CALIFORNIA
AIR RESOURCES BOARD

STANDARD OPERATING PROCEDURE FOR PREPARATION OF CALIBRATION AND CONTROL STANDARDS USING A MULTI-COMPONENT GAS BLENDING AND DILUTION SYSTEM

MLD074
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Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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Disclaimer: Mention of any trade name or commercial product in this standard operating procedure does not constitute endorsement or recommendation of this product by the California Air Resources Board. Specific brand names and instrument descriptions listed in the standard operating procedure are for equipment used by the California Air Resources Board's laboratory. Any functionally equivalent instrumentation is acceptable.

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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 blending and diluting system (mixer/diluter), volatile organic compound (VOC) gases in high pressure cylinders are diluted with nitrogen gas, also contained in a high pressure cylinder, and transferred into an electropolished, ceramic-coated, or silica-lined stainless steel air canister. The mixer/diluter works by controlling various mass flow controllers (MFCs) 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 canister to allow calculations of liquid standards that may be added to the output gas stream.

3. ACRONYMS

Acronym or Term	Definition
Cal/OSHA	California Division of Occupational Safety and Health
CARB	California Air Resources Board
CGA	Compressed Gas Association
ID	Identification
inHg	Inches of Mercury
LIMS	Laboratory Information Management System
MFC	Mass Flow Controller
MLD	Monitoring and Laboratory Division
NIST	National Institute of Standards and Technology
NLB	Northern Laboratory Branch
OLS	Organics Laboratory Section
PPB	Parts Per Billion
PSIA	Pounds Per Square Inch Absolute
PSIG	Pounds Per Square Inch Gauge
QC	Quality Control
SCCM	Standard Cubic Centimeter Per Minute

Acronym or Term	Definition
SDS	Safety Data Sheet
SOP	Standard Operating Procedure
UHP	Ultra-High Purity
VOC	Volatile Organic Compounds

4. INTERFERENCES AND LIMITATIONS

Interferences from contamination are an issue for this procedure. Only 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 reagent grade such as Nanopure. To determine the suitability of a new compressed gas cylinder and Nanopure water, a blank using the same volume of gas or water used to make the standard shall be placed in a stainless steel air canister and tested for compound concentrations exceeding blank criteria values. Any air canister used for standard production or suitability testing must pass OLS's contamination check. See MLD020 SOP for Cleaning Stainless Steel Air Canisters.

The MFCs 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.

Table 1. Flow Controller Ranges

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.

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.

5. PERSONNEL QUALIFICATIONS AND TRAINING

5.1. Prior to performing this procedure, new personnel must be trained by staff with expert knowledge of this procedure. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the procedure, the quality assurance components, and LIMS functionality pertaining to the program.

5.2. Personnel should provide an initial demonstration of capability prior to performing this procedure on real-world samples (i.e., data for record).

5.3. Training will be documented and maintained by the laboratory supervisor.

5.4. 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.

6. SAFETY REQUIREMENTS

6.1. Refer to safe handling practices regarding compressed gases when moving and installing cylinders (Cal/OSHA Title 8, §4650).

6.2. 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 SDS prior to handling.

6.3. 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.

6.4. 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 CARB Injury and Illness Prevention Program.

6.6. 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.

7. HAZARDOUS WASTE

The liquid standards of acrolein, acetonitrile, and acrylonitrile are considered extremely hazardous and toxic. The hazardous waste must be disposed within 90 days upon accumulation of 1.0 kg (approximately two pounds). The NLB Health & Safety Officer should be notified upon accumulation of 1.0 kg of this waste to arrange for disposal. Waste vials containing acrolein, acetonitrile, and acrylonitrile are stored in a small 48-ounce waste bucket. The waste bucket must be properly labeled with appropriate hazardous waste labels indicating the contents and start date of accumulation.

