California Environmental Protection Agency

Air Resources Board

Northern Laboratory Branch
Monitoring and Laboratory Division

STANDARD OPERATING PROCEDURE FOR PREPARATION OF CALIBRATION AND CONTROL STANDARDS USING A GAS MIXER/DILUTION APPARATUS

SOP MLD074
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DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure (SOP) does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the SOP are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

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1. Scope

This method describes the procedures followed by Monitoring and Laboratory Division (MLD) staff to prepare working standards and controls for the calibration of analytical instrumentation used in the analysis of ambient air samples. The use of gaseous and liquid standards is described. This standard operating procedure (SOP) was developed by staff in the Organic Laboratory Section (OLS) of the Northern Laboratory Branch (NLB).

2. Summary of Method

Using a gas mixing and diluting system (mixer/diluter) gases in high pressure cylinders are diluted with nitrogen gas, also contained in a high pressure cylinder, and transferred into a SUMMA canister. The mixer/diluter works by controlling various mass flow controllers whose output is blended into a lower concentration. The mixer/diluter also controls the final pressure of gas delivered to the canister. A mass totalizer is included in the system to measure the volume of gas placed in the cylinder to allow calculations of liquid standards that may be added to the output gas stream.

3. Personal Qualifications

Personnel performing this procedure should be familiar with proper operation of the gas dilution system and other laboratory equipment used in the preparation of standards. Familiarity with the safe handling of compressed gases, toxic compounds, and general laboratory techniques is also required. This method involves the application of the Ideal Gas Law, density, molality, and gas volume calculations with the potential use of spreadsheets which requires knowledge of these concepts.

4. Safety

This method uses high pressure gases. Refer to the safe handling practices regarding compressed gases when moving and installing the cylinders.

The compounds used by this method are toxic and precautions should be taken to limit the potential for inhalation of these compounds. Gloves and eye protection are recommended for the handling of the liquid standards when used in this method. Refer to safety data sheets (SDS) prior to handling.

There are potentially dangerous voltages used by the equipment and care should be exercised when the unit's cover is removed or water is handled near the device.

Laboratory staff are responsible for following the established work procedures and safety guidelines identified in the Chemical Hygiene Plan and all other components of the ARB Injury and Illness Prevention Program.

5. Interferences and Limitations

Interferences from contamination are an issue for this procedure. Only ultra-high purity (UHP, 99.995% or better) gases should be used for dilution and passed through a hydrocarbon scrubber. Water used in the preparation of standards must be VOC (volatile organic compound) free. To determine the suitability of a new compressed gas cylinder and organic free water a blank using the same volume of gas or water used to make the standard shall be placed in a SUMMA canister and tested for compound concentrations exceeding blank criteria values. Any SUMMA canister used for standard production or suitability testing must pass OLS's contamination check. See MLD020 Standard Operating Procedure (SOP.)

The mass flow controllers must not be set below 10 percent or greater than 90 percent of their maximum flow rates. The usable ranges for various controllers are detailed in the following table.

Flow Controller	Range
10 sccm	1 – 9 sccm *
100 sccm	10 – 90 sccm
1 Liter/minute	100 – 900 sccm
10 Liter/minute	1 – 9 Liter/minute

*Recommendation not less than 1.5 sccm.

If multiple cylinders are connected to make a dilution gas each standard cylinder should be tested by filling and analyzing a canister with a single gas of comparable concentration to the multi-cylinder dilution to make certain it does not contain any contaminant that would affect any other component of the diluted gas.

Each compound should be checked to make certain it does not react with any internal wetted part of the mixer/diluter. This is done by analyzing a standard made with the dilution system and comparing it to either a certified standard of comparable concentration or one prepared using syringe volumetric dilution from the high pressure cylinder standard which replicates the dilution system's final canister concentration. Results of these tests must meet method SOP replicate criterion for which these standards are used.

