.

3.20 Laboratory notebook for recording data or an electronic database.

4.0 Preparation of 5% Coating Solution

***Note*:** Minimal exposure of reagent chemicals and solvents to ambient air is required to keep ammonia values in the blank sample(s) low. *Exhaled breath contains ammonia*.

4.1 Record all information in a laboratory data notebook and directly to an electronic database. At a minimum, the labeling for bottles must show the date of preparation, content, initial volume, and the name of the person preparing the contents.

4.2 Use the following steps to prepare a 5% Phosphorous Acid Coating Solution.

Note: Solutions at other percentage concentrations are prepared by adjusting the amount of phosphorous acid weighed.

4.2.1 Using a laboratory balance readable to the nearest 10 mg, zero the balance and then tare a clean, dry, polystyrene weigh boat. Weigh out 12.5 g of phosphorous acid crystals. Do this quickly to avoid absorption of ammonia gas from the air.

4.2.2 Working in a fume hood, fold two sides of the weigh boat to almost meet and then transfer the phosphorous acid crystals directly into a pre-labeled, 250 mL glass volumetric flask. Use a graduated cylinder containing 25 mL of deionized water to rinse any residue remaining in the weigh boat into the volumetric flask.

4.2.3 Add methanol to the flask until the total volume reaches 250 mL. Cap the volumetric flask, swirl, and invert several times until phosphorous acid is dissolved. Set flask aside for use in coating denuders.

5.0 Preparation and Use of Glove Cabinet

5.1 Ensure interior surfaces of the glove cabinet are clean; wipe down with a clean sponge or paper towel that is moist with deionized water. Line the bottom of the cabinet with clean, dry, paper towels.

5.2 Pour citric acid crystals into 3 or 4 polystyrene weigh boats to a depth of about 0.25 inch. Place the dishes inside, along the back of the cabinet, at a point away from the area where you will be manipulating denuders during the coating and extraction processes. The dishes will stay inside the cabinet during use to absorb ammonia should any be present.

5.3 Determine what procedures you plan to conduct inside the glove cabinet and load needed equipment into the main section of the cabinet and into the side section of the cabinet. Equipment may include the following: clean denuders to be coated; a flask or bottle containing the coating solution; rinse bottles containing water or methanol; beakers and watch glasses for covering beakers, freshly-coated denuders; a box of laboratory wipes (KimWipes® or equivalent); a large glass beaker to serve as a "sink" for waste liquids; a plastic bag to contain discarded laboratory wipes; pre-labeled bottles to receive rinses from extracted denuders; pre-labeled plastic bags to contain coated denuders when they are dry and ready to be removed from the cabinet.

5.4 Connect a source of nitrogen (high purity house nitrogen or high purity compressed gas cylinder) via Teflon® or plastic tubing to an inlet on the glove cabinet. Slightly open the plastic zippers on the front, side, and interior of the cabinet so that a significant flow of nitrogen can pass freely through the cabinet interior and out the openings; do not over-pressurize the flexible plastic cabinet. After about 5 minutes, close one of the exterior zippers and allow a slow, excess flow of gas to continue while one is working inside the cabinet.

Note: Clean house air may be substituted for nitrogen.

5.5 Depending on personal preferences and convenience, hand access to the glove cabinet interior can occur in several ways:

- By way of the built-in plastic gloves that are laminated to the front plastic wall of the cabinet.
- Since the built-in gloves are bulky and do not provide good tactile qualities, the hand ends of the built-in gloves can be cut off. The user then dons laboratory gloves and uses large rubber bands or stretchable Velcro to make a snug fit of the built-in glove

sleeves to the forearm. If this method is used, be sure to roll up and clamp or clip the sleeves of the built-in gloves when they are not in use to prevent entry of room air to the cabinet interior.

- So long as a noticeably positive flow of air or nitrogen from within the cabinet to the outside is maintained, the user may partially open the front zipper and insert a gloved hand (or both hands) in the opening to maneuver within the cabinet. Do not leave the zipper open any longer than necessary to coat a denuder, extract a denuder, etc.

- Close the zipper between distinct operations. Be sure the clean gas flow ceases or is lowered when the zipper is closed or nearly closed; this prevents over-pressurizing the chamber walls.

