VOLATILE ORGANIC COMPOUNDS (VOC) AUDIT

by

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CAUTION

Disclaimer: This Standard Operating Procedure has been developed for use by ManTech Environmental Technology, Inc. in support of the National Performance Audit Program (NPAP) under contract to the U.S. Environmental Protection Agency and may not be applicable to the activities of other organizations.

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PROCEDURAL SECTION

1.0 Scope and Application

1.1 Title 40, Code of Federal Regulations, Part 58 requires States to establish Photochemical Assessment Monitoring Stations (PAMS) as part of the State Implementation Plan in areas of ozone non-attainment. These monitoring stations will collect ambient air quality data including quantitative data on potential ozone precursors.

1.2 This Standard Operating Procedure (SOP) describes how ManTech Environmental Technology Inc. prepares dilute gaseous mixtures of aromatic and aliphatic hydrocarbons to be used as audit materials. These mixtures are prepared in high pressure cylinders or low pressure canisters and consist of hydrocarbons that contain between two and twelve carbon atoms.

2.0 Summary of Method

2.1 Before sample preparation, a closing date is determined, a list of registered participants is generated received, and up to 3 referee labs are determined by EPA. Mailing labels and data sheets are generated from this list.

2.2 Cylinder Method

2.2.1 A sufficient quantity of cylinders and regulators are cleaned to supply all the participants. Mixtures of target compounds are then prepared in clean, high pressure 1.5 liter aluminum cylinders. These cylinders have been treated, by the manufacturer, in a way to minimize the active sites of the cylinder walls.

2.2.2 The mixtures are diluted from stock cylinders at higher concentrations, using a high pressure gas transfer system (GTS).

2.2.3 The cylinders containing the gaseous mixture are packaged with a clean, high purity regulator and distributed to the participants.

2.2.4 When returned, the cylinder and regulator are re-cleaned and set aside for future use.

2.3 Canister Method

2.3.1 Canisters are received from participants, their ID's recorded in the "NPAP VOC Prep" logbook and NPAP bar coded labels are attached for ManTech tracking purposes.

2.3.2 Each canister is assigned to a batch. Each batch should contain at least one canister from a referee lab. EPA will designate referee labs for each audit.

2.3.3 A batch of canisters are attached to the manifold and one by one their background pressure is measured and then adjusted to a common background pressure.

2.3.4 A mixture of target compounds is added to the canisters.

2.3.5 The mix is diluted with VOC free nitrogen.

2.3.6 The canisters are repackaged with data sheets and instructions and returned to participants.

2.4 The data sheets are reviewed and the data is entered into a participant result database. Each participant receives a report that shows how their individual data compares to the target values.

3.0 Health & Safety Warnings

3.1 The manifold used to prepare the gas mixtures is capable of operation at pressures as high as 3000 psi. The master cylinders are attached directly to the manifold without the benefit of pressure reduction. The manifold itself includes nine separate valves and two gauges that must be monitored closely to prepare the final mixture. There may exist concurrently several different pressure domains in the cylinder/manifold system.

3.2 This complex and dynamic continuum of vacuum to high pressure requires the operator to maintain a constant high state of awareness during the filling process.

3.3 In addition to the high pressure concerns, knowledge of potential injury due to heat and chemical toxicity are also important because the manifold is heated to approximately 90 degrees C, liquid cryogen is used in the vacuum system, and the operator is usually preparing a dilution of a high ppb or ppm master cylinder.

3.4 Wear safety glasses at all times. Use thermal gloves when handling the liquid cryogen.. Be aware that the manifold operates at approximately 90°C (194°F). Safety glasses and thermal gloves must be used but are no substitute for training and knowledge.

3.4 Toxic VOC's at the ppb and ppm levels are in the master cylinder.

4.0 Apparatus & Materials

4.1 Note: The materials used in the preparation of the audit mixtures have been chosen to provide consistent and reliable results. Details of the experiments performed to determine the operating characteristics of the gas transfer system can be found in the articles listed in the bibliography.

