

# Standard Operating Procedure for Coating and Extracting Denuders for Capture of Ammonia and Its Measurement

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## Contents

<b>Section</b>	<b>Page</b>
1.0 Purpose and Applicability.....	3
2.0 Safety Precautions.....	3
3.0 Equipment and Materials .....	3
4.0 Preparation of Coating Solution .....	4
5.0 Preparation and Use of Glove Cabinet .....	5
6.0 Cleaning, Coating, and Storage of Honeycomb Denuders .....	6
7.0 Extraction of Honeycomb Denuders.....	7
8.0 Storage and Handling of Denuder Extract and Handling in the Ions Laboratory.....	8

## **Standard Operating Procedure for Coating and Extracting Denuders for Capture of Ammonia and Its Measurement**

### **1.0 Purpose and Applicability**

This document outlines procedures for coating a denuder with phosphorous acid (or other acidic material such as citric acid) and extracting the denuder for the collection and quantitation of gas-phase basic gases species in the ambient air, primarily ammonia. This standard operating procedure (SOP) applies to coating and extracting aluminum or glass honeycomb denuders of the type 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.

### **2.0 Safety Precautions**

- 2.1 Always wear clean, dry neoprene gloves when handling any component involved in these procedures.
- 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 (MSDS) for all chemicals involved in this procedure. Several chemicals are corrosive.
- 2.3 Always keep open chemical containers in properly operating fume hoods and wear adequate protective clothing, as outlined in the MSDS sheets for that chemical.
- 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 Chem Master neoprene gloves, medium. VWR Brand Cat. No. 32892-058 or equivalent.
- 3.2 Phosphorus acid, 97% or better. 500 g. Alfa Aesar Stock No. 89407.
- 3.3 Citric acid, monohydrate. 500 g. J.T. Baker Brand Cat. No. 0118-01.
- 3.4 Methanol, reagent grade. 4 liter. VWR Brand Cat. No. VW4300-3 or equivalent.
- 3.5 1000 mL, 500 mL, and 100 mL volumetric flasks, Pyrex Class A, VWR Brand Cat. No. 29610-182 or equivalent.
- 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 1000 mL polyethylene storage bottles, VWR Brand Cat. No. 16155-050.
- 3.8 Distilled water, laboratory grade.

- 3.9 Source of ammonia-free nitrogen gas or clean air to purge glove box.
- 3.10 Storage bottles, high-density polyethylene, 60 mL capacity, VWR Brand Cat. No. 16058-043.
- 3.11 Storage bottles, high-density polyethylene, 30 mL capacity, VWR Brand Cat. No. 16058-021.
- 3.12 Graduated cylinders, selection ranging from 10 to 50 mL capacity, VWR Brand Cat. No. 24711-295 or equivalent.
- 3.13 Glass baking dishes, various sizes, clear. Pyrex 2.2 quart, rectangular. Local purchase.
- 3.14 Plastic powder funnels, sized to fit inside neck of various volumetric flasks.
- 3.15 Various laboratory supplies (fine-tipped plastic and/or stainless steel tweezers, glass graduated cylinders, beakers, watch glasses, plastic rinse bottles containing deionized water and methanol, laboratory tissue wipes, marking pen, labels, etc.). From laboratory stock.
- 3.16 Wristwatch or small electronic timer.