6.0 Cleaning, Coating, and Storage of Compact Parallel-plate Denuders

6.1 This procedure is written for use with quartz, parallel-plate denuders with dimensions that allow them to fit into the MetOne sampling module. Any changes in the size and design of the denuder will necessitate revisions to this section of the SOP. Each denuder comes with a set of "caps" which screw onto the ends of the denuder. These caps are used to protect the device from exposure to air and dust after it has been sampled, cleaned, or coated and stored. Figure 1a and Figure 1b, adopted from Reference 1, illustrate details of the parallel-plate denuder and show how it is mounted inside the MetOne SASS sampling module.

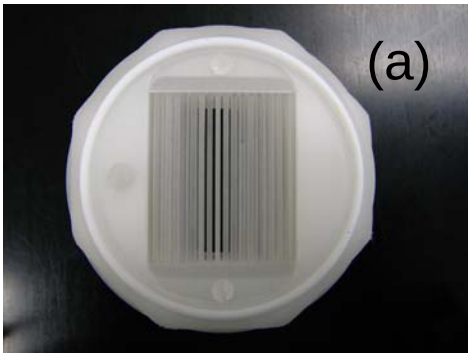
6.2 Wear gloves when conducting the steps in the following cleaning process. This cleaning process may be used to prepare the denuder when first received from the manufacturer or for removing an acidic coating from a previous sampling event.

6.2.1 Disassemble the denuder by removing the top and bottom caps. There is an o-ring in the top of the denuder and one in the bottom cap. Remove the o-rings from their grooves. The o-ring must be cleaned in the same manner as the denuder and the end caps.

6.2.2 Rinse the denuder, o-ring, and end caps in a running stream of hot tap water. Rinse all openings in the denuder, invert it and rinse from the other end as well. Rinse the exterior of the denuder and the interior and exterior of each end cap. Carefully shake out excess tap water. To help the water to drain from each piece, place them on a stack of laboratory paper towels.

6.2.3 Rinse the o-rings in a stream of running of DI water. Pat them dry with paper towels

6.2.4 Rinse the top and bottom caps by filling each with DI water, swishing, and discarding the rinse. Repeat three times. To help the water drain from the end caps turn each upside down on paper towels.



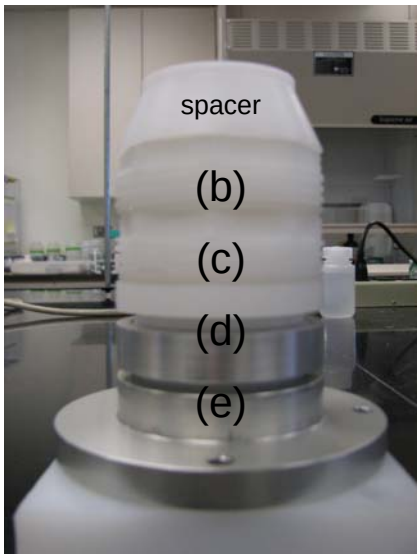


Figure 1a. SASS sampling canister featuring Prototype 2 denuders: (a) Prototype 2 integrated slide denuder; Prototype 2 sampling train assembled (b) Denuder A, (c) Denuder B, (d) Filter 1, and (e) Filter 2. This assembly is enclosed by the cover and spacer shown in Figure 1b.

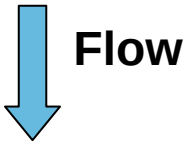


Figure 1b, SASS sampling mounted in plastic block for ease of handling. (f) sharp cut PM2.5 cyclone, (g) canister cover, (h) canister extender.

6.2.5 Rinse the denuder with DI water for approximately 10 seconds. Ensure that the water runs into the channels between the plates of the denuder and makes contact with each plate wall. Rinse the outside threads of the denuder.

6.2.6 Place the denuder in the top cap and then fill the cap with DI water. Fill the bottom cap with DI water.

6.2.7 Set the caps and denuder aside and allow them to soak for ~ 5 minutes.

6.2.8 Repeat steps 6.2.3 through 6.2.6 three additional times. When repeating step 6.2.6 shake the denuder back and forth for thirty seconds, open the denuder and then discard the rinse. It is not necessary to repeat the 5-minute soaking in step 6.2.7.

6.2.9 After the final rinse in Step 6.2.8, take care not to drop or bump the denuder, use relatively vigorous shaking to remove the excess water from the channels of the denuder and the caps.

