Standard Operating Procedure for the Determination of Compounds in Aerosol Consumer Product Propellant by Gas Chromatography

SAS05
Revision 4.0

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.

Table of Contents

Standard Operating Procedure Determination of Compounds in Aerosol Consumer Product Propellant by Gas Chromatography

1 Introduction

This standard operating procedure (SOP) describes the analysis of aerosol consumer product propellant compounds. This SOP follows Method 310 as required by the California Consumer Products Regulations. This SOP is based on ASTM D3063-94, ASTM D3064-97, ASTM D3074-94, and US EPA Method 18.

2 Summary of Method

An aerosol container is vented and the propellant is collected in an evacuated propellant collection bag. A sample from the propellant collection bag is analyzed on a gas chromatograph, fitted with a thermal conductivity detector (GC/TCD), and compounds present are identified and quantified. Aerosol propellant compounds of interest are: nitrogen, ethane, carbon dioxide, 1,1-difluoroethane (HFC-152a), 1,1,1,2-tetrafluoroethane (HFC-134a), propane, 1,3,3,3-tetrafluoroprop-1-ene (HFO-1234ze), dimethyl ether, isobutane, and butane.

The data produced from the GC/TCD is in volume based units, therefore density measurement is needed to convert the data into a mass based format.

3 Acronyms and Definitions

Acronym or Term	Definition
ACS Grade	Chemicals meeting standards set by the American Chemical Society.
Aliquot	A representative portion of a non-aerosol sample or the non-propellant portion of an aerosol sample.
Analytical Batch	A set of samples analyzed together as a group for a particular analysis.
APDO/APDD	Antiperspirant and/or Deodorant
ASTM	ASTM International, formerly known as American Society for Testing and Materials
Calibration Verification Standards	Gas standards of known composition obtained from a source other than that of the primary standards that are analyzed to confirm the stability of the calibration.
CARB	California Air Resources Board
°C	Degrees Celsius
Control/Check Standard	A gas standard of known composition obtained from a source other than that of the primary standards that is analyzed to verify the calibration. This QC standard is

Acronym or Term	Definition
	also separately identified as a control standard and a check standard.
CFR	Code of Federal Regulations
Duplicate	A second analysis of a sample submitted for analysis under Method 310.
g	Gram
gal	US gallon, 3.78541178 L
GC	Gas Chromatograph
GC/TCD	Gas Chromatograph fitted with Thermal Conductivity Detector
H&SC	Health and Safety Coordinator
HFC	Hydrofluorocarbon
HFC-134a	1,1,1,2-tetrafluoroethane
HFC-152a	1,1-difluoroethane
HFO	Hydrofluoroolefin
HFO-1234ze	1,3,3,3-tetrafluoroprop-1-ene
Holding Time	Maximum amount of time a sample may be stored prior to performing an operation.
i.d.	Inner diameter
L	Liter
LIMS	Laboratory Information Management System
LIMS Manual	Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)
m	Meter
MDL	Method Detection Limit
MFC	Mass Flow Controller
mL	Milliliter
mm	Millimeter
NIST	National Institute of Standards and Technology
NLB	Northern Laboratory Branch
OD	Outer Diameter
Propellant Blank	Helium without the target compound(s) analyzed to determine interferences or contamination during analysis.
psi	Pounds per square inch
PTFE	Polytetrafluoroethylene
QC	Quality Control
QCM	Quality Control Manual
Replicate	An additional analysis of the same sample propellant portion. The sample must be chosen at random.
RL	Reporting Limit
RPD	Relative Percent Difference
rpm	Revolutions per minute
Sample	The sample submitted for analysis under Method 310.

Acronym or Term	Definition
Sample Batch	A set of samples analyzed together under Method 310.
SAS	Special Analysis Section
sd	Standard deviation
SOP	Standard Operating Procedure
U.S. EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound(s)
v/v	Volume/volume—measure of the concentration of a substance in a solution

4 Interferences

4.1 Ambient air is 78 percent nitrogen and may be present in the propellant collection system prior to sample collection. This is minimized by sweeping out any connecting lines to the propellant collection bag with product prior to sample collection.

4.2 Components are identified by retention time. Components having similar retention times to the compounds of interest listed in Section 2 may co-elute and can lead to misidentification.

4.3 Analysis of the sample propellant portion must be completed within two days. Propellant collection bags are semi-permeable thus the longer the bags sit before analysis, the more likely the presence of nitrogen can occur from the atmosphere. For each analytical sequence, fresh bags of propellant blank, calibration verification standards, and control/check standards are prepared.

4.4 Allot the non-propellant portion of vented aerosol samples no later than one day after venting to assure that high end volatile compounds are not lost, and that ambient moisture does not infiltrate the sample container.

5 Personnel Qualifications and Training

5.1 Prior to performing this method, new personnel must be trained by staff with detailed knowledge of this method. Personnel must be trained to understand the program’s requirements per any applicable State and federal regulations and/or guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, 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 method on real-world samples (i.e., data for record).

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

6 Safety Requirements

6.1 All personnel must follow the general health and safety requirements found in NLB's Chemical Hygiene Plan.

6.2 Analysts should acknowledge any sample labeling for safety warnings and take appropriate safety measures.

6.3 Method involves piercing or opening of pressurized containers which occurs under a fume hood. During these procedures, the fume hood sash should be lowered as low as possible. Ensure fume hood is operating properly (i.e., alarm measuring face velocity is operating properly and not disabled).

7 Hazardous Waste

For all vented sample containers, evaluate the sample contents for guidance on proper disposal management. During content evaluation, samples can be temporarily stored in individual containers. Samples should be segregated and disposed of by chemical category. Waste samples should be categorized by halogenated or non-halogenated organic solvents, acidic aqueous, caustic aqueous, or in some cases, the product may contain a chemical requiring special handling or disposal. If a product's categorization is uncertain, consult with the NLB Health and Safety Coordinator (H&SC) or the Industrial Hygiene Safety Section.

Satellite containers used for temporary storage should not be allowed to reach more than 75% capacity before either moving to the main hazardous waste storage area or transfer to the appropriate bulk storage drum. The NLB H&SC should be notified when any satellite container is moved to the main storage area and when waste is ready for pickup by the hazardous waste disposal contractor.

Store empty sample containers in a secure location until release of custody.

8 Equipment, Supplies, and Chemicals

8.1 Top-Loader Balance, capacity of at least 1000 g x 0.01 g readability

8.2 100 g Mass, ASTM class 1 or better

8.3 Propellant Collection System, for metal containers (Appendix A, Figure 1), with house vacuum and helium

8.4 Sample Venting Platform, for metal containers (Appendix A, Figure 2), fitted with a piercer (Appendix A, Figure 3) and Viton gasket (Appendix A, Figure 4)

8.5 Propellant Collection System, for glass containers (Appendix A, Figure 5), with house air

8.6 Sample Venting Platform, for glass containers (Appendix A, Figure 6), fitted with an inverted adapter (Appendix A, Figure 7) and a size 109 Viton o-ring

8.7 Gas Mixing System, (e.g., Environics Series 4000)

8.8 Software for gas mixing system

8.9 Density Meter, capable of measuring five decimal places, (e.g.,Mettler-Toledo DE 50)

8.10 Gas Chromatograph (GC), fitted with a Thermal Conductivity Detector (TCD) and autosampler

8.11 Laboratory workstation

8.12 Software for data acquisition and data analysis (e.g., Agilent Chemstation)

8.13 GC Capillary Column, 30 m x 0.53 mm i.d. Restek RT-QPLOT column or equivalent

8.14 Platform Shaker, capable of holding sample cans of various diameters and heights

8.15 Refrigerator, capable of maintaining temperature between 0 ºC and 10 ºC (e.g., Walk-In Arctic model C-36X78)

8.16 Chemical fume hood

8.17 Propellant Collection Bags, ranging 0.25 L – 1.0 L, equipped with slip valve and septum

8.18 Cork Rings, 80 x 32 mm

8.19 Tubing, PTFE, 1/4” OD, 3/16” i.d.

8.20 Jar, glass, 500 mL, wide mouthed with lid

8.21 40 mL Amber Vials, screw top with caps

8.22 Parafilm

8.23 Vacutainer Needles, pediatric sized, with holders

8.24 Pipe Cutters of various sizes ranging from 1/8’’ to 3 ½” in diameter

8.25 Containers, of various types and sizes (e.g., 20 mL to 2.5 gal)

8.26 Scissors

8.27 Cable Ties

8.28 Wrenches, open-ended of various sizes ranging from ½" to 9/16"

8.29 Syringes, luer slip, ranging from 3 mL to 60 mL

8.30 Instrument Gases

8.30.1 Air, compressed

8.30.2 Air or Nitrogen, Ultra Zero

8.30.3 Helium, Grade 5

8.31 Calibration Gases

8.31.1 Helium, Grade 5

8.31.2 Nitrogen, Grade 5

8.31.3 Carbon Dioxide, 99% or greater

8.31.4 Ethane, 99% or greater

8.31.5 HFC-152a, 99% or greater

8.31.6 HFC-134a, 99% or greater

8.31.7 Propane, 99% or greater

8.31.8 HFO-1234ze, 99% or greater

8.31.9 Dimethyl Ether, 99% or greater

8.31.10 Isobutane, 99% or greater

8.31.11 Butane, 99% or greater

8.32 Calibration Verification Standard Gases

8.32.1 Calibration Verification Standard #1, 33% v/v mixture of HFC-134a, HFC-152a, and Carbon Dioxide

8.32.2 Calibration Verification Standard #2, 25% v/v mixture of Propane, Dimethyl Ether, Isobutane, and Butane

8.32.3 Calibration Verification Standard #3, 33% v/v mixture of Nitrogen, Ethane, and HFO-1234ze

8.33 Control/Check Standard consisting of 76% HFC-152a, and 24% Isobutane

8.34 Density Meter Calibration Gases and Reagent

8.34.1 Helium, Grade 5

8.34.2 HFC-152a, 99% or greater

8.34.3 Water, ASTM Type 1

8.34.4 Acetone, ACS Grade

9 **Procedure**

9.1 Shake aerosol sample container and store in the walk-in refrigerator in an inverted orientation for at least twelve hours prior to venting. Refer to SAS13 Section 9 for sample custody transfer and creation of sample batch.

9.2 Propellant Collection Bag Preparation:

Select appropriately sized propellant collection bag. Attach the bag to Output 1 of the Metal Aerosol Propellant Collection System and open valve on the bag (Appendix A, Figure 1). Use the vacuum to evacuate the bag completely. Then fill the bag with helium. Repeat this process three times. Evacuate to completely flush the bag, then close the valve on the bag and disconnect.