#### **4.0 Preparation of Coating Solution**

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

- 4.1 Preparation of 2% Phosphorous Acid Coating Solution. Note: 5% or 10% solutions are prepared by adjusting the amount weighed.
  - 4.1.1 Using a laboratory balance readable to the nearest mg, tare a clean, dry 100 mL glass beaker. Weigh out 5.00 g of phosphorous acid crystals using laboratory balance. Do this quickly to avoid absorption of ammonia gas from the air.
  - 4.1.2 Transfer phosphorous acid crystals via a powder funnel to a prelabeled, dated 250 mL glass volumetric flask. Rinse any residue remaining in beaker and funnel, with 25 mL of deionized water (use graduated cylinder to measure), into the volumetric flask.
  - 4.1.3 Add methanol to the flask until the total volume reaches 250 mL. Cap volumetric flask, swirl, and invert several times until phosphorous acid is dissolved. Set flask aside for use in coating denuders.
- 4.2 Preparation of 2% Citric Acid Coating Solution. Note: 5% or 10% solutions are prepared by adjusting the amount weighed.
  - 4.2.1 Tare a clean, dry, 100 mL glass beaker. Weigh out 5.00 g of citric acid crystals using laboratory balance readable to nearest mg.

- 4.2.2 Promptly transfer citric acid via a powder funnel to a pre-labeled, dated 250 mL glass volumetric flask. Rinse any residue remaining in beaker and funnel, with 25 mL of deionized water (use graduated cylinder to measure), into the volumetric flask.
- 4.2.3 Add methanol to the volumetric flask to reach the 250 mL mark. Cap volumetric flask, swirl, and invert several times until citric 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 laboratory paper towels.
- 5.2 Pour citric acid crystals into a Pyrex baking dish to a depth of about 0.25 inch. Place the dish inside the cabinet at a point away from the area where you will be manipulating denuders during the coating and extraction processes. The dish 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 for immersing the denuders during coating; watch glasses to cover the beakers to minimize evaporation; another Pyrex dish, lined with laboratory wipes to receive the moist, freshly-coated denuders and provide a place for them to dry; volumetric flasks to measure out coating solutions; 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 ammonia-free nitrogen (house nitrogen) or air (clean house air) via Teflon or plastic tubing to an inlet in the glove cabinet. Slightly open the plastic zippers on the front, side, and interior of the cabinet so that a significant flow of nitrogen or air 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 flow of gas to continue while one is working inside the cabinet.
- 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 Neoprene or latex 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 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 Honeycomb Denuders**

- 6.1 This procedure is written for use with either an aluminum or glass honeycomb denuder with dimensions that allow it 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.
- 6.2 Ensure that the honeycomb denuder is clean, well-rinsed with deionized water, and dry. The cleaning process follows the steps below when removing acidic coatings, such as phosphorous acid or citric acid (both very soluble in water):
- Rinse the denuder well in a running stream of hot tap water. Rinse all openings and invert the denuder and rinse from the other side as well. Rinse the exterior well. Shake out excess tap water and place the denuder on a stack of several laboratory paper towels for a minute to allow the water to wick from the honeycomb orifices. Do not allow the denuder to dry.
  - Use a spray or rinse bottle containing deionized water to rinse the exterior and interior of the denuder. Repeat the rinsing from the other side of the denuder openings. Repeat this process three times, taking care to rinse all openings. Shake excess water from the denuder and place the denuder on a laboratory wipe to drain and dry. To speed the drying process, the denuder is held in front of a stream of clean nitrogen or air to dislodge water from the openings and dry all openings.
- 6.3 Working inside the ammonia-free, purged glove cabinet, insert the denuder with openings facing up and down into a 100-mL glass beaker. Pour sufficient coating solution over the denuder in order to just cover the denuder surfaces. Gently tap the beaker up and down against the floor of the cabinet to ensure the liquid enters all honeycomb pores. Bubbles will rise to the surface as the filling solution displaces air. Add additional coating solution if needed. Insert the tips of fine-tipped stainless steel or plastic tweezers into several denuder openings; move the denuder up and down four times to ensure coating has entered the openings. Use the tweezers to pull the denuder from the beaker, shake off

excess coating solution into the beaker, and set the moist denuder on a stack of three or four crumpled laboratory tissues to dry. 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(s) in place in the cabinet for an hour or two to ensure the solvents of the coating solution have evaporated. Test the evaporation 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. During this process, maintain a flow of clean air or nitrogen in the glove cabinet to prevent entry of laboratory air.