6.2.10 To speed the drying process, dislodge water droplets by holding the denuder in front of a moderately flowing stream of nitrogen. Repeat the nitrogen drying with each cap.

6.2.11 Place the denuder, o-rings, and the caps inside the glove box on a bed of laboratory toweling. To ensure complete drying, set the nitrogen purge to allow excess gas to flow from one opening in the glove cabinet. Ensure that all other openings are closed.

6.3 The following coating process is used to apply a phosphorous acid solution to the parallel plates in the denuder. Be sure to prevent intrusion of room air by maintaining an excess flow (slight positive pressure) from the nitrogen purge while working inside the glove cabinet.

6.3.1 Ensure that the o-rings are properly seated in the grooves on the denuder and the bottom end cap. Then screw the denuder firmly into the lower storage cap.

6.3.2 Transfer approximately 15 mL of the 5% phosphorous acid coating solution to a 25 mL beaker. Although the work is conducted inside the glove cabinet, care needs to be taken not to expose large volumes of the solution to the atmosphere.

6.3.3 Use the Thermo Scientific Finnpipette auto-pipette to deliver 6 mL of the coating solution into the denuder. Ensure that each channel between the plates receives some of the solution with this delivery.

Note: Deliver more solution if needed; however, ensure that the channels are not overfilled. The solution should not flow out onto the surface of the denuder.

6.3.4 Cover the denuder by threading the upper cap loosely onto the denuder. Allow the denuder to soak in the coating solution for 10 minutes.

6.3.5 Remove the top cap and then unscrew the denuder from the bottom cap. Remove most of the coating solution from the denuder by tapping it gently against the bottom cap or shaking the denuder gently over the bottom cap.

6.3.6 If a drying manifold is unavailable, place the denuder and caps on a bed of crumpled laboratory toweling and allow wicking to remove the excess coating solution from the denuder. Crumpling the tissues allows circulation of ammonia-free gases through the denuder channels. After a minute or two, grasp the denuder and turn it over. Leave the denuder in place in the cabinet for twenty minutes and then examine to determine if the solvents of the coating solution have evaporated.

6.3.7 Verify evaporation of the coating solution by viewing the denuder from one end to determine if all channels are open to light and that no liquid is visible or present as evidenced by touching the denuder to a dry laboratory tissue. To prevent possible contamination from room air, ensure that there is an excess nitrogen flow. Continue the drying process as necessary.

6.3.8 When the denuder is completely dry, it maybe installed directly into the sampling module or stored for later use.

6.4 If storing the denuder for future use, screw the top and bottom caps onto the denuder, place the assembly in zip-closing, plastic bag and store it in the refrigerator.

***Note*:** It is recommended that the denuder and bag be placed in another larger plastic bag to ensure no room air enters. At this point, it is very important that the denuder be uniquely identifiable so that it can later be associated with a sampling event/location. Use an indelible pen to write this information on both of the denuder end caps and the zip-closing bag. Record all this information in a laboratory notebook or directly into an electronic database.

6.5 If the MetOne sampling module is to be loaded at this time, use the following steps to conduct the loading procedure while inside the glove cabinet. Determine which filters are to be used in the sampling event and insert the appropriate filter cassettes. If filters are not required, use Teflon® spacers as necessary

6.5.1 Place MetOne sampling module into a plastic block having holes to contain the module's attachment flanges. This holds the module in a level position and maintains stability during placement of the denuder and closure of the total module assembly. (Refer to Figure 1b).

6.5.2 Loosen all of the module bolts before attempting to remove them completely. Remove module cover exposing the interior of the module.

6.5.3 Determine which filters will be used during sampling and insert the filters into the appropriate filter cassettes. Record the identification numbers for each filter being used. If using Teflon® filters, record the pre-weights for each filter as well as the filter ID numbers.

6.5.4 *Nylon filter*: insert the filter cassette into the "outlet" section of the sampling module. Place a stainless steel filter spacer on top of the nylon filter cassette. If the nylon filter is not used, insert a Teflon® spacer as a place holder for the filter in the assembly.

6.5.5 *Teflon® filter*: place the Teflon® filter cassette on top of the stainless steel (or Teflon®) filter spacer.

6.5.6 Place a plastic spacer on top of the Teflon® filter cassette. This spacer is used to separate the Teflon® filter and the parallel-plate denuder.

