

California Environmental Protection Agency



**Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division**

MLD SOP SAS05

**STANDARD OPERATING PROCEDURE FOR THE
DETERMINATION OF COMPOUNDS IN AEROSOL
CONSUMER PRODUCT PROPELLANT BY GAS
CHROMATOGRAPHY**

August 18, 2010, Revision 3.2

DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory.

1 INTRODUCTION

This document describes a procedure for the analysis of aerosol consumer product propellant compounds as identified under Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Articles 1 - 3, Sections 94500-94528. For more information see ARB Method 310, ASTM D 3063-94, ASTM D 3064-89 and ASTM D 3074-94.

2 SUMMARY OF METHOD

An aerosol container is vented and the propellant is collected in an evacuated Tedlar bag. A sample from the Tedlar 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, CO₂, 1,1-difluoroethane (HFC-152a), 1,1,1,2-tetrafluoroethane (HFC-134a), propane, dimethyl ether (DME), isobutane, and n-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 INTERFERENCES/LIMITATIONS

- 3.1 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 Tedlar bag with product prior to sample collection.
- 3.2 Components with similar retention times to the compounds of interest listed in Section 2 will interfere in this procedure.
- 3.3 Analysis of the propellant sample must be completed within three days. Tedlar 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 analysis, fresh bags of helium blank, check and standard should be prepared.
- 3.4 The non-propellant portion of metal and piston aerosol samples must be aliquotted 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.

4 APPARATUS AND MATERIALS

- 4.1 Balance, capable of accurately weighing to 0.01 g.

- 4.2 Propellant Collection System, for metal containers (Figure 1), with house vacuum and helium.
- 4.3 Sample Venting Platform, for metal containers (Figure 2), fitted with a piercer (Figure 3) and Viton gasket (Figure 4).
- 4.4 Propellant Collection System, for glass containers (Figure 5), with house air.
- 4.5 Sample Venting Platform, for glass containers (Figure 6), fitted with an inverted adapter (Figure 7) and a size 109 Viton o-ring.
- 4.6 Density Meter, capable of measuring five decimal places, Mettler-Toledo DE 50.
- 4.7 Gas Chromatograph (GC), Agilent 7890 equipped with a TCD and a Wasson-ECE 16 position autosampler using ChemStation software.
 - 4.7.1 GC Capillary Column, 30 m x 0.53 mm ID Restek RT Q- PLOT column.
 - 4.7.2 GC System Working Parameters:

Injector Temperature	200 °C
Detector Temperature	160 °C
Split Ratio	1:1

 Temperature Program:

Initial:	100 °C for 3.0 min.
Rate:	10 °C/min to 220 °C
Hold time:	2.0 min
Column Flow Rate:	7.0 mL/min
- 4.8 Platform Shaker, capable of holding sample cans of various diameters and heights.
- 4.9 Walk-In Refrigerator, capable of maintaining temperature between 0 °C and 10 °C.
- 4.10 Tedlar Bags or equivalent, equipped with slip valve and septum.
 - 4.10.1 1 L, SKC part # 232-01.
 - 4.10.2 0.5 L, SKC part # 232-02.
 - 4.10.3 0.25 L, SKC part # CPM051204-003.

- 4.11 Vial, 40 mL, amber, with septa cap, for archival sampling.
- 4.12 Vial, 20 mL, clear, with septa cap, for working sample aliquot.
- 4.13 Cork Rings, 80 x 32 mm.
- 4.14 Tubing, PTFE, 1/4" OD, 3/16" ID.
- 4.15 Jar, 500 mL, wide mouthed with lid, for sample collection and aliquot of glass aerosol samples.
- 4.16 Parafilm.
- 4.17 Vacutainer Needles, pediatric sized, with holders.
- 4.18 Pipe Cutters.
 - 4.18.1 1/8" – 1 1/8" size.
 - 4.18.2 1/4" - 2 5/8" size.
- 4.19 Containers, of various types and sizes (e.g. 400mL to 2.5 gal), for liquid.
- 4.20 Scissors.
- 4.21 Cable Ties.

5 GASES AND REAGENTS

- 5.1 Helium, Grade 5.
- 5.2 HFC-152a, 98% or greater.
- 5.3 HFC-134a, 98% or greater.
- 5.4 n-Butane, 98% or greater.
- 5.5 Carbon Dioxide, 98% or greater.
- 5.6 Dimethyl Ether, 98% or greater.
- 5.7 Isobutane, 98% or greater.
- 5.8 Propane, 98% or greater.

