

Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

QSM Approval: _____

Coating and Extraction of Honeycomb Denuders

1 INTRODUCTION

- 1.1 The following procedures are used for the coating of honeycomb denuders with citric acid and sodium carbonate solutions, and their extraction.
- 1.2 This work is part of the NAPS - PM2.5 Speciation Program.

2 SAMPLE REQUIREMENT

- 2.1 Denuders should be coated and prepared for shipment within a week.
- 2.2 Sampled denuders should be stored in the refrigerator until extraction (Consult SOP 2.06/*.*/*S).
- 2.3 Extracts should be analysed within 24 hours.

3 APPARATUS and MATERIALS

Clean-air drying system

- Pure air generator (Aadco Instruments, Inc.) supplying an Ammonia free source of dry air
- Manifold for drying the denuders

Honeycomb Denuders

- Denuders used for coating with citric acid are marked with a red dot.
- Clean red caps (polyethylene caps, size EC-32, CAPPLUGS Division, Protective Closures, Inc) with and without hole
 - 10 mL bottle-top dispensers
 - Clean plastic trays and/or containers
 - Racks with scintillation vials
 - Powder-free nitrile gloves

THIS DOCUMENT MUST NOT BE PHOTOCOPIED

Any hard copies of this document missing any pages, or without a copy number and the initials of the Quality Systems Manager is uncontrolled. Any electronic copy of this document anywhere but on SharePoint is uncontrolled.

DO NOT USE THIS DOCUMENT FOR OPERATIONAL PURPOSES IF IT IS AN UNCONTROLLED COPY

Page:

1 of 9



Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

4 REAGENTS and SOLUTIONS

- 4.1 If available, all reagents are analytical grade, otherwise, the best available grade is used.
- 4.2 Water: use high-purity de-ionized (DI) water (resistance >18 M-ohm cm) obtained by treating tap water with reverse osmosis and ion exchange (Millipore, Model RIOS 30 and Model Super Q). (Consult SOP 19.04/*.*./S)

4.3 Stock Solutions

- 4.3.1 1 N Hydrochloric Acid (HCl): add 83 mL of concentrated (38%) HCl to approximately 900 mL of DI water in a 1000 mL volumetric flask. Dilute to the mark, and mix thoroughly. Prepare this solution in a well ventilated fumehood.
- 4.3.2 2% Sodium Carbonate (Na₂CO₃): dissolve 20 g of sodium carbonate in DI water, dilute to 1000 mL in volumetric flask, and mix thoroughly.
- 4.3.3 4% Citric Acid (C₆H₈O₇): dissolve 40 g of citric acid in DI water, dilute to 1000 mL in volumetric flask, and mix thoroughly.
- 4.3.4 2% Glycerol (C₃H₈O₃): combine 20 mL of glycerin and 980 mL of methanol in the plastic bottle, mix.
- 4.3.5 Store the stock solutions in labeled plastic bottles in the refrigerator. Prepare fresh every 4 months and record the date of preparation.

4.4 Coating Solutions

- 4.4.1 Sodium Carbonate Coating Solution: combine equal volumes of 2% sodium carbonate and 2% glycerol in the labeled dispensing bottles. Prepare fresh weekly.
- 4.4.2 Citric Acid Coating Solution: combine equal volumes of 4% citric acid and 2% glycerol in the labeled dispensing bottles. Prepare fresh weekly.
- 4.4.3 On the day of preparation of coating solutions, Lab Blank denuders are made and sent for chemical analysis.

5 CLEANING (Pre-Coating)

5.1 Red Caps

- 5.1.1 Place all caps in the container. Fill container with DI water; soak caps for approximately 5 minutes, then drain off the water. Repeat three times.
- 5.1.2 Place caps in the plastic basket, thoroughly rinse them with a jet of DI water, and dry on a Kimwipe-covered clean plastic tray/or tabletop.
- 5.1.3 Store all cleaned caps in the labeled, closed containers.