4.2 High Pressure Cylinders (1.5 Liter)
4.3 High Purity Nitrogen (99.999 %, Total Hydrocarbons < 100 ppbV)
4.4 High Purity Regulators, Scott Model 19 VOC™
4.5 Gas Mixtures Containing Target Compounds
4.6 High Pressure Gas Manifold with digital pressure gauges with ranges 0 to 100 psig and 0 to 3000 psig
4.7 CGA to VCR Fittings: CGA 660 to ¼ inch VCR 55 fittings
4.8 Heating Blankets
4.9 Low Pressure Manifold with pressure guage with a range of 0 to 100 psia reading to 0.01 psia
4.10 Vacuum and air pumps

5.0 Cleaning of Cylinders and Regulators

WARNING

Wear safety glasses at all time. Use thermal gloves when handling the liquid cryogen. Be aware that the manifold operates at approximately 90°C (194°F).
Safety glasses and thermal goves must be used but are no substitute for Training and knowledge.

5.1 Cleaning Cylinders

1. Attach the cylinders to the GTS. (See figure 1).
2. Attach the heating blankets and heat until the cylinder reaches 40 °C.
3. Open valves 4, 8, and 9 to vent any excess gas.
4. Close valve 4.
5. Open the vacuum system (valve 2).
6. Open valves 5, 8, and 9.
7. Evacuate the cylinders to at least 50 100 millitorr.
8. Close valve 2.

9. Open valve 1 and fill cylinders to 400 - 600 psi with high purity N_2.
10. Repeat Steps 3 - 9 two additional times.

5.2 Cleaning Regulators

1. Clean the regulator by attaching it to a cylinder containing high purity nitrogen.
2. Allowing the nitrogen to flow through it at a minimum of 50 milliliters per minute for 60 minutes.

6.0 Making the Samples Using the Gas Transfer System (GTS)

WARNING

The manifold used to prepare the high pressure cylinder gas mixtures is capable of operation at pressures as high as 3000 psi. **The master cylinders are attached directly to the manifold without the benefit of pressure reduction.** The manifold itself includes nine separate valves and two gauges that must be monitored closely to prepare the final mixture. There may exist concurrently several different domains in the cylinder/manifold system.

This complex and dynamic continuum of vacuum to high pressure requires the operator to maintain a constant high state of awareness during the filling process.

In addition to the high pressure concerns, knowledge of potential injury due to heat and chemical toxicity are also important because the manifold is heated to approximately 90 degrees C, liquid cryogen is used in the vacuum system, and the operator is usually preparing a dilution from a high ppb or ppm master cylinder.

6.1 Choose gas mixtures in master cylinders from the cylinders on hand. One or more master cylinders may be used to satisfy the qualitative and quantitative purposes of the audit sample.

6.2 Make mixtures containing all target compounds and having concentrations from 1.5 ppbC to 500 ppbC are made.

6.3 Typical mixtures are in the 5 ppbC to 50 ppbC range and include a variety of hydrocarbons from the target list.

6.4 Mixtures may be prepared to test a variety of critical parameters. These include possible differential collection and desorbtion of light and heavy compounds, proper identification of closely eluting compounds, and misidentification of common non-target compounds.

6.5 Purging the Manifold

6.5.1 Note: Procedures in 6.5.2 and 6.5.3 should be done using low pressure and low flow. This may be achieved by setting the regulator to a setting just above zero psig. An audible hiss will be heard from the gas exit points.

6.5.2 Prior to use, purge the cryogenic trap by opening both the inlet line valve and the vacuum line valve (valves 1 and 2). See Figure 1. This purges the trap with high purity nitrogen to remove water build up.

6.5.3 Purge the manifold when changing cylinders and when the manifold has not been used for extended periods of time. This is done by opening the inlet valve and all exit valves.