For Propellant Blank, fill the propellant collection bag with helium.
For Calibration Verification Standards, fill individual propellant collection bags with Calibration Verification Standard #1, #2, and #3.
For Control/Check Standard, fill the propellant collection bag with the Control/Check Standard.
For Sample propellant portion collection, refer to Section 9.4.

Label each filled propellant collection bag with its contents, date, and analyst's initials.

9.3 Balance Accuracy Check:

9.3.1 Ensure the accuracy of the top-loader balance by performing a Balance Control. Using forceps, place the 100 g mass on the top-loader balance. When the reading becomes stable, record the value in LIMS using the Balance QC Application. QC criteria is seen in Section 11.1.

9.3.2 Perform a Balance Check by weighing the 100 g mass after each weighing session is complete (after all full cans, all vented cans, and all empty cans are weighed). Follow procedure seen in Section 9.3.1. QC criteria is seen in Section 11.1.

9.4 Sample Propellant Portion Collection:

9.4.1 Record all can weights for aerosol containers in LIMS following procedures outlined in the LIMS Manual.

9.4.2 For metal aerosol containers, refer to Appendix B.

9.4.3 For glass aerosol containers, refer to Appendix C.

9.4.4 For pouch aerosol containers without grommet, refer to Appendix D.

9.4.5 For bladder and piston aerosol containers with grommet refer to Appendix E.

9.5 Aerosol Sample Analysis Preparation

Enter the analytical batch into LIMS following the procedures outlined in the LIMS Manual. LIMS will randomly assign a replicate for the analytical batch.

9.6 Aerosol Sample Propellant Analysis

9.6.1 Perform a calibration of the gases listed in Section 2 at least annually (refer to Appendices F and G).

9.6.2 Instrument preparation for samples

9.6.2.1 Verify helium and ultra zero air cylinder pressures are above 500 psi. Replace cylinder(s) as necessary prior to analysis.

9.6.2.2 Prepare the autosampler: Attach propellant collection bags filled with the Propellant Blank, Calibration Verification Standards, Control/Check Standard, and sample propellant portions to a port on the GC autosampler manifold. Make certain to snug the attaching nut ¼ turn past finger tight, then open the bag.

9.6.2.3 Load the method in the GC software and verify the following conditions:

Parameter	SAS05 Method	
	System N	System X and Y
Inlet		
Mode	Split	Split
Heater	200°C	200°C
Split Ratio	1:1	5:1
Thermal Aux 1	n/a	50°C

Parameter	SAS05 Method	
	System N	System X and Y
Thermal Aux 2	n/a	50°C
Column		
Control Mode	Constant Flow	Constant Flow
Flow	7.0 mL/min	7.3 mL/min
Oven		
Initial Temperature	100°C	100°C
Hold Time	4.00 min	3.00 min
Ramp	10°C/min to 160°C, hold 2 minutes	25°C/min to 125°C, hold 6 minutes, 20°C/min to 200°C, hold 3 minutes
Run Time	12 min	16.75 min
Post Run Temperature	100°C	230°C
Post Run Time	0.1 min	2 min
Detector/TCD		
Heater Temperature	160°C	220°C
Reference Flow	15 mL/min	15 mL/min
Data Rate	5 Hz	10 Hz
Min Peak Width	0.04 min	0.02 min

9.6.2.4 Analytical Sequence

Each analytical run includes the following quality control samples as listed below with a maximum of ten samples between control and check standards, ending with a check standard. The recommended order of analysis is as follows:

Propellant blank
Calibration verification standard #1
Calibration verification standard #2
Calibration verification standard #3
Propellant blank
Control standard
Propellant samples
Replicate (one of ten or fewer samples in the analytical batch)
Propellant blank
Check standard

Repeat propellant samples, propellant blank, and check standard as necessary.

9.6.2.5 Verify or input the following parameters in the sequence:

Sample location
Sample names
Method name
Number of injections (2 for the sample assigned as the replicate, 1 for all others)
Sample type (i.e., “sample” for samples)

9.6.2.6 Verify the instrument is directed to go into the standby mode at the end of the sequence.

9.6.2.7 Verify analyst initials are associated with the analytical sequence.

9.6.2.8 Save and print the sequence.

9.6.3 Sample Analysis

9.6.3.1 Verify the positions of the propellant collection bags on the autosampler match the vial location in the sequence.

9.6.3.2 Run the sequence.

9.6.3.3 Print and review the chromatograms.

9.6.3.4 Verify the data has met the QC criteria in section 11.1.

9.6.3.5 Any anomalies occurring during the analysis that affect the data shall be documented, and all affected samples shall be reanalyzed or invalidated. Notify management and proceed under their direction.

9.6.3.6 Any instrument issues or maintenance shall be documented in the instrument logbook to be kept with the instrument at all times.

9.6.4 After sequence completion, remove the propellant collection bags from the autosampler, and ensure that the STANDBY method is loaded.

9.6.5 Upload data to LIMS (refer to LIMS Manual: Propellant Analysis).

10 **Propellant Density Analysis**

10.1 Density Measurement is necessary for a Consumer Product that contains both exempt and non-exempt compounds as listed in the California Consumer Products Regulations, or for APDO, APDD, Aerosol Coatings, or Reactivity samples.

10.2 Density is determined from the same propellant collection bag using a density meter, refer to Appendix H or Appendix I. The resulting data is used to calculate the mass (g) of propellant found in the product.

11 Quality Control

11.1 Table of Quality Controls

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Balance Control	Before each weighing session	±2 sd of the target	If outside control criteria, recalibrate the balance manually per the manufacturer's instructions. After the calibration, re-weigh the Balance Control and record in LIMS. If the weight is still outside the control limits, there may be a problem with the balance or the mass standard. Contact appropriate personnel for service.
Balance Check	After each weighing session	±2 sd of the target	If outside criteria, the weighing session is invalid. See corrective actions for Balance Control and reperform the weighing session. If weight is still outside the control limits, the affected sample results shall be invalidated and only qualitative results reported on a Qualitative Results Report.
Propellant Collection Bag Holding Time	All	Analyze samples within two days of collection.	If criteria is not met, affected sample results shall be invalidated and only qualitative results reported on a Qualitative Results Report.
Vented Aerosol Holding Time	All	The non-propellant portion of aerosol samples must be collected within 1 day of venting.	If criteria is not met, the analytical batch shall be invalidated for quantitative results. Only qualitative data will be reported on a Qualitative Results Report.

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Propellant Blank	At minimum before the calibration standard, calibration verification standard #1, and control/check standard	The target compound concentration in the propellant blank must be less than the lowest calibration level.	If the blank result is < the lowest calibration level, no action is taken. If the blank result is ≥ the lowest calibration level, and the affected samples are ≥ ten (10) times higher than the blank value, then no action is taken. If the blank is ≥ the lowest calibration level and the sample result < ten (10) times higher than the blank value, then the result for the affected sample(s) shall be invalid and the cause investigated. The affected sample(s) may be reanalyzed, if there is sample available.
Calibration	Annually	Must have a correlation coefficient greater than 0.98.	If criteria are not met, reanalyze the calibration curve or prepare new propellant collection bags of the affected propellant calibration gas.
Calibration Verification Standards	Annual calibrations and each analytical batch	Upper and lower control limits set at ± 10 percent of the target value.	If criteria is not met, then all affected sample results are invalid. The conditions are evaluated, and samples are reanalyzed. If the calibration verification standard continues to be outside of the control limits, the affected analytes will be recalibrated.
Control/Check Standard	Control/check standard is analyzed after calibration verification standard #3, and after every ten or fewer samples, and at the end of the analytical sequence. The control/check standard is always preceded by a propellant blank.	Upper and lower control limits set at ± 10 percent of the target value. Upper and lower warning limits set at ± 8 percent of the target value.	If criteria is not met, then all affected sample results are invalid. Take action to bring the system back into control and reanalyze the control/check standard and any sample(s) not bracketed by successful control/check standards. Three consecutive control standards falling between the warning and control limits require investigation and corrective action as described in the QCM.

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Replicate	One of ten or fewer samples in the analytical batch	For replicate results ≥ 5x RL: RPD ≤ 25	If the replicate pair does not meet criteria, the analytical batch should be re-analyzed or invalidated if re-analysis is not possible.
Duplicate	One of ten or fewer samples in the sample batch	No QC criteria for this SOP. Evaluate duplicate results after calculating total VOC per SAS13.	Not applicable. Refer to SAS13 for overall %VOC criteria.

11.2 Table of Quality Controls for Density

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Calibration (Density Meter DE50)	Monthly	Calibration “ok” on instrument report	If criteria not met, repeat calibration.
Calibration (Density Meter D5)	Daily	ρ Air = 0.00121 g/cm^3 ± 0.00012 g/cm^3 at 20°C ρ Water = 0.99820 g/cm^3 ± 0.09982 g/cm^3 at 20°C	If criteria not met, repeat calibration.
Instrument Check (Helium Density (ρ He))	Instrument check is performed at the beginning of the analytical sequence, after every ten or fewer samples, and at the end of the analytical sequence.	ρ He = 0.00018 g/cm^3 ± 0.00002 g/cm^3 at 20°C	If an analysis is out of the control limits, the conditions are evaluated, and the instrument check and any results not bracketed by successful instrument checks will be invalidated and reanalyzed.
Density (ρ) Control/Check	Density Control is performed after the	ρ HFC-152a = 0.00279 g/cm^3 ±	If an analysis is out of the control limits, the conditions are evaluated, and the Density

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
(HFC-152a Density (ρ HFC-152a))	Instrument check, after every ten or fewer samples, and at the end of the analytical sequence	0.00007 g/cm^3 at 20°C	Control/check and any results not bracketed by successful Density control/checks will be invalidated and reanalyzed.
Replicate	One of ten or fewer samples in the analytical batch	For replicate results ≥ 5x RL: RPD ≤ 25	If the replicate pair does not meet criteria, the analytical batch should be re-analyzed or invalidated if re-analysis is not possible.
Duplicate	One of ten or fewer samples in the sample batch	No QC criteria for this SOP. Evaluate duplicate results after calculating total VOC per SAS13.	Not applicable. Refer to SAS13 for overall %VOC criteria.

11.3 Equipment Maintenance and Service Repair

11.3.1 The balances require calibration by an outside source annually.

11.3.2 The 100 g mass is calibrated by an outside source annually.

11.3.3 Mass Flow Controllers require annual certification. The Gas Mixing System(s) must be sent to the manufacturer at least every two years for recertification, preventative maintenance, and updates.

11.3.4 The MDL for the compound groups should be verified annually following procedures outlined in the CARB NLB Laboratory Quality Control Manual.