6. Apparatus and Equipment

   6.1. Summa polished stainless steel canisters

   6.2. Environics Model 2040 mixer/diluter

   6.3. Sierra Smart-Trak flowmeter

   6.4. Cylinder regulators (CGA 580, CGA 350, CGA 180)

   6.5. Nafion® humidifier

   6.6. Teflon separatory funnel

   6.7. Analytical balance, syringes, and vials for liquid standards

7. Reagents and Supplies

   7.1. Nitrogen, ultra-high pure (UHP), 99.999%

   7.2. High concentration gas standards

   7.3. Liquid standards

   7.4. VOC free water (see section 4)

   7.5. Hydrocarbon gas scrubber

8. Calibration Standards

   The OLS uses a custom blend of gaseous standards prepared by the National Institute of Standards and Testing (NIST). This blend is at concentrations higher than ambient levels to maintain stability and must be diluted prior to use. Additional compounds not contained in this standard mixture that are target compounds or compounds of interest may be added using liquid standards, gas tight syringe injections from gaseous standards, or from auxiliary ports on the dilution system. Liquid and gas tight syringe compounds are added via injection while the standard canister is being filled with the gaseous standards.

9. Standard Storage

9.1. High pressure cylinders are stored at room temperature. All cylinders must be secured and capped when not in use.

9.2. Neat materials are those that have not been mixed or changed in any way that may be combined with others or diluted to be used as standards. A stock solution is a concentrated solution that will be diluted to some lower concentration for actual use. Neat materials and stock solutions have accurate known concentrations. All neat, stock, and working solutions must be stored in accordance with procedures recommended by their supplier.

10. Standard Preparation

10.1. Mixer/Diluter Initial Setup

The mixer/diluter is energized and allowed to stabilize for at least 30 minutes. The pressure regulators are connected from the diluter's inlet port to the appropriate standard cylinder. The main cylinder valves are opened and the regulators adjusted to approximately 40 psig. If post regulator shut-off valves are present they are opened. Liquid working standards are removed from the refrigerator and allowed to warm to room temperature prior to injection.

10.2. Mixer/Diluter Setup

The mixer/diluter is placed in concentration mode and the required dilution program is recalled from the unit's preprogrammed memory. The program is derived by determining the dilution of the standard gas by a diluent gas and entering the correct value. Since gas mixtures are used the standard gas's concentration is given an arbitrary value of 100. As an example if you require a one hundredth dilution of the standard gas a value of one is entered for the port the standard gas is attached to. The canister fill pressure is set to 25 psig. The mixer/diluter's output line is loosely attached to the SUMMA canister with the three-way valve set in the by-pass position. The <Start> button is depressed and the gas flows are monitored to make certain the proper dilution was selected and that they are functioning normally. The stopcock on the separatory funnel is opened if a humidified standard is to be made. See detailed instructions for operation in OLS-MLD-Mixer/Diluter.

10.3. Making a Standard

After the system has stabilized and equilibrated, which takes approximately five minutes, the standard may be prepared. The three-way valve is turned so the gas output is directed to the SUMMA canister. The lines downstream of the valve are

purged with approximately 200 milliliters of gas. The valve is returned to the by-pass position and the output line's fitting on the canister is tightened (closed.) The flow totalizer's display is reset to zero. The canister valve is opened and a liquid or gaseous standard is prepared for injection if one is to be added to the canister. A solvent flush technique must be used when injecting a liquid standard. The syringe is inserted into the septa-equipped tee until it just touches the wall of the tee opposite the septa. For a gaseous standard the syringe is flushed at least three times prior to filling and the syringe's pressure is allowed to come to atmospheric pressure prior to injecting in the gas flow directed to the canister. The three-way valve is turned so flow is directed to the canister and the liquid or gaseous standard is slowly injected. Approximately one liter of gas is allowed to flow into the canister before removing the syringe. It is recommended that injections into the canister take place while the canister pressure is less than -20 psig. A canister tag detailing the contents is prepared while the canister is being filled. See section 12. The standard must not be used for at least 24 hours to allow it to equilibrate in the canister

11. Quality Control

11.1. Gases

Only ultra-high purity gases are used as the diluent gas.

11.2. Calibration Standard

Certified gas standards are purchased from The National Institute of Science and Technology (NIST) when available. The gases must not be used passed their expiration date unless otherwise authorized by laboratory management. Gases may continue to be used if they are recertified by their supplier or NIST. Liquid standards must be certified by their supplier and stored according to supplier recommendations. The calibration standard dilution must be different from the control standard to verify the mass flow controllers are responding to the unit's computer control.