6.6 Conditioning the Manifold

6.6.1 Condition the manifold with high purity nitrogen, after purging, by alternately evacuating the manifold to 100 millitorr followed by pressurization with high purity nitrogen to approximately 30 psia.

6.7 **Connecting Masters and Audit Cylinders to Manifold**

WARNING

Toxic VOCs at the ppb and ppm levels are in the master cylinder.

1. Begin with all valves closed.
2. Attach the CGA to VCR adaptor to the master and audit cylinders.
3. Open the inlet line valve so that high purity nitrogen flows out the selected ports at low pressure while the cylinders are being attached. **Do not open** the cylinder valves at this point.
4. Attach the master cylinder(s) to ports 6 and/or 7.
5. Attach the audit cylinders to ports 8 and/or 9.
6. Wrap the audit cylinders with the heating blankets.
7. Turn the blankets on and wait approximately one hour before filling.

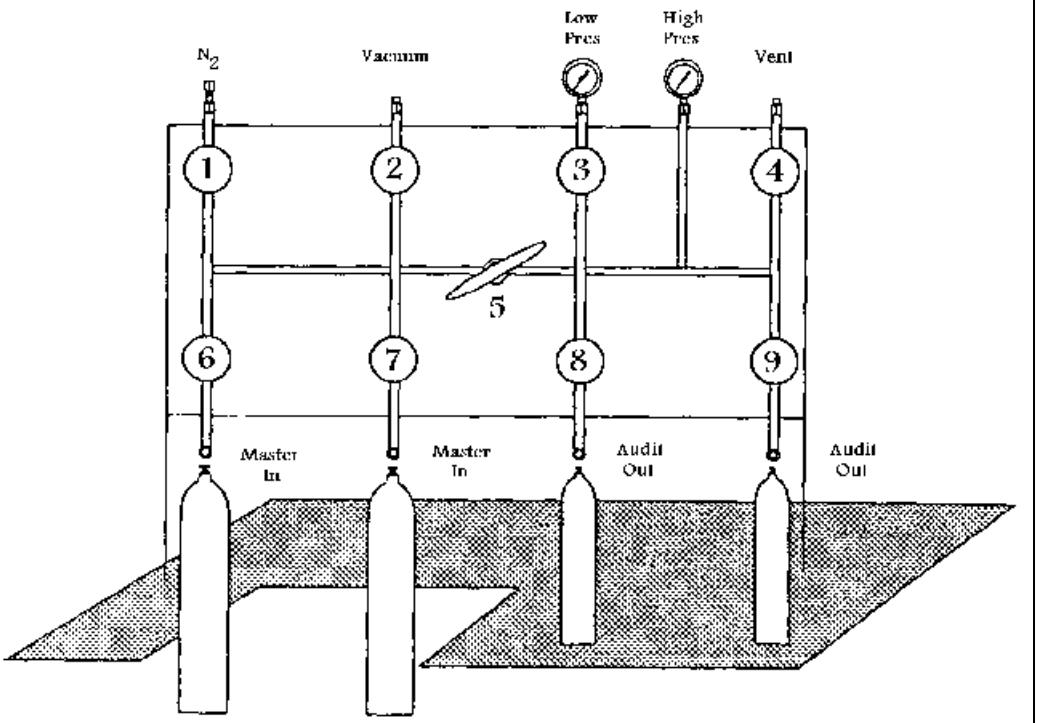

Figure 1 The Gas Manifold with Attached Cylinders.

6.8 Venting Pressurized Cylinders

NOTE: Always assume that the audit cylinders are pressurized.

1. Close all valves.
2. Open the audit cylinder valves slowly.
3. Open valves 8 and 9.
4. If the pressure gauge reads greater than 15 psi, open valve 4 to release the pressure and contents to the exhaust.