11.3.5 Service repairs and preventative maintenance are performed by contractors.

11.4 Troubleshooting

Basic troubleshooting can consist of changing the gas absorbent traps, septum nut, inlet septum, inlet liner, liner O-ring, gold seal, column nut, column ferrule, column detector nut, detector ferrule, split vent traps, and lines or other consumables.

11.4.1 Externally and internally check the system for leaks and measure flow with a flow meter at the split vent or septum purge vent.

11.4.2 Column cutting and re-installation is permitted.

11.4.3 Baking out or conditioning inlet, oven and detectors is permitted.

11.4.4 Consult the instrument manufacturer’s online database of instructional videos for assistance performing tasks.

11.4.5 Reference the troubleshooting manual published by the manufacturer tht is associated with the specific model of gas chromatograph (i.e., Agilent 7890A, 7890B) for other detailed troubleshooting efforts.

11.4.6 Contact the instrument manufacturer’s customer support call center for assistance. (i.e., Agilent Technologies, 1-800-227-9770).

12 **Sample and Data Management**

12.1 Data management consists of samples logged into the LIMS, documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are to be kept with the

instrumentation at all times.

12.2 Information that has been designated as confidential, proprietary, or trade secrets must be maintained in a locked file cabinet in a secure area. Access to this file cabinet is subject to management approval.

13 Calculations

13.1 Molar volume (V_m) using ideal gas law approximation (PV = nRT):

$$V_m = \frac{V}{n} = \frac{RT}{P} = \frac{\left(0.082057\ \left(\frac{L \times atm}{K \times mol}\right) \times 298.15\ K\right)}{1\ atm} = 24.5\ L/mol$$

Where:

P = Pressure at 1 atm

T = Temperature at 25°C = 298.15 K

R = Ideal Gas Constant = 0.082057 ((L x atm)/(K x mol))

13.2 LIMS will automatically calculate mass (g) of each propellant compound for a Consumer Product that contains both exempt and non-exempt compounds, or for APDO, Aerosol Coatings, or Reactivity samples as follows:

$$\text{Compound Conc.}\ \left(\frac{g}{L}\right) = \left(\frac{\text{MW of Compound (g/mol)}}{V_m\ (L/mol)}\right) \times \text{Compound Fraction (v/v)}$$

Where:

V_m = 24.5 L/mol (as derived in section 13.1)

MW = Molecular Weight

Then,

$$\text{Compound Mass (g)} = \text{Compound Conc.}\ \left(\frac{g}{L}\right) \times \left(\frac{\text{Total Propellant Mass (g)}}{\text{Total Propellant Density}\ \left(\frac{g}{cm^3}\right)\left(\frac{1\ cm^3}{1\ mL}\right)\left(\frac{1000\ mL}{1\ L}\right)}\right)$$

13.3 Relative Percent Difference shall be calculated as follows:

$$RPD = \frac{(Y-X)}{((Y+X)/2)} \times 100$$

Where:

X = the sample result

Y = the replicate result

14 References

14.1 The California Consumer Products Regulations, Title 17, California Code of Regulation, Division 3, Chapter 1, Subchapter 8.5, Article 1 – Article 5

14.2 Method 310 Determination of Volatile Organic Compounds (VOC) in Consumer Products and Reactive Organic Compounds (ROC) in Aerosol Coating Products, August 1, 2022

14.3 ASTM D3063-94, Standard Test Methods for Pressure in Glass Aerosol Bottles (November 15, 1994), with the modifications found in Appendix A to this Method 310

14.4 ASTM D3064-97, Standard Terminology Relating to Aerosol Products (September 10, 1997)

14.5 ASTM D3074-94, Standard Test Methods for Pressure in Metal Aerosol Containers (November 15, 1994), with the modifications found in Appendix A to this Method 310

14.6 US EPA Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography, Title 40 CFR Part 60, Appendix A, (July 1, 1996)

14.7 CARB NLB Laboratory Quality Control Manual, Revision 5.0, December 7, 2021 or current

14.8 MLD076 Standard Operating Procedure for Preparation of Northern Laboratory Branch's Standard Operating Procedures, Revision 1.0, December 30, 2021

14.9 Chemical Hygiene Plan for Northern Laboratory Branch, 1927 13th Street, 1900 14th Street, July 19, 2023 or current

14.10 Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS), May 23, 2023 or current

14.11 SOP SAS13 Standard Operating Procedure for Consumer Product Sample Batch Management and Reporting, August 5, 2019 or current

14.12 SOP SAS14 Standard Operating Procedure for Consumer Product Sample Preparation, August 5, 2019 or current

14.13 Environics Series 4000/4040 User Manual (Revision 1, 2017-10-02)

14.14 Mettler Toledo. (2023). Reference Manual for Density Meter Excellence D4, D5 and D6. Retrieved from https://www.mt.com/us/en/home/library/operating-instructions/lab-analytical-instruments/excellence-density-meter-d4-d5-d6-manual.html.

15 SOP Revision History

SOP/Addendum Identification	Approval Date	Description of Change
MLD SOP304 Revision 1	October 16, 1996	Analysis is by an initial screening method for the presence of R-152a or R-134a. If present a four-point calibration is made and the samples reanalyzed. The oven temperature and run time has been extended to remove propellants like isobutane and dimethyl ether from the column to minimize interference. Carbon dioxide, if present, will be 100% and given full exemption.
Unknown	March 10, 1998	Adjusted document font to Times New Roman 12. Inserted Appendix A and B formerly a stand-alone document.
MLD SOP ES05 Revision 3	December 10, 1999	The analysis is now on a Varian 3800, with valve controllers and the Star software system. The column is a Restek Q-PLOT megabore. Included is the SOP for the Mettler density determination, Appendix C.
MLD SOP SAS05 Revision 2.1	October 17, 2003	SOP updated to reflect the various modifications made to the propellant analysis. Changes include optimizing GC analysis, including a five-point calibration and clarifying the calculation equation. Additional changes include font (Arial 12) conversion, grammar and nomenclature corrections, and enumeration correction.
MLD SOP SAS05 Revision 2.2	April 8, 2004	SOP updated to reflect the various updates and modifications made to the propellant analysis. Changes include adding appendices for glass aerosol, bladder and piston aerosol venting. In addition, Figures 1-3 were updated to reflect all recent modification. Figure 4 was added to detail the Glass Aerosol Sample Venting Platform. All associated enumeration corrections were performed.
Unknown	June 9, 2008	SOP updated to reflect the various updates and modifications made to the propellant analysis. The most notable change – analysis now performed on Agilent 7890 with Wasson-ECE valve controlled autosampler system. All associated enumeration corrections were performed.

SOP/Addendum Identification	Approval Date	Description of Change
Unknown	September 29, 2009	SOP updated to reflect various updates and modifications made to the propellant analysis. All figures updated, including additional detailed drawings of key components.
MLD SOP SAS05 Revision 3.2	August 18, 2010	SOP updated to reflect updates made to the propellant analysis. Changes include optimizing GC analysis and a six-point calibration. All associated enumeration corrections were performed.
SAS05 Revision 4.0	July 16, 2024	Reviewed for grammar and content, and compliance with the most recent versions of the Laboratory Quality Control Manual Revision 5.0 and MLD076 Revision 1.0. Miscellaneous additions/deletions made. Added additional propellant calibration verification standard QC and added a new control/check standard. Added procedure for Agilent 7890 (Systems X and Y) with Custom Solutions valve control and incorporating use of Environics Gas Mixer.

APPENDIX A

Appendix A is a collection of figures referred to in this SOP.

Figure 1

PROPELLANT COLLECTION SYSTEM
METAL AEROSOL CONTAINER

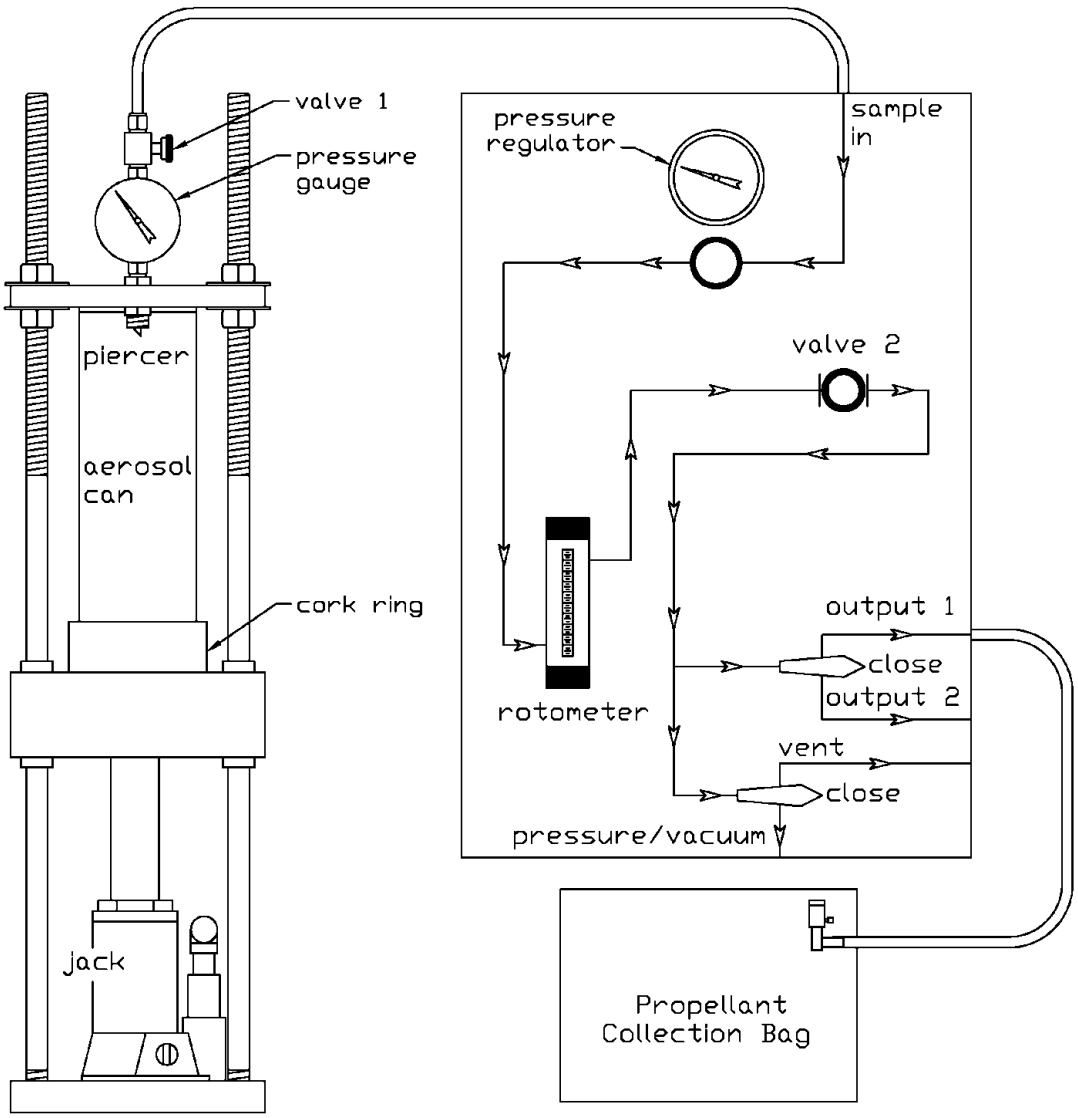
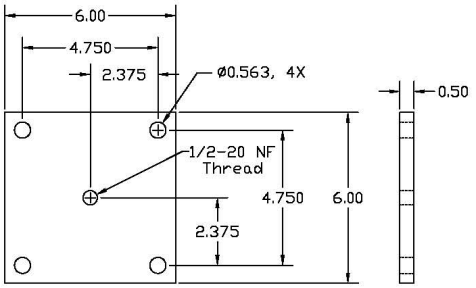
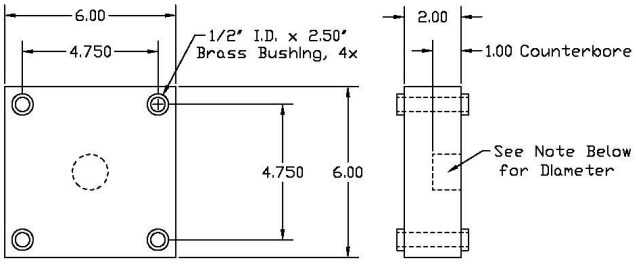