<p>THIS DOCUMENT MUST NOT BE PHOTOCOPIED Any hard copies of this document missing any pages, or without a copy number and the initials of the Quality Systems Manager is uncontrolled. Any electronic copy of this document anywhere but on SharePoint is uncontrolled. DO NOT USE THIS DOCUMENT FOR OPERATIONAL PURPOSES IF IT IS AN UNCONTROLLED COPY</p>	<p>Page: 2 of 9</p>
---	--------------------------------



Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

5.2 Honeycomb Denuders

- 5.2.1 All new denuders must be soaked in 1N hydrochloric acid overnight.
- 5.2.2 Clean citric acid coated denuders separately from those that are carbonate coated to avoid cross contamination.
- 5.2.3 Thoroughly wash all new and used denuders by flushing with a jet of DI water 3 times, then ultrasonicate the denuders for 5 minutes (ensuring that all denuders are submerged, with the honeycomb channels unobstructed), followed by 3 more rinses with a jet of DI water.
- 5.2.4 Gently tap the denuders on the clean Kimwipe to shake all of the water out of the denuder channels. Place all cleaned denuders on the Kimwipe-covered clean plastic tray. Put additional Kimwipes on top of the denuders, and allow them to air dry.
- 5.2.5 If it is necessary to dry denuders rapidly, rinse them with approximately 10 mL of methanol and allow them to air dry on the Kimwipe-covered tray, or use the clean-air drying system.
- 5.2.6 After drying, store denuders in closed, labeled containers prior to coating.

6 COATING

6.1 Citric acid coating of Denuders (with red dots)

- 6.1.1 Have polyethylene caps ready before coating denuders. To balance the denuder pressure during coating, half of the caps must have a hole in the middle. Use a needle to make the hole in the centre, and mark the caps by cutting a small piece of each cap's edge.
- 6.1.2 Be sure to minimize exposure of denuders to room air during coating because the acid gases and ammonia in the laboratory air can cause contamination. To decrease drying time and to protect the denuders from contamination, pass clean, dry air through the freshly coated denuders until they are dry.
- 6.1.3 Make sure that all components of the drying system are connected properly. Wipe the manifold ports with Kimwipes moistened with de-ionized water to remove residue of previous coating.
- 6.1.4 Before beginning the coating and drying procedure, put on powder-free gloves, then rinse your gloved hands with DI water and dry them with Kimwipes.
- 6.1.5 Confirm that bottle-top dispensers are functioning correctly by dispensing 10 mL of each solution into a graduated cylinder prior to coating.

THIS DOCUMENT MUST NOT BE PHOTOCOPIED

Any hard copies of this document missing any pages, or without a copy number and the initials of the Quality Systems Manager is uncontrolled. Any electronic copy of this document anywhere but on SharePoint is uncontrolled.

DO NOT USE THIS DOCUMENT FOR OPERATIONAL PURPOSES IF IT IS AN UNCONTROLLED COPY

Page:

3 of 9

Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

- 6.1.6 Remove one cap from a clean, dry denuder. Be sure to leave the other on the bottom of the denuder.
- 6.1.7 Using a bottle-top dispenser, gently add 10 mL of coating solution to the open end of the denuder.
- 6.1.8 Cap this end with a clean cap with a hole leaving a space between denuder and cap so coating solution can reach all of the denuder channels.
- 6.1.9 Hold the denuder by placing your thumb on the cap without the hole, and your middle finger on the cap with the hole. Cover the hole with your index finger to avoid any leakage when inverting the denuder.
- 6.1.10 Gently invert the denuder 10 times to mix the coating solution. Then rotate the denuder about 120 degrees along its axis and repeat the inverting process. This will ensure that all channels in the denuder are completely coated. To prevent leakage, do not shake the denuder during coating.
- 6.1.11 Remove the cap with the hole.
- 6.1.12 Pour out the excess coating solution into the waste beaker.
- 6.1.13 Remove the other cap.
- 6.1.14 Gently tap the denuder on a stack of Kimwipes. This will ensure that there are no liquid bubbles inside the channels of the denuder.
- 6.1.15 Place the denuder into an open manifold port, cover with a Kimwipe and let it dry (for 30 to 60 minutes).
- 6.1.16 Remove the dry denuder and wipe its outer surface with a Kimwipe moistened with DI water. Cap (without hole) both ends of the denuder, or load immediately into the ChemComb cartridge if shipping the same day.
- 6.1.17 Repeat steps 6.1.5 - 6.1.16 to coat all denuders.
- 6.1.18 Keep the coated denuders on Kimwipes inside closed, labeled container(s).

6.2 Sodium carbonate coating of Denuders

- 6.2.1 Follow steps in Section 6.1.1 to 6.1.18.



Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

7 EXTRACTION

7.1 Citric acid coated Denuders

- 7.1.1 To minimize contamination of the denuders wear clean powder-free gloves at all times during procedure.
- 7.1.2 Prepare rack with clean scintillation vials and labeled caps.
- 7.1.3 Check a bottle-top dispenser by weighing the needed volume of de-ionized water on a top loading balance (record results on the control chart).
- 7.1.4 Rinse your gloved hands with DI water and dry with Kimwipes.
- 7.1.5 Remove cap from one end. Wipe the outer surface of the denuder with a Kimwipe moistened with DI water.
- 7.1.6 Using a bottle-top dispenser, add 10 mL of degassed DI water to the open end of denuder.
- 7.1.7 Immediately cap this end with a clean, dry cap with a hole. Avoid excessive pressure while applying cap. This will cause the extracting solution to leak out of the caps during extraction. When the denuder is uncapped, be sure to hold it only by its outer surface. Do not touch either end of uncapped denuder.
- 7.1.8 Hold the denuder by placing your thumb on the cap without hole, and your middle finger on the cap with hole. Cover the hole with your index finger to avoid any leakage while inverting the denuder.
- 7.1.9 Gently invert the denuder 10 times, then rotate the denuder about 120 degrees along its axis and invert another 10 times. Rotate the denuder again 120 degrees along its axis and invert and reverse a third 10 times. This will ensure that all channels inside the denuder have been rinsed with extraction solution.
- 7.1.10 Hold the denuder by keeping the end with the holed-cap on top, then shake denuder to force the liquid to the bottom, letting the extraction solution fill up the bottom cap.
- 7.1.11 Remove the top cap (with hole) from the denuder. Hold the bottom cap firmly, and carefully remove the denuder from the cap. Most of the extraction solution should be in the bottom cap. If the extraction solution does not come out, gently shake the denuder again to get the solution out into the cap.
- 7.1.12 Pour the extraction solution into a scintillation vial and cover with labeled cap.
- 7.1.13 Repeat steps 7.1.4 – 7.1.12 to extract all denuders.
- 7.1.14 Extracts should be analyzed within 24 hours. 4.1.10 Store the residue of extracts in a freezer up to 6 months (SOP 2.6/*.*/*S).
- 7.1.15 Place used caps and denuders on the tray and clean them as soon as possible.

THIS DOCUMENT MUST NOT BE PHOTOCOPIED

Any hard copies of this document missing any pages, or without a copy number and the initials of the Quality Systems Manager is uncontrolled. Any electronic copy of this document anywhere but on SharePoint is uncontrolled.

DO NOT USE THIS DOCUMENT FOR OPERATIONAL PURPOSES IF IT IS AN UNCONTROLLED COPY

Page:

5 of 9

Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

7.2 Sodium carbonate coated Denuders.

- 7.2.1 When sodium carbonate denuder extracts are to be analyzed for Sulphate, follow the extraction steps as described in Section 7.1 with the following exceptions. Use 0.09% Hydrogen Peroxide as the extraction solution and keep extract at room temperature until next day for analysis.
- 7.2.2 Preparation of 0.09% Hydrogen Peroxide (H₂O₂) solution: carefully add 3.0 mL of 30% H₂O₂ to approximately 500 mL of DI water in 1000 mL volumetric flask. Dilute to the mark, and mix thoroughly.
- 7.2.3 When sodium carbonate denuder extracts are to be analyzed only for nitrite and nitrate, follow all extraction steps as described in Section 7.1.

8 COATING and EXTRACTION CONCERNS

8.1 High blank value for ammonia

- 8.1.1 Denuder is not clean enough. - Soak it in 1N HCl overnight and flush with de-ionized water 3times. Remember to keep denuder away from your body by placing it inside the fume hood. Exhaled breath contains a lot of ammonia, which might be absorbed by the denuder's coating.
- 8.1.2 The coating solution is not fresh or was not prepared inside a fume hood.

8.2 High blank value for Sulphate

- 8.2.1 Denuder is not clean enough. – The denuder was etched during production with a solution containing a high concentration of Sulphate. Therefore the denuder must be flushed with DI water longer before the first coating. Repeat flushing process until a low level of Sulphate in the blank is achieved. Concentration of Sulphate is a good indicator for testing denuder cleaning skills.

8.3 Caps leak during coating

- 8.3.1 The end cap is too tight. - (a) Be certain that a cap with a hole was used. (b) The denuder was held too tightly. This can generate some pressure that pushes the solution out of the denuder. Wipe the denuder with a Kimwipe moistened with DI water. Change the Kimwipes covering the work space if they become wet due to sample spillage to avoid cross contamination.

Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

9 APPLICABLE SOPs

- 2.01/*.* /S “Gravimetric Measurement”
- 19.02/*.* /S “Volumetric Measurement - Micro Pipettes and Bottle-Top Dispensers”
- 2.04/*.* /S “Fumehoods”
- 2.06/*.* /S “Laboratory Refrigerators and Freezers”
- 6.02/*.* /S “Labware Cleaning”
- 19.04/*.* /S “AAQS Water Purification System”

10 REVISIONS

- April 2003:** Authors: Ewa Dabek and Maria Piechowski; New Document.
- June 2003:** Reviewers: Maria Piechowski, David Mathieu
 Minor changes in sections 3, 6, and 11 due to installation of new device for clean-air drying system.
- Sept 2004:** Reviewer: Maria Piechowski
 Minor changes in section 7.2.; paragraph 7.2.1. contains information about extraction of sodium carbonate coated denuders destined for nitrite and nitrate analysis; and new paragraph 7.2.2 - for sulphate analysis.
- July 2007:** Reviewers: Maria Piechowski, Alicia Berthiaume
 “(4°C)” removed through text; minor changes due to additional editing.
- May 2009:** Reviewers: Maria Piechowski, David Mathieu
 Paragraph 2.1 “the same day” changed to “within a week”; paragraphs 4.7.1 and 4.7.2 “daily” changed to “weekly”; paragraph 4.7.3 is new; paragraph 6.1.3. “Lay out the Teflon manifold on clean paper towels.” is removed; paragraph 6.1.14. “(approximately 30 minutes)” changed to “(for 30 to 60 minutes)”; section 9. “2.02/*.* /S” changed to “19.02/*.* /S”.
- May 2011:** Reviewers: David Mathieu, Maria Piechowski
 Section 1.2, Change project to program
 Change vinyl gloves to nitrile gloves in section 3.7.
 Change RO 20 to RIOS 30 in section 4.2. to reflect new reverse osmosis system.

THIS DOCUMENT MUST NOT BE PHOTOCOPIED

Any hard copies of this document missing any pages, or without a copy number and the initials of the Quality Systems Manager is uncontrolled. Any electronic copy of this document anywhere but on SharePoint is uncontrolled.

DO NOT USE THIS DOCUMENT FOR OPERATIONAL PURPOSES IF IT IS AN UNCONTROLLED COPY

Page:

7 of 9

Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

Remove note pertaining to soaking of citric acid denuders in 1 N HCL to all denuders overnight and make it 5.2.1, change numbering of all subsequent sections.

Remove references to polypropylene test tubes in sections 3.6., 7.1.2, 7.1.12 and 7.1.14 and rephrase sentences.

Switch positions of sections 7.2.2 with 7.2.1, since the extraction for Sulphate is the routine procedure, and clarify text for the Nitrite/Nitrate extraction.

Section 8.1.1 Change the word “longer” regarding denuder soaking to “overnight”, and water rinsing from “longer” to “three times”.

Remove section 8.4 as it is addressed in SOP 2.04/*.*/*S –Fumehoods.

Sept 2013:

Reviewers: Michal Suski, David Mathieu

Change “HCs” to Denuders

Section 4.2 Add reference the DI water SOP

Section 4.3 re-title to “Stock Solutions” to align with section 4.4

Section 6.1.5 new reference to checking bottle top dispenser

Section 7.1.14 Remove the reference to “storing vials in refrigerator” and renumber the rest of section accordingly. Add comment about freezing the extract remainder

Add the DI water SOP to Applicable SOPs section

11 REFERENCES

1. Operating Manual, ChemComb Model 3500 Speciation Sampling Cartridge, January 2000, Revision A, Rupprecht & Patashnick Co., Inc.
2. Operating Instructions, Aadco 737 Series, Pure Air Generators, June 2002, Aadco Instruments, Inc.

Title: Coating and Extraction of Honeycomb Denuders		Copy No: ##
SOP No.: 6.09/1.6/S	Effective Date: September 13, 2013	Location: ###

Reviewer: David Mathieu
Title: Supervisor, Particulate Characterization Unit

Reviewer: Michal Suski
Title: Chemist, Particulate Characterization Unit

Approved by: Ewa Dabek
Title: Head, Particulate Characterization Unit

UNCONTROLLED IF PRINTED