- 5.9 Propellant Standard #1, 33% v/v mixture of HFC-134a, HFC-152a and CO₂.
- 5.10 Propellant Standard #2, 25% v/v mixture of propane, dimethyl ether, isobutane, and butane.

6 PROCEDURE

- 6.1 Sample Preparation.
 - 6.1.1 Shake aerosol sample container prior to storage.
 - 6.1.2 Store aerosol sample containers in the walk-in refrigerator, in an upside down orientation, for at least 24 hours prior to venting.
 - 6.1.2.1 Freezing aerosol shaving cream samples one hour prior to venting may benefit propellant collection.
- 6.2 Tedlar Bag Preparation:
 - 6.2.1 Attach sample Tedlar bag to Output 1 of the Metal Aerosol Propellant Collection System and open valve on the bag.
 - 6.2.2 Fully evacuate the bag using vacuum.
 - 6.2.3 Fill bag with helium.
 - 6.2.4 Repeat steps 6.2.2 through 6.2.3 three times, then evacuate, to completely flush bag.
 - 6.2.5 Close the valve on the bag and disconnect.
- 6.3 Propellant Collection:
 - 6.3.1 For metal aerosol containers, see Appendix A.
 - 6.3.2 For glass aerosol containers, see Appendix B.
 - 6.3.3 For pouch aerosol containers without grommet, see Appendix C.
 - 6.3.4 For bladder and piston aerosol containers with grommet, see Appendix D.
- 6.4 Propellant Analysis:
 - 6.4.1 Perform propellant analysis, see Appendix E.

6.4.1.1 For a Consumer Product - a 100% exemption is given if a sample only contains one or more of the following exempted compound: nitrogen, CO₂, HFC-152a or HFC-134a.

6.5 Density Measurement:

6.5.1 Density is determined from the same Tedlar bag on density meter, see Appendix F. The resulting data is used to calculate the grams of exempt propellant found in the product.

6.5.1.1 Density measurement is necessary under the following circumstances:

6.5.1.1.1 for a Consumer Product that contains both exempt and non-exempt compounds, or

6.5.1.1.2 for APDO, Aerosol Coatings or Reactivity samples.

7 QUALITY CONTROL

7.1 Helium Blank must be analyzed for each batch of samples. Any analyte concentration in the blank must be less than 0.1% wt/volume. A helium blank is run before and after the calibration controls and before calibration checks to prevent carry over from the previous sample.

7.2 A six-point calibration is performed annually on each of the compounds mentioned in Section 2. The correlation coefficient for each compound's calibration must be greater than 0.98. If any calibration fails, corrective action is implemented. Corrective action may include rerunning the calibration of one or more compound.

7.2.1 Calibration Controls and Checks provide ongoing verification that the annual calibration is still valid

7.2.2 A complete calibration is run following any major modification to the analytical instrumentation.

7.3 Propellant Standards #1 & #2 are used as Calibration Controls and Calibration Checks.

7.4 Calibration Control is run prior to each sample set. Control values must fall within the established control limits for all compounds of interest. If any control is outside the control limits, corrective action is implemented.

Corrective action may include recalibration of the instrument and rerun of the sequence.

- 7.5 Calibration Check is run at the end of the run. Check values must fall within the established control limits for all compounds of interest. If any check is outside the control limits, corrective action is implemented. Corrective action may include recalibration of the instrument and rerun of the sequence.
- 7.6 LIMS assigns at least one duplicate sample for every sample set. If the designated duplicate is an aerosol, that sample will be analyzed twice. The duplicate analysis should not have an absolute difference greater than $\pm 3\%$.
- 7.7 The density meter is calibrated monthly – see Appendix F, Section 1.
- 7.8 HFC-152a is used as the control and check for density measurement.