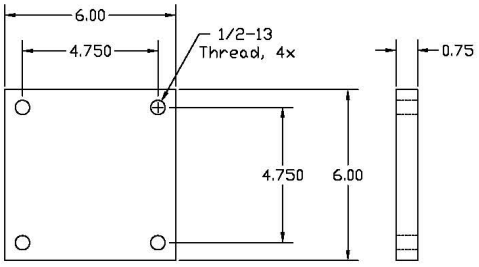
Figure 2
SAMPLE VENTING PLATFORM
METAL AEROSOL CONTAINER



Aluminum Piercing Plate



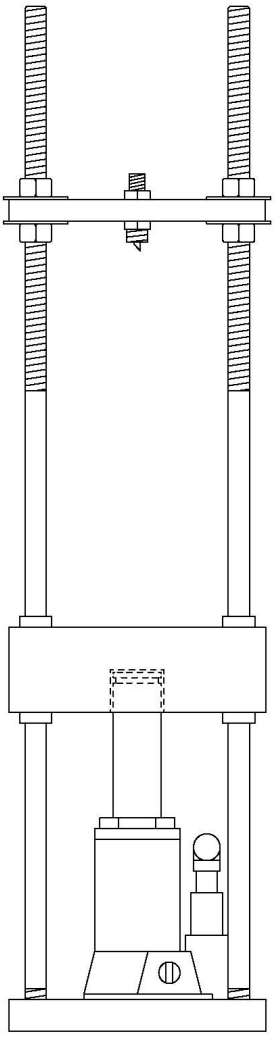
Aluminum Jack Plate

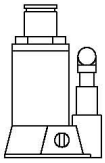


Aluminum Base Plate

1/2" Nut, 8x

1/2" Washer, 8x

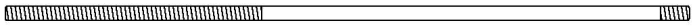




Note: Aluminum jack plate counterbore diameter should be 0.25" larger than the diameter of the bottle jack piston.

Manual Hydraulic Bottle Jack (2 Ton)