6.9 Evacuating the Manifold and Cylinders

1. Close all valves.
2. Start the vacuum pump.
3. Open the vacuum system valve 2.
4. Open valves 5, 8, and 9.
5. Evacuate both sides of the manifold to at least 50 millitorr.
6. Open the cylinder valves.
7. Evacuate the entire manifold/cylinder system to 50 millitorr.

8. Close all valves.

6.10 Filling the Audit Cylinders

1. Open the valves on the master cylinder.
2. Open the valve on the manifold that is in line with the master cylinder.
3. Open the audit cylinder valves.
4. Throttle the regulating valve 5 until the audit cylinders are filled to the desired pressure.
5. Close all valves on the manifold.
6. Open valve 2.
7. Evacuate to 100 millitorr.
8. Close Valve 2.
9. Open valve 1 to the nitrogen diluent.
10. Open valves 8 and/or 9 to the audit cylinder(s).
4. Throttle the regulating valve until the audit cylinders are filled to the desired final pressure with high purity nitrogen.
12. Close all valves.

6.11 Disconnecting Master and Audit Cylinders

1. Open all appropriate valves (5, 6, 7, 8, and 9).
2. Set the regulator pressure on the high purity nitrogen to 30 psi or less.
3. Open valve 1.
4. Disconnect the cylinders at the attachment to the manifold, being sure that low pressure, high purity nitrogen is flowing from the ports.
5. Replace the plugs.
6. Close all valves.
7. Return the master cylinders to the storage facility.
8. Disconnect the adaptor from the cylinder.
9. Label the audit cylinders with the date, initials of operator, and audit identification.

6.12 Standby State for the Manifold

6.12.1 Replace the plugs that may have been removed from the ports.

6.12.2 Condition the manifold with high purity nitrogen. Leave the manifold in the pressurized state at approximately 30 psi.

6.12.3 Close all valves.

7.0 Calculations

7.1 Note: After the initial quantitative and qualitative determinations have been made, in accordance with the purpose of the audit, calculate the actual pressures used in preparing the mixtures. Formulas and examples are found in the following sections.

7.2 Convert ppbV to ppbC

$C_A(ppbC) = (ppbV) \times N_C$

where C_A = concentration of analyze
N_C = number of carbons in analyze molecule
ppbC = part per billion carbon
ppbV = part per billion volume

7.3 Calculate the dilution ration for the master cylinder.

$DR = C_D/C_M$

where DR = Dilution Ration
C_D = Concentration desired in audit cylinder
C_M = Concentration in master cylinder

7.4 Example for high pressure cylinders: A master cylinder is chosen to provide 28 of the target compounds. This cylinder contains the compounds at 45 ppbV. The desired concentration is 1.5 ppbC at a final pressure of 2000 psia.

1. What is the concentration of benzene in ppbC?

   Calculate the concentration of the compound in ppbC by multiplying the number of carbon atoms contained in the compound by the concentration in ppbV.

   $C_A (ppbC) = (ppbV) \times N_C$

   Benzene = 45 ppbV x 6 carbon atoms = 270 ppbC

b) What pressures are needed to prepare the mixture?

1. Calculate the dilution ratio by choosing one of the target compounds and divide the desired concentration (15 ppbC) by the concentration in the master cylinder (270 ppbC).

   DR - C_D/C_M

   DR = 15 ppbC/270 ppbC - 0.05556

2. To obtain the pressure needed using the master cylinder, multiply this dilution ratio by the final pressure desired in the audit sample.

   DR x C_D = 0.05556 x 40 psia = 2.22 psia

Solution: Fill the audit canisters to 2.22 psia greater than the background pressure with contents of the master cylinder and then pressurize to 40 psia with high purity nitrogen.

7.5 Example for low pressure canisters: A master cylinder is chosen to provide 28 of the target compounds. This cylinder contains the compounds at 45 ppbV. The desired concentration is 15 ppbC at a final pressure of 40 psia.

a) What is the concentration of benzene in ppbC?

Calculate the concentration of the compound in ppbC by multiplying the number of carbon atoms contained in the compound by the concentration in ppbV.