11.3. Control Standard

Control gases must be obtained from approved sources and not used beyond their expiration dates unless otherwise authorized by laboratory management. Liquid standards must be made from sources other than those of the calibration standards. If no other source is available a different lot number from the supplier may be used.

11.4. Mixer/Diluter

The mixer/diluter must have the mass flow controllers certified at least annually by MLD's standards laboratory. The mixer/diluter must be sent to the manufacturer at least every two years for recertification, preventative maintenance, and updates.

12. Troubleshooting

Problem	Possible Corrective Action
Gas mixer does not power up	Check power cable and power circuit
Gas mixer set points lost due to battery failure	Submit unit to MLD Instrument Shop or return to manufacturer
Improper gas concentrations in standards	Check that correct gases are attached to proper ports Check that correct gas flow values are entered into the diluter Check standard expiration date Verify correct liquid standard and volume was added to canister
No gas flow	Check compressed cylinder connections and that all valves are open and regulators are set to their proper pressures. If determined to be instrument problem return to manufacturer

13. Calculations

Dilutions may be calculated based either on mass flow controller settings or absolute flow. The mixer/diluter calculates the flow required based on concentrations entered by the user. Since most of the standard and control gases are mixtures with varying compound concentrations an arbitrary value of 100 is used for the gas mixture. Standards using the 100 value are calculated by the unit's concentration software to make the appropriate dilution.

Example: A one-fiftieth dilution is required. Set the concentration of the port for the standard gas to 2: 100/50 = 2

To verify that the flows are correct press the <OGC/Flow> button to observe the flows in sccm.

Example: one-fiftieth dilution with a total flow of 800 sccm should display standard flow of 16 sccm with a diluent flow of 784.

Liquid calculations are done using the ideal gas law. It is assumed the low ppb levels of compounds added to the cylinder represent a near infinite dilution and the slightly elevated atmospheric pressure of nitrogen in the container does not invalidate the use of the ideal gas law.

$$PV=nRT$$

Where

P = pressure in atmospheres
V = volume in liters
n = moles of compound
T = temperature in degrees Kelvin
R = ideal gas law constant 0.082 atmosphere * liters / mole * degree K

To calculate the canister concentration, the nanomoles of compound injected is divided by the moles of diluent gas to give part per billion (mole basis) concentrations in the canister. Alternately the volume of diluent gas is measured by a gas totalizer for use in the calculation.

14. Tracking Procedure

Canister tags shall be attached to every standard or control produced. Minimum information shall include the following:

- Stock gas mixture ID
- Standard Source (cylinder identification or liquid working standard)
- Dilution value
- Date and preparer's initials
- Whether the canister has been humidified
- Canister ID
- Final pressure of canister (canister gauge)
- Atmospheric pressure
- Volume of gas in canister
- Laboratory temperature
- Any deviations in the preparation of the gas standard dilution

A logbook of prepared standards must be kept near the mixer/diluter which includes the same information as the tag.

15. References

15.1. Operating Manual Series 2014 Computerized Volatile Organic Compounds Gas Dilution System, Environics, Inc. 69 Industrial Park Road East, Tolland, CT 06084-2805, 860-872-1111

15.2. Operator Manual Addendum Canister Filling and Humidifier Options, Environics, Inc., Dec., 2007

15.3. MLD QC Manual, Revision 3.0, 2014

15.4. MLD020 SOP for Canister Cleaning, Revision 4.0, 4/9/2013

15.5. Cal/OSHA Title 8, §4650. Storage, Handling, and Use of Cylinders

15.6. MLD Injury and Illness Prevention Plan

16. Appendix

16.1. OLS-MLD074-A1: Revision Log

16.2. OLS-MLD074-A2: Annual Review Log

OLS-MLD074-A1
Revision Log

Revision Made and Reason	Approval Date	Approved By	Start Date

OLS-MLD074-A2
Annual Review Log

Review Date	Reviewed By	Changes Needed	Comments