Piercer and Viton Gasket



1/2-13 Steel Retaining Rod – 30" Length, 4x

Figure 3
SAMPLE VENTING PLATFORM PIERCER
METAL AEROSOL CONTAINER

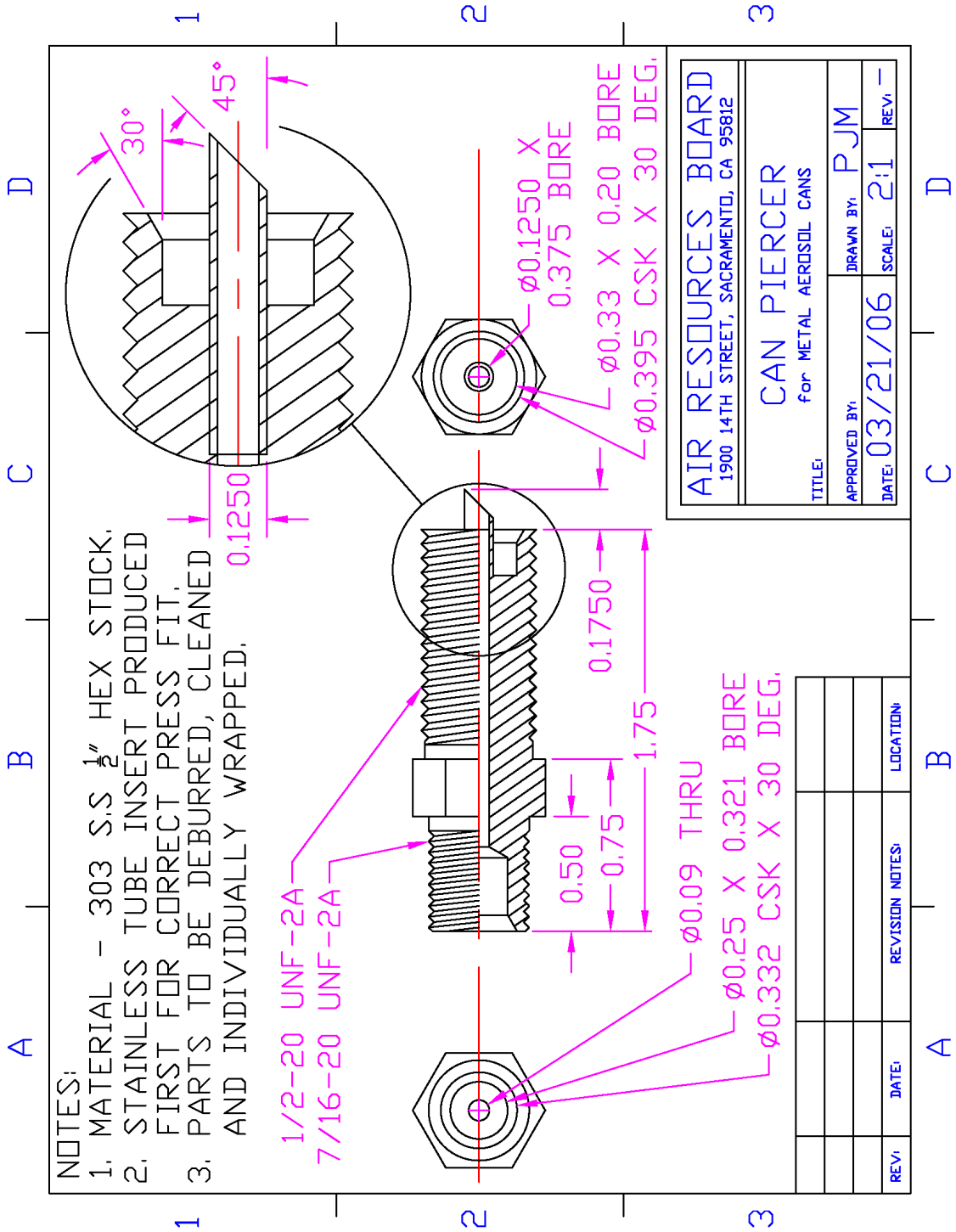


Figure 4
SAMPLE VENTING PLATFORM VITON GASKET
METAL AEROSOL CONTAINER

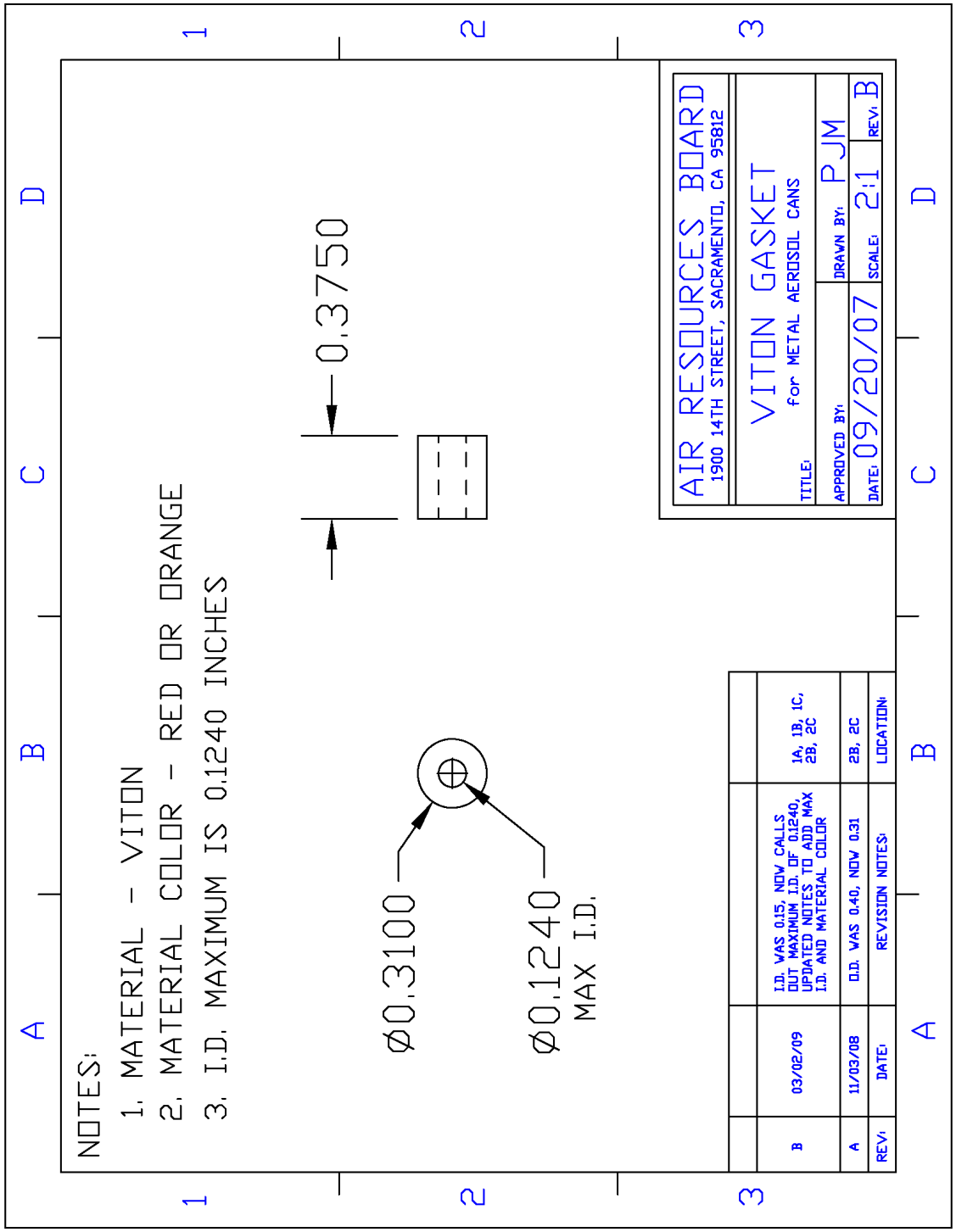


Figure 5
PROPELLANT COLLECTION SYSTEM
GLASS AEROSOL CONTAINER

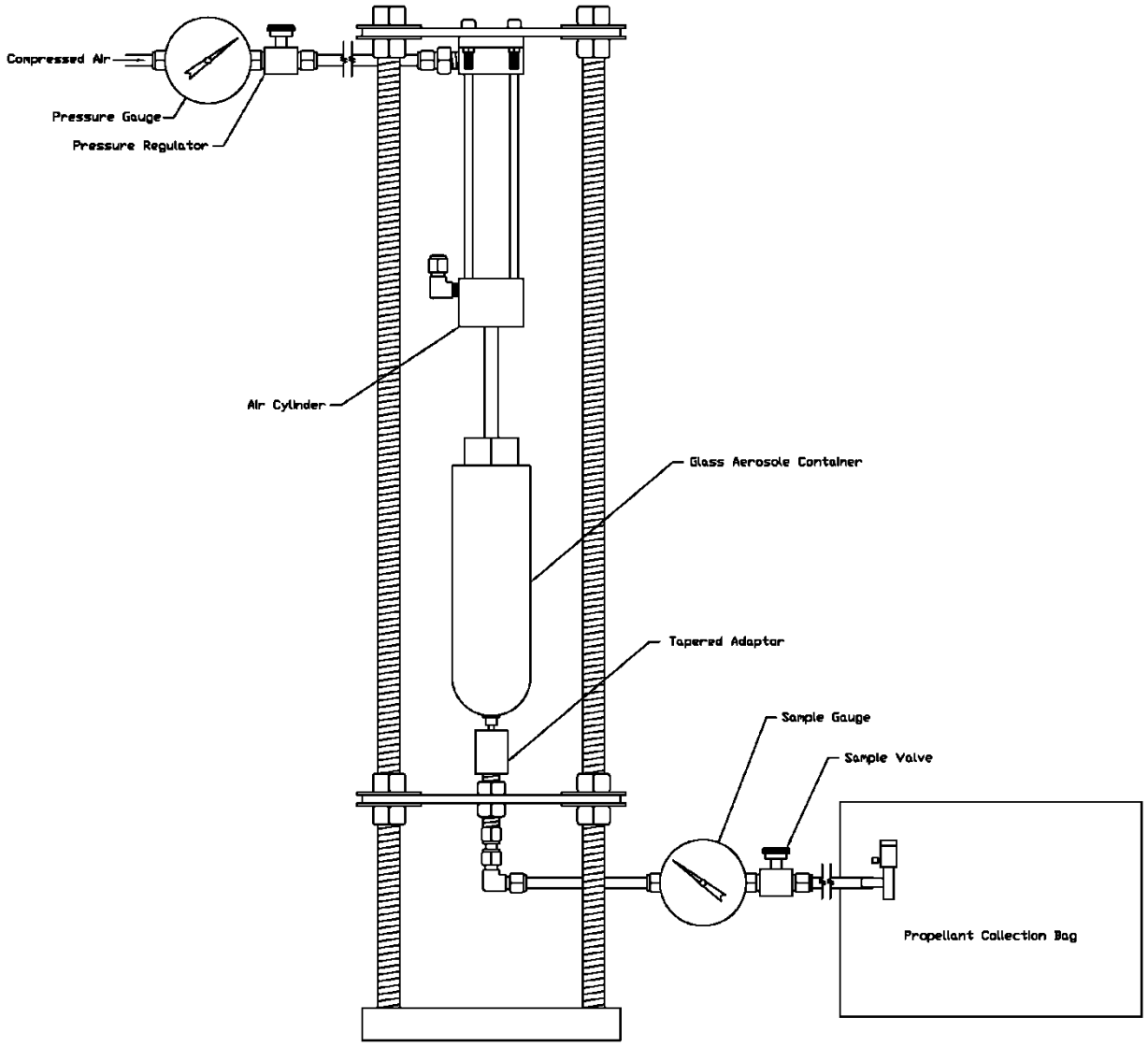
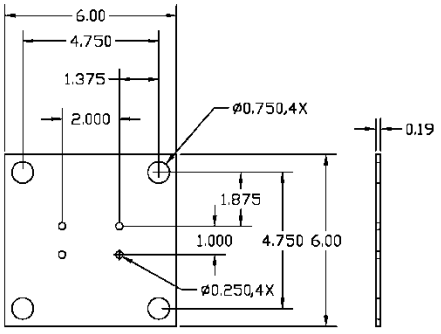
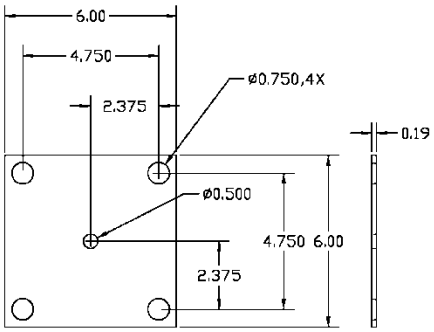


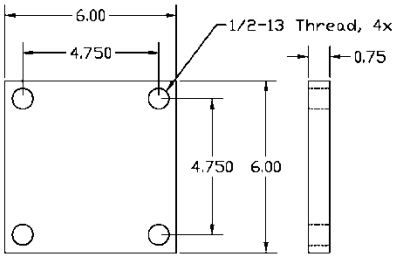
Figure 6
SAMPLE VENTING PLATFORM
GLASS AEROSOL CONTAINER



Air Cylinder Mounting Plate



Tapered Adapter Mounting Plate

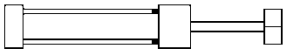


Base Plate

Tapered Adaptor and □-Ring

1/2" Nut, 8X 1/2" Washer, 8X

Air Cylinder Rear Flange Mounting Plate



Air Cylinder, nonrotating drop-in tie rod, 1-1/8" bore, 4" stroke

1/2-13 Threaded Rod - 24" Length, 4X

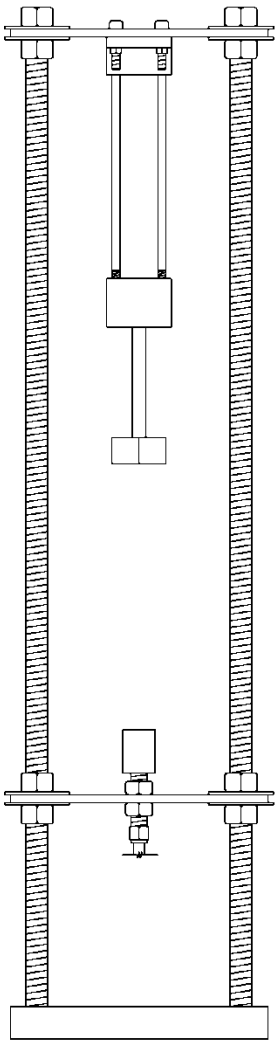
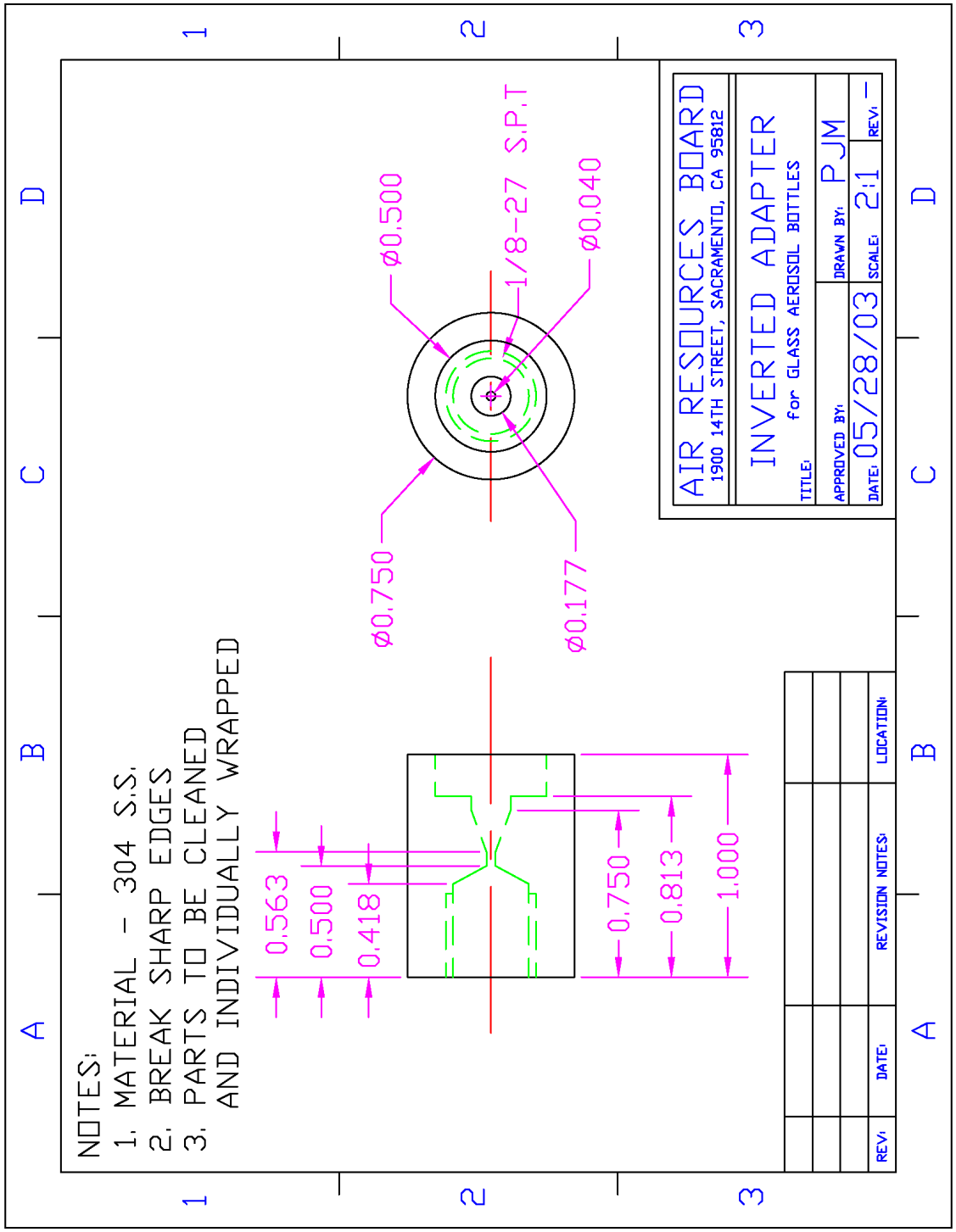


Figure 7
SAMPLE VENTING PLATFORM INVERTED ADAPTOR
GLASS AEROSOL CONTAINER



APPENDIX B

COLLECTION OF PROPELLANT FROM METAL AEROSOL CONTAINERS

DAY 1

1. Attach sample venting platform to the propellant collection system (Appendix A, Figure 1) using about 20 feet of PTFE tubing. The PTFE tubing should be coiled (and secured with cable ties) into about 4 loops, to capture any non-propellant sample that comes over with the venting propellant.