6.5.7 Place a coated parallel-plate denuder onto the spacer. To ensure a secure fit, align the spacer pins with the denuder pins. Ensure that the black o-ring is properly seated in the groove on top of the denuder

6.5.8 Place the conical spacer on top of the denuder. To ensure a tight seal against the conical spacer, the denuder's o-ring must face upwards in the assembly.

6.5.9 Place an o-ring on the top of the conical spacer. This o-ring will ensure a tight seal against the "inlet" section of the sampling module.

6.5.10 Without disturbing the alignment of the filter cassettes, spacers, and denuder, carefully place the "inlet" section of the sampling module over the assembly.

6.5.11 Insert the module bolts and tighten each bolt one half turn in sequence to ensure the sampling module seals evenly.

Note: It is important that the data records link the identity of the denuder to the identifying information assigned to the sampling module.

7.0 Quantitative Extraction of Compact Parallel-Plate Denuders

In order to avoid exposure to room air, the module containing the sampled denuder must be opened while inside the nitrogen-purged glove cabinet. It is okay to loosen the bolts on the module before placing it inside the cabinet. Wear laboratory gloves when conducting the extraction. Proceed as shown below to extract an exposed denuder for subsequent analysis:

7.1 Disassemble the module, remove the denuder, ensure that the o-ring is in place, and then screw the denuder firmly onto its bottom cap.

7.2 Use the auto-pipette to deliver 6 mL DI water (extracting solution) into the denuder and then screw the top cap on firmly.

7.3 Shake the denuder to move the extracting solution back and forth through the channels for a minute or two. Rotate the denuder top to bottom a few times while shaking it.

7.4 Place the denuder inside the glove cabinet and then unscrew the top cap and set it aside.

Note: Use caution when unscrewing the top cap because the denuder could unscrew from the bottom cap at the same time.

7.5 While holding the bottom cap firmly against the bench top, slowly and gently unscrew the denuder from the bottom cap.

7.6 When the denuder detaches from the bottom cap gently tap it against the bottom cap or shake it gently over the bottom cap to dislodge any solution trapped between the denuder plates.

7.7 Carefully decant the extract from the bottom cap into an appropriately labeled, 15 mL sample bottle.

7.8 Attach a label with the appropriate sample information to a 15 mL sample bottle. Prepare a blank sample by pipetting 6 mL of DI water into the bottle.

7.9 Submit the blank and the denuder's extract to the laboratory for analysis of ammonium or refrigerate the samples while awaiting analysis. Ensure that the denuder's extract is analyzed within the established holding time.

Note: Sampling could be conducted using two parallel-plate denuders in a single sampling module. To process the second denuder, repeat the steps in this section. It is important to label the bottles to receive the extracts to ensure one knows which denuder's extract is in the bottle.

8.0 Storage and Handling of Denuder Extract and Handling in the Ions Laboratory

8.1 Store the extract in a labeled sample bottle. Store the sample bottle in a chemical free refrigeration unit capable of maintaining temperatures between 1 and 5 degrees C until it is time to transfer custody of the solution to the analytical laboratory.

8.2 Alert the analytical laboratory that it will be necessary to take precautions to limit exposing the samples to room air when pouring the extract from the 15 mL bottle into analysis vials for use with the ion chromatograph or automated colorimeter. The analyst should seal the analysis vials securely to prevent intrusion of air that may contain ammonia while the vials await their turn for analysis.

9.0 Corrective Action

9.1 High laboratory or field blank values are the usual causes for concern. If this occurs, repeat the cleaning procedure for the denuder, evaluate the ammonium content of the coating solution, and conduct a peer evaluation the processes used to clean, coat, install, and check the laboratory and field blank samples. Repeat the coating and recheck the blank extract solutions for acceptable values. Past experience (Reference 2) has shown a blank laboratory value of 1.0 µg NH_4^+ per denuder can be achieved.

10.0 References

1. Schurman, Misha Iris, Fall 2009. Master of Science Thesis: "Developing and Testing Prototype Compact Denuders for Ambient Air Sampling Applications." Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado.

2. Eaton, W. Cary, Wall, Constance V., and Walters, Steven J., October 2009. "Refinement and Field Testing of Denuder Technology for Quantification of Basic and Acidic Gases to Support EPA PM2.5 and CASTNET Ambient Air Monitoring Network Research." RTI International Institutional Research and Development Final Report.