- 6.4 For the MetOne system, the honeycomb denuder is next placed inside an aluminum sleeve that is, in turn, placed inside the MetOne sampling module. The freshly coated denuder, in its sleeve, may be temporarily stored inside a reclosable thick plastic bag. It is recommended that the denuder and bag be further stored in another larger plastic bag to ensure no room air enters. **Note:** At this point, it is very important that the denuder sleeve be identified so that it can later be associated with a sampling event/location. Use an indelible pen to write such information on both the aluminum sleeve and the reclosable bag. Record all this information in a laboratory data notebook and in any electronic database provided. Conduct all these operations inside the glove cabinet.
- 6.5 If the MetOne or other style sampling module is to be loaded at this time, conduct the normal loading procedure while inside the glove cabinet. Determine which, if any, filters are to be used in the module and insert the filter cassette. Assemble the module, tighten all bolts, seal all openings with plastic CaPlugs™, and deliver the sampling module to the requestor or to the Sample Handling and Archival Laboratory (SHAL) for further handling. **Note:** Once again, it is important to match the identity of the denuder with the identifying bar code or label of the sampling module so that when the denuder is later extracted and the extract sent for analysis, the sampling location, date, etc., is clearly linked to the denuder identity. Record all information in a laboratory data notebook and in any electronic database provided.

## 7.0 Extraction of Honeycomb Denuders

To avoid exposure to room air, the module containing the exposed denuder must be opened while inside the purged glove cabinet. It is OK to loosen the bolts on the module before placing the module inside the cabinet. Proceed as shown below.

- 7.1 Disassemble the module, remove the denuder (if it is inside an aluminum sleeve, push the denuder out of the sleeve and set the sleeve aside), and place it on a clean laboratory tissue.

**Note:** From this point forward, it is assumed that the denuder cannot be sealed on each end to allow extraction. If the denuder is glass and can be sealed with plastic plugs, the extraction method will differ. This SOP will be modified to describe this process.

- 7.2 Use a graduated cylinder to deliver exactly 30 mL of deionized water to a clean 50-mL glass beaker.
- 7.3 Using fine-pointed stainless steel or plastic tweezers, grasp the denuder in the middle of the honeycomb section and lower the denuder into the water in the beaker. 30 mL of water should just cover the denuder surface when the denuder is in the water with channels facing upward.
- 7.4 Immediately (time: zero minutes) use the tweezers to move the denuder into and just barely out of the water 10 times (using an up/down pumping motion) to fully fill the denuder cavities with water (some air bubbles should rise from the channels when this is done).
- 7.5 Cover the beaker with a watch glass to minimize evaporation; allow the denuder to remain immersed in the water for 10 minutes.
- 7.6 After 10 minutes has passed, use the tweezers to move the denuder up and down 10 more times.
- 7.7 Allow the denuder to rest immersed in the water for 10 more minutes.
- 7.8 Use tweezers to lift the denuder out of the water and hold it above the beaker; gently shake out most of the extraction solution from the denuder into the beaker. Move the denuder to a glass dish for later cleaning and reuse.
- 7.9 The beaker now contains 20 mL or more of extract.
- 7.10 Pour a portion of the water extract into a labeled 15 mL volume HDPE narrow-mouth bottle having a polypropylene linerless cap. Cap the bottle and refrigerate at ~ 4°C until submittal to the laboratory for analysis of ammonium and other cations.

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

- 8.1 Store the extract in the labeled receiving bottle at temperatures below 5°C until it is time to transfer the solution to the analytical laboratory.
- 8.2 It may be necessary to provide a “blanket” of nitrogen or another ammonia-free glove cabinet while pouring the denuder extract from the 20 mL bottle into analysis vials for use with the ion chromatograph or automated colorimeter.
- 8.3 Seal the analysis vials securely to prevent intrusion of air that may contain ammonia as the vials await their turn for analysis.