2. Verify that all valves and outputs on the propellant collection system are closed, including the hydraulic jack valve.

3. Obtain sample container from walk-in refrigerator.

   Assess the stability of the packaging to assure that the lid and the actuator will not compress during sample venting. If so, it will be necessary to remove actuator and/or lid prior to Step 4.

4. Weigh the container, to the nearest 0.01 g. Record this as the “full” weight.

5. Center container on the sample venting platform (Appendix A, Figure 2), still in the upside down orientation, stabilized by cork rings.

6. Raise the jack so that the sample container is quickly and evenly pierced. Observe that the can pressure of the container is visible on the pressure gauge.

7. Open valve 1 to pressurize the system.

8. Open output 1 and valve 2, sequentially.

9. Slowly turn the pressure regulator knob until constant flow is established on the rotometer. Adjust as necessary to maintain a constant flow.

10. When propellant fumes are visually confirmed from output 1, attach an appropriate sized prepared propellant collection bag (refer to SAS05, Section 9.2).

11. Open the propellant collection bag valve to collect the propellant.

    Monitor any non-propellant sample that appears in the PTFE tube.

12. Close the propellant collection bag valve and disconnect the propellant collection bag when either the propellant collection bag is full, or the non-propellant portion

of the sample advances to within the last loop of the PTFE tube. Should this happen:

12.1 Close off valve 1.

12.2 Close the propellant collection bag valve.

12.3 Disconnect the PTFE tube at the panel.

12.4 Secure the end of the PTFE tube in a tared container with Parafilm for the remainder of the venting process. The weight difference is added to the "vented" weight, to ensure the correct proportion of propellant and non-propellant. Additional tared containers may be necessary, depending on how vigorously the non-propellant portion sample proceeds.

12.5 Disconnect the propellant collection bag. The sample propellant collection bag is now ready for GC analysis (refer to SAS05, Section 9.6).

13. When the non-propellant sample is no longer coming through the PTFE tubing, open vent output on the propellant collection system. Periodic adjustments to the pressure regulator knob will be necessary, until the full open position is reached.

14. When the pressure gauge indicates zero pressure and the rotometer no longer indicates flow, gently tap sample container periodically, until no flow is indicated. The container is ready for removal when flow no longer registers.

15. Turn the hydraulic jack valve open, and carefully lower the sample container. Close the hydraulic jack valve.

16. Remove the sample container and transfer it to the platform shaker. Set platform shaker to around 85 rpm and allow the sample container to agitate for a minimum of 2 hours.

17. If applicable, weigh the looped PTFE tubing to account for any non-propellant sample carry over. Clean and dry the PTFE tubing, weighing again. The weight difference is added to the "vented" weight, to ensure the correct proportion of propellant and non-propellant. Put the cleaned sampling tube back on the sample venting platform. The weight differential of any additional containers used must also be added to the "vented" weight.

<u>DAY 2</u>

18. Remove the sample container from the platform shaker.

19. Weigh the container, to the nearest 0.01 g. Record this as the "vented" weight.

20. Refer to SAS14 for opening sample container and dispensing aliquots. Additionally, SAS14 addresses procedures for handling and disposal of the remaining non-propellant portion.

21. If there are any “mixing” devices within the can, such as marbles or steel balls, thoroughly clean and weigh them. This weight will be added to the “empty” weight, to ensure the correct proportion of propellant and non-propellant weights.

22. Rinse sample container to remove any residues. Use water for aqueous samples and solvent for non-aqueous samples. Dispose any hazardous waste as described in Section 7. Allow the container to dry completely. Visually inspect to ensure that there is no liquid remaining in the container.

23. Weigh sample container, to the nearest 0.01 g. Record this as the “empty” weight.

APPENDIX C

COLLECTION OF PROPELLANT FROM GLASS AEROSOL CONTAINERS

PART 1

1. Attach propellant collection system (Appendix A, Figure 5) to ultra zero air.

2. Set pressure regulator knob to approximately 25 psi to allow the air cylinder arm to fully extend.

3. Attach about 3’ of PTFE tubing to the sample valve, to be employed as a sampling tube. Close sample valve.

4. Weigh an empty wide mouthed sampling jar and lid. Record this weight.

5. Obtain sample container from walk-in refrigerator.

6. Remove the actuator from the valve stem and weigh the container, to the nearest 0.01 g. Record this as the “full” weight.

7. Center sample container on the inverted adaptor, still in the upside-down orientation. Manually extend the arm of the air cylinder to hold the sample container in place.

8. Pressurize the air cylinder to actuate the sample container valve onto the inverted adaptor. Increase the pressure to the air cylinder to approximately 30 psi.

9. Evacuate the sampling tube with house vacuum, then immediately attach an appropriately sized prepared propellant collection bag.

10. Open prepared propellant collection bag valve (refer to SAS05, Section 9.2).

11. Open sample valve to collect propellant.

12. Close the propellant collection bag valve, close the sample valve and disconnect the propellant collection bag when either the propellant collection bag is full, or the non-propellant portion of the sample reaches to within 12” of the end of the sampling tube.

    The propellant collection bag is now ready for GC analysis (refer to SAS05, Section 9.6).

13. Place the end of the sampling tube into the sampling jar, secured with Parafilm. Allow venting to continue until there is no more visible movement of the non-propellant portion in the sampling tube. Given the variety of samples available in

this type of packaging, the time factor for this step can vary from a couple of hours up to overnight.

PART 2

14. When venting ceases:

14.1 Close sample valve. Decrease pressure on air cylinder. Remove the sample container from the venting platform. Turn sample container to its upright orientation.

14.2 Remove jar from sampling tube and attach lid. Weigh the jar with the total amount of sample collected. The difference between this and the tare weight is added to the “vented” weight, to ensure the correct proportion of propellant and non-propellant. Place the lid on the jar, until just snug (since it can contain residual entrained propellant) and place the jar in the walk-in refrigerator.

15. Separate the sampling tube from the sample valve. Obtain weight of the sampling tube both before and after cleaning and drying. The weight difference is added to the “vented” weight, to ensure the correct proportion of propellant and non-propellant weights.

16. The sampling assembly is made up of all of the components from the inverted adaptor to the sample valve. To remove this assembly, separate the inverted adaptor from the rest of the assembly. Obtain weights for both before and after cleaning and drying. Both weight differences are added to the “vented” weight, to ensure the correct proportion of propellant and non-propellant weights.

17. Punch a very small hole into the top of the crimp, just next to the actuator valve.

18. Insert one end of a vacutainer needle into the hole and loosely place one of the vacutainer covers over the other end. The vacutainer cover will serve to protect against sharps hazard during this part of the venting process.

19. Place the sample container into a tared 400 mL beaker, on the platform shaker. Set platform shaker to around 85 rpm.

20. When there is minimal or no foaming when the sample container is swirled, remove vacutainer assembly from shaker.

21. Cut open the container where the valve assembly is crimped onto the container (do not remove the valve assembly at this point). Place the sample container back on the platform shaker until there is no visible foaming when swirled.

PART 3

22. Remove the sample container and tared beaker from the platform shaker.

23. Weigh the sample container to the nearest 0.01 g. Record this as the “vented” weight.

24. If applicable, weigh tared beaker to account for any sample carry over. Any weight difference is added to the “vented” weight, to ensure the correct proportion of propellant and non-propellant weights.

25. Retrieve sampling jar from walk-in.

26. Remove the valve assembly from the container. Mix and transfer the non-propellant portion to a 40 mL vial, with the remainder going into the sampling jar used throughout the venting process.
    When opening the sampling jar do so slowly, as there may be pressure from any residual entrained propellant.

27. Rinse sample container to remove any residues. Use water for aqueous samples and solvent for non-aqueous samples. Dispose any hazardous waste as described in Section 7. Allow the container to dry completely.

28. Weigh sample container to the nearest 0.01 g. Record this as the “empty” weight.

APPENDIX D

COLLECTION OF PROPELLANT FROM POUCH AEROSOL CONTAINERS WITHOUT GROMMET

1. Attach sample venting platform to the propellant collection system (Figure 1) using about 20 feet PTFE tubing. The PTFE tubing should be coiled (and secured with cable ties) into about 4 loops, to capture any non-propellant sample that comes over with the venting propellant.

2. Verify that all valves and outputs on the propellant collection system are closed, including the hydraulic jack valve.

3. Obtain sample container from walk-in refrigerator.

   Assess the stability of the packaging to assure that the lid and the actuator will not compress during sample venting. If so, it will be necessary to remove actuator and/or lid prior to Step 4.

4. Weigh the container, to the nearest 0.01 g. Record this as the “full” weight.

5. Center container on the sample venting platform (Appendix A, Figure 2), still in the upside down orientation, stabilized by cork rings.

6. Raise the jack so that the sample container is quickly and evenly pierced. Observe that the can pressure of the container is visible on the pressure gauge. Even if the initial pressure indication seems significant, these samples may not have a large amount of propellant to collect.

7. Open valve 1 to pressurize the system.

8. Open valve 2 and output 1, sequentially.

9. Slowly turn the pressure regulator knob until constant flow is established on the rotometer. Adjust as necessary to maintain the initial flow.

10. Attach an appropriately sized prepared propellant collection bag (refer to SAS05, Section 9.2).

11. Open the propellant collection bag valve to collect the propellant.

12. When the bag is full or when the flow decreases and it appears the bag is no longer filling, close the bag valve and disconnect the propellant collection bag. The propellant collection bag is now ready for GC analysis (refer to SAS05, Section 9.6).