C_A(ppbC) = (ppbV) x N_c

Benzene = 45 ppbV x 6 carbon atoms = 270 ppbC

b) What pressures are needed to prepare the mixture?

1. Calculate the dilution ratio by choosing one of the target compounds and divide the desired concentration (15ppbC) by the concentration in the master cylinder (270 ppbC).

   DR = C_D/C_M

   DR = 15 ppbC/270 ppbC = 0.05556

2. To obtain the pressure needed using the master cylinder, multiply this dilution ratio by the final pressure desired in the audit sample.

$$DR \times C_D = 0.05556 \times 40 \text{ psia} = 2.22 \text{ psia}$$

Solution: Fill the audit canisters to 2.22 psia greater than the background pressure with contents of the master cylinder and then pressurize to 40 psia with high purity.

8.0 Preparing Canisters

8.1 Make sure all manifold fitting are tight and the pumping system is anchored.

8.2 Evacuate the system and flush with VOC free nitrogen until a background pressure of at least 0.30 psia can be maintained for a least 2 min.

8.3 Attach a batch of canisters and evacuate and test the system again, tightening canisters connections as needed.

8.4 With the manifold evacuated and isolated open one canister valve and read its background pressure. Close the canister valve.. Evacuate the manifold again, Repeat for each canister in the attached batch. When all have been read, determine a common background pressure. Work with only one canister.

8.5 Adjust the pressure of each canister by adding VOC free nitrogen or evacuating as needed to reach the common background pressure. Work with only on canister at a time.

9.0 Filling Canisters

9.1 With all canisters isolated at a common background pressure, attach a standard VOCs mixture cylinder to the system, purge the lines with the mixture, and adjust the pressure to greater than the common background pressure of the canisters.

9.2 Slowly crack open the valve on the canister closest to the VOC cylinder, and then the next canister, etc. Increase the flow/pressure from the VOC cylinder as needed to maintain an increasing pressure as canisters are opened.

9.3 Gradually open all canister valves maintaining pressure on the system.

9.4 With all valves wide open, monitor the pressure and turn down the flow as the desired pressure approaches.

9.5 At the desired VOC pressure turn off the metering valve and allow 5-10 seconds to read the equilibrium pressure.

9.6 Close all canister valves.

9.7 Attach VOC free nitrogen to the system, evacuate and flush lines, and adjust the pressure to greater than the canisters' equilibrium pressure

9.8 With the VOC free nitrogen flowing, repeat steps 9.2 through 9.6 for the VOC free nitrogen.

9.9 Remove the canisters from the manifold and ship them with data sheets and instructions.

10.0 Data Management & Records Management

10.1 Participant Data: Audit data is sent directly to the Data Entry personnel and handled according to *NPAP-SOP-005: Computer Data Entry, Report Printing, and System Maintenance for the NPAP*.

10.2 Record all regulator cleaning data in the "Cylinder Pressure and Regulator Cleaning Log." Date and initial all entries.

10.3 Record all canister and cylinder filling data in the "NPAP VOC Prep" logbook. Date and initial all entries.

REFERENCE SECTION

1.0 Documentation on the Use of the Scott Gas Transfer Manifold; Research and Development Dept., Scott Specialty Gases, Inc.; October 23, 1992.

2.0 Mitchell, W., Streib, E., Crist, H., et al., "A Low Cost Procedure to Make Gaseous Pollutant Audit Materials", in Proceedings of the 1993 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, VIP-34; Air & Waste Management Association: Pittsburgh, 1993; pp 363-369.

3.0 Suggs, J., Crist, H., Mitchell, W., et al, "A QA Program For The Photochemical Assessment Monitoring Network", in Proceeding of the 1994 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, VIP-39; Air & Waste Management Association: Pittsburgh, 1994; pp 135-141.

4.0 NPAP-SOP–005: Computer Data Entry, Report Printing, and System Maintenance for the NPAP