8. EQUIPMENT AND SUPPLIES

8.1. Electropolished, ceramic-coated, and/or silica-lined stainless steel canisters.

8.2. Environics Model 2040 Multi-Component Gas Blending and Dilution System.

8.3. Sierra Smart-Trak flowmeter.

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

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

8.6. Compressed UHP Nitrogen.

8.7. Compressed high concentration gas standards.

8.8. Liquid standards.

8.9. Reagent grade water purification system, Barnstead NanoPure-Diamond model# D11951, or equivalent.

8.10. Hydrocarbon gas scrubber.

8.11. Calibrated gauge.

8.12. 9/16” compound wrench.

9. PROCEDURES

9.1. Mixer/Diluter Initial Setup

The mixer/diluter is powered on 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.

9.2. 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. For 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 air canister fill pressure is set to 25 psig and the diluter will stop filling until pressure is reached. The mixer/diluter's output line is loosely attached to the air canister with the three-way valve set in the bypass 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.

9.3. 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 air 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 fitting on the canister is tightened (closed). The flow totalizer's display is reset to zero. The canister valve is opened and a liquid and/or gaseous standard is prepared for injection.

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 vacuum is more than 20 inHg. A canister tag detailing the contents is prepared while the canister is being filled. See section 14 for troubleshooting. The standard canister must sit overnight to equilibrate before being analyzed.

9.4. Filling grab samples

Grab samples are received from the field at or near atmospheric pressure. Most grab samples will utilize a dilution factor of two. Knowing this factor can help in determining final canister pressure when filling with nitrogen. A simple calculation can determine the dilution factor, but using the dilution factor calculator can help with this determination. Record the canister vacuum using the calibrated gauge and enter this value into the calculator. Doing this will also calculate the final canister pressure to set on mixer/diluter. After the canister has been filled with nitrogen, it is set aside for five (5) minutes to equilibrate. The final pressure is recorded with the calibrated gauge and its value is entered into the calculator to display the dilution factor. By following this method, all canisters in a group of grab samples will have similar dilution factors. See section 11 (Calculations) for determining dilution factors.

10. QUALITY CONTROL

10.1. Gases

Only UHP gases are used as the diluent gas.

10.2. Calibration Standard

Certified gas standards are purchased from NIST when available. If NIST gases are not available, they may be NIST traceable. Certified gas must not be used beyond their expiration date unless otherwise authorized by laboratory management. Gases may continue to be used if their supplier or NIST recertifies them.

Liquid standards must be certified by their supplier and stored according to supplier recommendations. Liquid calibration standards must not be used beyond their expiration date unless otherwise authorized by laboratory management.

10.3. Control Standard

Control gas standards are purchased from NIST when available. If NIST gases are not available, they may be NIST traceable. Control gas must

be obtained from approved sources and may not be used beyond their expiration dates unless otherwise authorized by laboratory management.

Liquid control 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 or the control standard can be made on another day or by another analyst. Liquid calibration standards must not be used beyond their expiration date unless otherwise authorized by laboratory management.

10.4. Mixer/Diluter

The mixer/diluter must have the MFCs 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.

10.5. See NLB Laboratory Quality Control Manual for further details about QC.

Table 2. QC Reference

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Calibration Standard (Gas)	All certified cylinders	Should be NIST certified and not used beyond expiration date	1. If not NIST certified, should be NIST traceable. 2. Gases that are past expiration date can be used per supervisor approval.
Calibration Standard (Liquid)	All liquid standards	Must be certified and stored by supplier recommendations	Liquid control standards that are past expiration date can be used per supervisor approval.
Control Standard (Gas)	All cylinders	Should be NIST certified and not used beyond expiration date. Are obtained from approved sources	1. If not NIST certified, should be NIST traceable. 2. Gases that are past expiration date can be used per supervisor approval.
Control Standard (Liquid)	All liquid standards	If available, should be made from sources other than those of the calibration standard	1. Liquid control standards that are past expiration date can be used per supervisor approval. 2. If no other source is available, a different lot number from the supplier may be used, made by another analyst, or made on another day.