13. When the pressure gauge indicates zero pressure, the container is fully vented.

14. Turn the hydraulic jack valve open, and carefully lower the sample container. Close the hydraulic jack valve.

15. Remove the container from the sample venting platform.

16. Weigh the container, to the nearest 0.01 g. Record this as the “vented” weight.

17. Open sample container and cut open the inner pouch with scissors.

18. Refer to SAS14 for opening sample container and dispensing aliquots. Additionally, SOP SAS14 addresses procedures for handling and disposal of the remaining non-propellant portion.

19. Rinse sample container to remove any residues. Use water for aqueous samples and solvent for non-aqueous samples. Dispose any hazardous waste as described in Section 7. Allow the container to dry completely. Visually inspect to ensure that there is no remaining liquid in the container.

20. Weigh sample container, to the nearest 0.01 g. Record this as the “empty” weight.

APPENDIX E

COLLECTION OF PROPELLANT FROM BLADDER AND PISTON AEROSOL CONTAINERS WITH GROMMET

1. Obtain sample container from walk-in refrigerator.

2. Weigh the container, to the nearest 0.01 g. Record this as the “full” weight.

3. With the container secured in an upside-down orientation, locate the “rubber-like” grommet in the center.

4. Insert the shortest end of a vacutainer needle into the center of the grommet.

5. Immediately insert the other side of the vacutainer needle into the septa opening of the appropriately sized prepared propellant collection bag (refer to SAS05, Section 9.2).

   Monitor if foam enters the propellant collection bag during filling. Should a significant amount enter the bag, fill another bag to avoid potential damage to the GC autosampler.

6. When full, remove the propellant collection bag. The propellant collection bag is now ready for GC analysis (refer to SAS05, Section 9.6).

7. Place the sample container on the platform shaker, with the vacutainer needle still inserted, for up to 20 minutes at about 85 rpm.

8. When the propellant is done venting, remove the needle from the grommet.

9. Weigh sample container, to the nearest 0.01 g. Record this as the “vented” weight.

10. Refer to SAS14 for opening sample container and dispensing aliquots. Additionally, SAS14 addresses procedures for handling and disposal of the remaining non-propellant portion.

    If the sample is expected to foam, place the sample container in the walk-in refrigerator to bring it below room temperature to minimize sample loss prior to transfer.

11. Rinse sample container to remove any residues. Use water for aqueous samples and solvent for non-aqueous samples. Dispose any hazardous waste as described in Section 7. Allow the container to dry completely. Visually inspect to ensure that there is no remaining liquid in the container.

12. Weigh sample container, to the nearest 0.01 g. Record this as the “empty” weight.

APPENDIX F

INSTRUMENT CALIBRATION FOR SYSTEM N

Calibrate System N annually using a six-point calibration.

1 Calibration blank and standards preparation

1.1 Propellant Collection Bag Preparation:

Attach sample propellant collection bag to Output 1 of the Metal Aerosol Propellant Collection System and open valve on the bag (Appendix A, Figure 1). Use the vacuum to evacuate the bag completely then fill the bag with helium. Repeat this process three times. Evacuate to completely flush the bag, then close the valve on the bag and disconnect.

For Propellant Blank, fill the propellant collection bag with helium.
For Calibration Verification Standards, fill individual propellant collection bags with Calibration Verification Standard #1, #2, and #3.
For Control/Check Standard, fill the propellant collection bag with the Control/Check Standard.

1.2 Fill a 1 Liter prepared propellant collection bag with each of the calibration standards described in SAS05 Section 2.

1.2.1 Fill the propellant collection bags until it appears that each bag is no longer filling.

1.2.2 Label each propellant collection bag with the contained propellant blank and calibration standard and the date filled. i.e., “Propane 04/14/2020”.

2 Instrument preparation for calibration

2.1 Verify Helium and Air cylinder pressures are above 500 psi. Replace cylinder(s) as necessary prior to analysis.

2.2 Prepare the autosampler by attaching each propellant collection bag to a port on the GC autosampler manifold. Make certain to snug the attaching nut ¼ turn past finger tight, then open.

2.3 The calibration levels are achieved using the same GC system working parameters as are used for sample analysis, changing only the split ratios to represent each of the six calibration levels, as follows:

Calibration Level	Split Ratio	Method
5%	47.114:1	5_PERCENT CALIBRATON
10%	22.843:1	10_PERCENT CALIBRATON
20%	10.707:1	20_PERCENT CALIBRATON

50%	3.425:1	50_PERCENT CALIBRATON
75%	1.8:1	75_PERCENT CALIBRATON
100%	1:1	SAS_05

2.4 Load the method(s) in the GC software and verify the following conditions:

Acquisition Parameter	**Setting**
Inlet	
Mode	Split
Heater	200°C
Split Ratio	1:1
Thermal Aux 1	n/a
Thermal Aux 2	n/a
Column	
Control Mode	Constant Flow
Flow	7.0 mL/min
Oven	
Initial Temperature	100°C
Hold Time	4.00 min
Ramp	10°C/min to 160°C, hold 2 minutes
Run Time	12 min
Post Run Temperature	100°C
Post Run Time	0.1 min
Detector/TCD	
Heater Temperature	160°C
Reference Flow	15 mL/min
Data Rate	5 Hz
Min Peak Width	0.04 min

2.5 Calibration Sequence

The recommended order of analysis for the calibration is as follows:

a) Propellant Blank
b) Calibration Standards for first calibration gas 5%
c) Calibration Standards for first calibration gas 10%
d) Calibration Standards for first calibration gas 20%
e) Calibration Standards for first calibration gas 50%
f) Calibration Standards for first calibration gas 75%
g) Calibration Standards for first calibration gas 100%
h) Propellant Blank

Repeat for steps b – h for all Calibration Standard gases

Verify calibration by analyzing the following sequence:
- Propellant Blank
- Calibration Verification Standard #1
- Calibration Verification Standard #2
- Calibration Verification Standard #3
- Propellant Blank
- Check standard

2.6 Verify or input the following parameters in the sequence:

- Sample location
- Sample names
- Method name
  - Ensure the correct method is listed using the various calibration methods to represent the split ratios of the calibration levels.
- Number of injections (should be “1” for all)
- Sample type (“calibration” for calibrators and “sample” for all others)
- For the calibration standards:
  - Calibration levels
  - Response factors will be replaced
  - Retention times will be averaged

2.6.1 Verify the instrument in directed to go into standby mode at the end of the sequence.

2.6.2 Verify analyst initials are associated with the analytical sequence.

2.6.3 Save and print the sequence.

3 Calibration Analysis

3.1 Verify the propellant collection bag position on the autosampler matches the vial location in the sequence.

3.2 Run Sequence.

3.3 Print and review chromatograms, calibration curve, and QC.

3.4 Verify the data has met the QC criteria in SAS05 Section 11.1.

3.5 Following a successful calibration, analyze the Calibration Verification Standards, which provides ongoing verification that the annual calibration remains valid.

3.6 After sequence completion, remove the propellant collection bags from the autosampler, and ensure that the STANDBY method loaded. Place caps on autosampler sampling ports.

APPENDIX G

INSTRUMENT CALIBRATION FOR SYSTEMS X AND Y

Calibrate Systems X and Y annually using a minimum six-point calibration curve. For Systems X and Y, the calibration is achieved using the same GC system working parameters as are used for sample analysis. A Gas Mixing System equipped with various mass flow controllers (MFC) is used to prepare the calibration standards from pure gas standards.

1 Propellant Collection Bag Preparation

Attach sample propellant collection bag to Output 1 of the Metal Aerosol Propellant Collection System and open valve on the bag (Appendix A, Figure 1). Use the vacuum to evacuate the bag completely then fill the bag with helium. Repeat this process three times. Evacuate to completely flush the bag, then close the valve on the bag and disconnect.

For Propellant Blank, fill the propellant collection bag with helium.
For Calibration Verification Standards, fill individual propellant collection bags with Calibration Verification Standard #1, #2, and #3.
For Control/Check Standard, fill the propellant collection bag with the Control/Check Standard.

2 Gas Mixing System

There are two Gas Mixing Systems each equipped with six MFCs. The systems are connected to a single laboratory workstation configured with the Gas Mixing System software.

2.1 System 8631 is configured with MFC #1 at 1 L and all other MFCs at 0.1 L. This system is connected to the laboratory workstation via COM port 3 and is preprogrammed to prepare 1%, 5%, 10%, and 25% blends.

2.2 System 8632 is configured at 1 L. This system is connected to the laboratory workstation via COM port 4 and is preprogrammed to prepare 25%, 50%,75%, and100% blends.

2.3 The six MFCs of both systems are sized for multiple gases and can blend all of the gases present in the table below:

MFC #	GAS	SIZED FOR
1	HELIUM	X
2	HFC-152A	X
2	ETHANE	
2	DIMETHYL ETHER	
3	HFO-1233ZD	X
3	HFO-1234ZE	
3	N-BUTANE	
3	ISOBUTANE	
4	HFC-134A	X
4	PROPANE	
5	NITROGEN / AIR	X
6	CARBON DIOXIDE	X

3 Calibration Standard Preparation

3.1 Prepare gas calibration standards using the Gas Mixing System. The recommended concentrations for each calibration standard level:

Calibration Standard Level 1 - 1% (optional)
Calibration Standard Level 2 – 5%
Calibration Standard Level 3 - 10%
Calibration Standard Level 4 - 25%
Calibration Standard Level 5 - 50%
Calibration Standard Level 6 - 75%
Calibration Standard Level 7 - 100%

3.2 Turn on the Gas Mixing System. Attach the appropriate gas cylinder(s) to the corresponding port(s) on the Gas Mixing System. Adjust the regulators to approximately 26 psi.

3.3 To run the software, follow the Environics Series 4000/4040 Manual (Revision 1, 2017-10-02). After opening the software, initialize the appropriate system, and access the preprogrammed concentration profile. Refer to the table in Section 2.3 to ensure that the MFC ports are assigned to the correct gasses. Click “Start” and wait for the gas flow(s) to stabilize (up to two minutes for low concentrations).

3.4 Fill propellant collection bags in the concentrations listed in Section 3.1 for each calibration standard described in SAS05 Section 2.

3.5 Fill the propellant collection bags until it appears that each bag is no longer filling.

3.6 Label each propellant collection bag with the contained calibration standard and the date filled. i.e., “Propane 04/14/2020”.

4 Instrument Preparation for Calibration

4.1 Verify Helium and Air cylinder pressures are above 500 psi. Replace cylinder(s) as necessary prior to analysis.

4.2 Prepare the autosampler by attaching each propellant collection bag to a port on the GC autosampler manifold. Make certain to snug the attaching nut ¼ turn past finger tight, then open the bag.

4.3 Load the method in the GC and verify the following parameters:

Acquisition Parameters	**Settings**
Inlet	
Mode	Split
Heater	200°C
Split Ratio	5:1
Thermal Aux 1	50°C
Thermal Aux 2	50°C
Column	
Control Mode	Constant Flow
Flow	7.3 mL/min
Oven	
Initial Temperature	100°C
Hold Time	3.00 min
Ramp	25°C/min to 125°C, hold 6 minutes, 20°C/min to 200°C, hold 3 minutes
Run Time	16.75 min
Post Run Temperature	230°C
Post Run Time	2 min
Detector/TCD	
Heater Temperature	220°C
Reference Flow	15 mL/min
Data Rate	10 Hz
Min Peak Width	0.02 min

4.4 Calibration Sequence

The recommended order of analysis for each calibration is as follows:

Propellant blank
Calibration Standard Level 1
Calibration Standard Level 2
Calibration Standard Level 3
Calibration Standard Level 4
Calibration Standard Level 5
Calibration Standard Level 6
Calibration Standard Level 7
Propellant blank

Verify calibration by analyzing the following sequence:
Propellant Blank
Calibration Verification Standard #1
Calibration Verification Standard #2
Calibration Verification Standard #3
Propellant Blank
Check standard

4.5 Verify or input the following parameters in the sequence:

Sample location
Sample names
Method name
Number of injections (should be “1” for all)
For the calibration standards:
Calibration levels
Response factors will be replaced
Retention times will be averaged

4.5.1 Verify the instrument is directed to go into the standby mode at the end of the sequence.

4.5.2 Verify analyst initials are associated with the analytical sequence.

4.5.3 Save and print the sequence.

5 Calibration Analysis

5.1 Verify the propellant collection bag position on the autosampler matches the vial location in the sequence.

5.2 Run Sequence.

5.3 Print and review chromatograms, calibration curve, and QC.

5.4 Verify the data has met the QC criteria in SAS05 Section 11.1.

5.5 Following successful calibration, the Calibration Verification Standards provide ongoing confirmation that the annual calibration remains valid.

5.6 After sequence completion, remove the propellant collection bags from the autosampler, and ensure that the STANDBY method loaded. Place caps on autosampler sampling ports.

APPENDIX H

PROPELLANT DENSITY ANALYSIS FOR INSTRUMENT DE50

The Consumer Products Regulation requires data be reported in a mass-based format. Since the GC propellant data is volume based, density measurement is necessary for data conversion and quantitation.

1 **CALIBRATION (monthly):**

1.1 Inspect the desiccant in the cartridge on top of the instrument to make sure it is satisfactory for analysis by visual confirmation that the indicator grains are blue. Change the desiccant if the indicator grains have changed to an off - white color.

1.2 Remove purge line from the deionized water trap and dry it thoroughly. It is important to have all traces of water removed from the purge line in order to accurately calibrate the instrument.

1.3 Place purge line into the desiccant port labeled “**DP**” on right side of instrument.

1.4 Press **PUMP**, allowing dry air to fill the measuring cell.

1.5 Press **CALIBRATE**; pump will turn off.

1.6 Press **ENTER** when the instrument calls for “**Purge Ok?**”

1.7 When instrument calls for “water”, remove clear intake tubing from the lower intake port. Remove the purge tubing from the desiccant port and place it into the deionized water trap, with the end below the surface of the water.

1.8 Inject approximately 3 mL of ASTM Type 1 water into the lower intake port, making sure that the water passes through the measuring cell and out the purge line. Do not remove the syringe.

1.9 Press **ENTER**.

1.10 The instrument will complete the calibration and print out a report. If calibration report states “Calibration OK”, record value in instrument lab book and press **RESET**. If calibration report states “Calibration failed”, repeat steps 1.1 through 1.9.

1.11 Inject about 3 mL of acetone followed by several syringes full of air to completely dry the measuring cell. Inspect that all droplets of liquid are gone before proceeding to next step.

1.12 Remove purge line from the deionized water trap and dry it thoroughly. It is important to have all traces of water removed from the purge line.

1.13 Place purge line into the desiccant port.

1.14 Press **PUMP**, allowing air to dry the measuring cell. Press **PUMP** again to shut off.

1.15 Replace purge line to the deionized water trap. Replace clear intake tubing in the lower intake port.

2 Density Analysis

2.1 Enter the analytical batch into LIMS following the procedure outlined in the LIMS Manual. LIMS will randomly assign a replicate for the analytical batch.

2.2 Use the following sequence to determine sample density:

Helium Instrument Check
HFC-152a Density Control
Sample(s) up to 10
Replicate (one of ten or fewer samples in the analytical batch)
Helium Instrument Check
HFC-152a Density Check

2.3 Inspect the desiccant in the cartridge on top of the instrument to make sure it is satisfactory for analysis by visual confirmation that the indicator grains are blue. Change the desiccant if the indicator grains have changed to an off-white color.

2.4 Perform Instrument Check - criteria ρ He = 0.00018 g/cm^3 ± 0.00002 g/cm^3 at 20°C.

2.4.1 Prepare propellant blank (refer to SAS05, Section 9.2). Attach propellant blank collection bag, opening valve at least one turn. Purge dry measuring cell with Helium prior to actual measurement by gently pressing on propellant collection bag.

2.4.2 Press **CHECK**.

2.4.3 Lightly press the propellant collection bag to introduce gas into the measuring cell, noting a steady stream of bubbles in the deionized water trap. Close propellant collection bag, leaving it attached.

2.4.4 Press **ENTER**.

2.4.5 The instrument will complete the check and print out a report. Verify that the criteria are met for ρ He. Refer to SAS05 Section 11.2.

2.4.5.1 If the check value fails, repeat steps 2.4 -2.4.5

2.4.5.2 If the check still does not pass, recalibrate (Appendix H Section 1) and start over.

2.4.6 Record instrument check value in instrument lab book.

2.4.7 Press **RESET** and disconnect helium propellant collection bag.

2.5 Perform Density Control/Check Sample Analysis - criteria ρ HFC-152a = 0.00279 g/cm^3 ± 0.00007 g/cm^3 at 20°C.

2.5.1 Prepare propellant collection bag (refer to SAS05, Section 9.2). Fill the bag with HFC-152a. Attach propellant collection bag filled with HFC-152a, opening bag valve at least one turn.

2.5.2 Lightly press the propellant collection bag to introduce gas into the measuring cell, noting a steady stream of bubbles in the deionized water trap. Close propellant collection bag, leaving it attached.

2.5.3 Press **MEASURE**.

2.5.4 The instrument will complete the measurement and print out a report.

2.5.5 Verify the data has met the QC criteria in SAS05 Section 11.2.

2.5.6 Record value in instrument lab book.

2.5.7 Press **RESET** and disconnect propellant collection bag.

2.6 Perform Sample Analysis

2.6.1 The sample density is obtained from sample propellant analysis bags. Attach sample propellant collection bag, opening bag valve at least one turn to introduce sample.

2.6.2 Lightly press the propellant sample bag to introduce gas into the measuring cell, noting a steady stream of bubbles in the deionized water trap. Close propellant sample bag, leaving it attached.

2.6.3 Press **MEASURE**.

2.6.4 The instrument will complete the measurement and print out a report.

2.6.5 Record value in instrument lab book.

2.6.6 Press **RESET** and disconnect propellant sample bag.

2.6.7 Repeat steps 2.6.1 – 2.6.6 for all samples.

2.7 Perform Check Sample Analysis

2.7.1 The Density Control/Check (HFC-152a) is analyzed after every ten or fewer samples and after the last sample by repeating Sections 2.5 through 2.5.7.

2.7.2 Verify that the Density Control/Check recoveries are within the control limits in SAS05 Section 11.2. If any of the checks are not within the control limits, invalidate and reanalyze the affected samples. This may require recalibrating the instrument prior to reanalysis.

2.8 Upload density data into LIMS (refer to LIMS Manual: Propellant Density).

APPENDIX I

PROPELLANT DENSITY ANALYSIS FOR INSTRUMENT D5

The Consumer Products Regulation requires data be reported in a mass-based format. Since the GC propellant data is volume based, density measurement is necessary for data conversion and quantitation.

1. Calibration (daily):

1.1. Inspect the DryPro air pump desiccant to make sure it is satisfactory for analysis by visual confirmation (refer to the manufacturer's instructions for color change). Change the desiccant if needed.

1.2. Perform air check.

1.2.1. Fill the measuring cell with air and measure density. The criteria is 0.00121 g/cm^3 ± 0.00012 g/cm^3 at 20°C.

1.2.2. Dry the measuring cell.

1.3. Perform water check.

1.3.1. Fill the measuring cell with ultrapure water and measure density. The criteria is 0.99820 g/cm^3 ± 0.09982 g/cm^3 at 20°C.

1.3.2. Dry the measuring cell.

2. Density Analysis

2.1. Enter the analytical batch into LIMS following the procedure outlined in the LIMS Manual. LIMS will randomly assign a replicate for the analytical batch.

2.2. Prepare helium instrument check and HFC-152a density control/check.

Attach propellant collection bag to Output 1 of the Metal Aerosol Propellant Collection System and open valve on the bag (Appendix A, Figure 1). Use the vacuum to evacuate the bag completely. Then fill the bag with helium. Repeat this process three times. Evacuate to completely flush the bag, then close the valve on the bag and disconnect.

For helium instrument check, fill the propellant collection bag with helium.
For HFC-152a density control/check, fill the propellant collection bag with HFC-152a.

2.3. Use the following sequence to determine sample density:

Helium Instrument Check
HFC-152a Density Control
Sample(s) up to 10
Replicate (one of ten or fewer samples in the analytical batch)
Helium Instrument Check
HFC-152a Density Check

2.4. For each density analysis:

2.4.1. Fill the measuring cell by connecting the propellant bag to the cell adapter and squeezing the bag gently. Keep the propellant bag attached and measure density at 20°C. Record measured density.

2.4.2. Dry the measuring cell.

2.5. Verify that the Density Control/Check recoveries are within the control limits in SAS05 Section 11.2.

2.5.1. The density criteria for helium is 0.00018 g/cm^3 ± 0.00002 g/cm^3 at 20°C.

2.5.2. The density criteria for HFC-152a is 0.00279 g/cm^3 ± 0.00007 g/cm^3 at 20°C.

2.6. If any of the blanks and checks are not within the control limits, invalidate and reanalyze the affected samples. This may require adjusting the measurement accuracy prior to reanalysis.

2.7. Upload density data into LIMS following LIMS Manual: Propellant Density Section.