11. CALCULATIONS

Dilutions may be calculated based on either MFC 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 sccm

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 the compound injected is divided by the moles of diluent gas to give ppb (mole basis) concentrations in the canister. Alternately, the volume of diluent gas is measured by a gas totalizer for use in the calculation. A dilution factor calculator is available on the OLS Drive in the Standards folder.

Dilution Factor for Grab Samples

$$\text{Dilution Factor} = \frac{(\text{psig after dilution} + \text{psia lab atmosphere})}{(\text{psia lab atmosphere} - (\text{vacuum inHg before dilution} \times 0.491))}$$

*0.491 = Conversion factor from inHg to psig

12. DATA MANAGEMENT

Internal and external instrument calibration reports are to be kept with the instrumentation at all times. SDSs and cylinder certificates of accuracy are to be kept near the mixer/diluter.

13. MAINTENANCE AND REPAIRS

13.1. The unit must be sent to the vendor every two years for a full equipment check and calibration.

13.2. On the year the unit does not go to the vendor, the unit must have the MFC evaluated and checked to ensure it is working properly. This is done internally by CARB.

14. TROUBLESHOOTING

Problem	Possible Corrective Action
Mixer/diluter does not power up	Check power cable and power circuit
Mixer/diluter set points lost due to battery failure	Submit unit to MLD Instrument Shop or return to manufacturer.
Improper gas concentrations in standards	1. Check that correct gases are attached to proper ports. 2. Check that correct gas flow values are entered into the mixer/diluter. 3. Check standard expiration date. 4. Verify correct liquid standard and volume was added to canister.
No gas flow	1. Check compressed cylinder connections and that all valves are open and regulators are set to their proper pressures. 2. If determined to be instrument problem, return to manufacturer.

15. TRACKING PROCEDURES

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

16. REFERENCES

16.1 California Air Resources Board MLD Northern Laboratory Branch: Final Chemical Hygiene Plan for Northern Laboratory Branch, 1927 13th Street, 1900 14th Street, June 2019.

16.2. California Air Resources Board MLD Northern Laboratory Branch: Laboratory Quality Control Manual, Revision 4.0, September 17, 2018. https://ww2.arb.ca.gov/sites/default/files/2018-10/nlbqcm.pdf

16.3. Cal/OSHA Title 8, §4650. Storage, Handling, and Use of Cylinders. https://www.dir.ca.gov/title8/4650.html

16.4. MLD020 SOP for Canister Cleaning, Revision 4.1, November 26, 2018. https://ww2.arb.ca.gov/sites/default/files/2018-11/mld020.pdf

16.5. Operating Manual Series 2014 Computerized Volatile Organic Compounds Gas Dilution System, Environics, Inc. 69 Industrial Park RoadEast, Tolland, CT 06084-2805, 860-872-1111. http://www.environics.com/hs-fs/hub/16612/file-2068017614-pdf/docs/gen2-manual-rev-8.pdf

17. REVISION HISTORY

Revision Number	Revision Date	Revision Made
0	5/11/2015	New SOP
1	August 13, 2019	Added Section 3. Table of Acronyms
1	August 13, 2019	Added Section 7. Hazardous Waste
1	August 13, 2019	Deleted Section 8. Calibration Standards
1	August 13, 2019	Added Section 9.4 Filling Grab Samples
1	August 13, 2019	Added QC Table to Section 10
1	August 13, 2019	Added Section 12. Data Management
1	August 13, 2019	Added Section 13. Maintenance & Repairs
1	August 13, 2019	Removed Appendixes for Revision Log and Annual Review Log
1	August 13, 2019	Added Section 17. Revision History
1	August 13, 2019	Added Section 18. Annual SOP Review Log

18. ANNUAL SOP REVIEW LOG

By signing this form, the analyst acknowledges that her or she understands the method SOP and follows the procedures when performing the associated analyses. Management initials each line to ensure changes and comments are communicated.

Review Date	Reviewed By	First Time Review? Yes/No	Changes Needed	Comments	Management Initials