8 CALCULATIONS

Calculate grams of each propellant compound of interest as follows (assuming 25°C):

$$\text{Compound, } \frac{\text{grams}}{\text{L}} = \left(\frac{\text{Molecular Weight of Compound, grams}}{24.5\text{L}} \right) \times (\text{Compound, v/v})$$

Then,

$$\text{Compound, grams} = \left(\text{Compound, } \frac{\text{grams}}{\text{L}} \right) \times \left(\frac{\text{Total Propellant, grams}}{\left(\text{Propellant Density, } \frac{\text{grams}}{\text{mL}} \times \frac{1000\text{mL}}{\text{L}} \right)} \right)$$

Figure 1
PROPELLANT COLLECTION SYSTEM
METAL AEROSOL CONTAINER

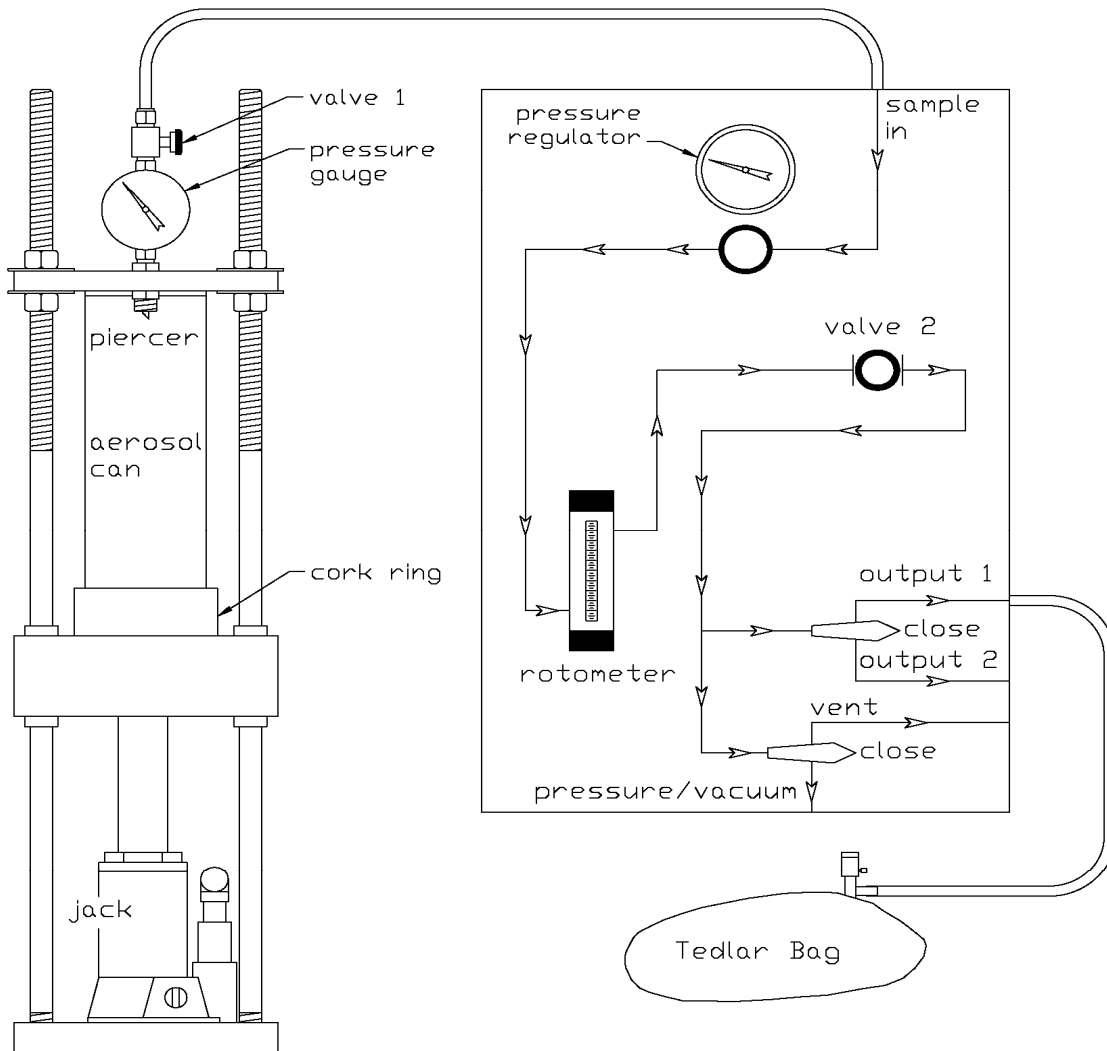


Figure 2 SAMPLE VENTING PLATFORM METAL AEROSOL CONTAINER

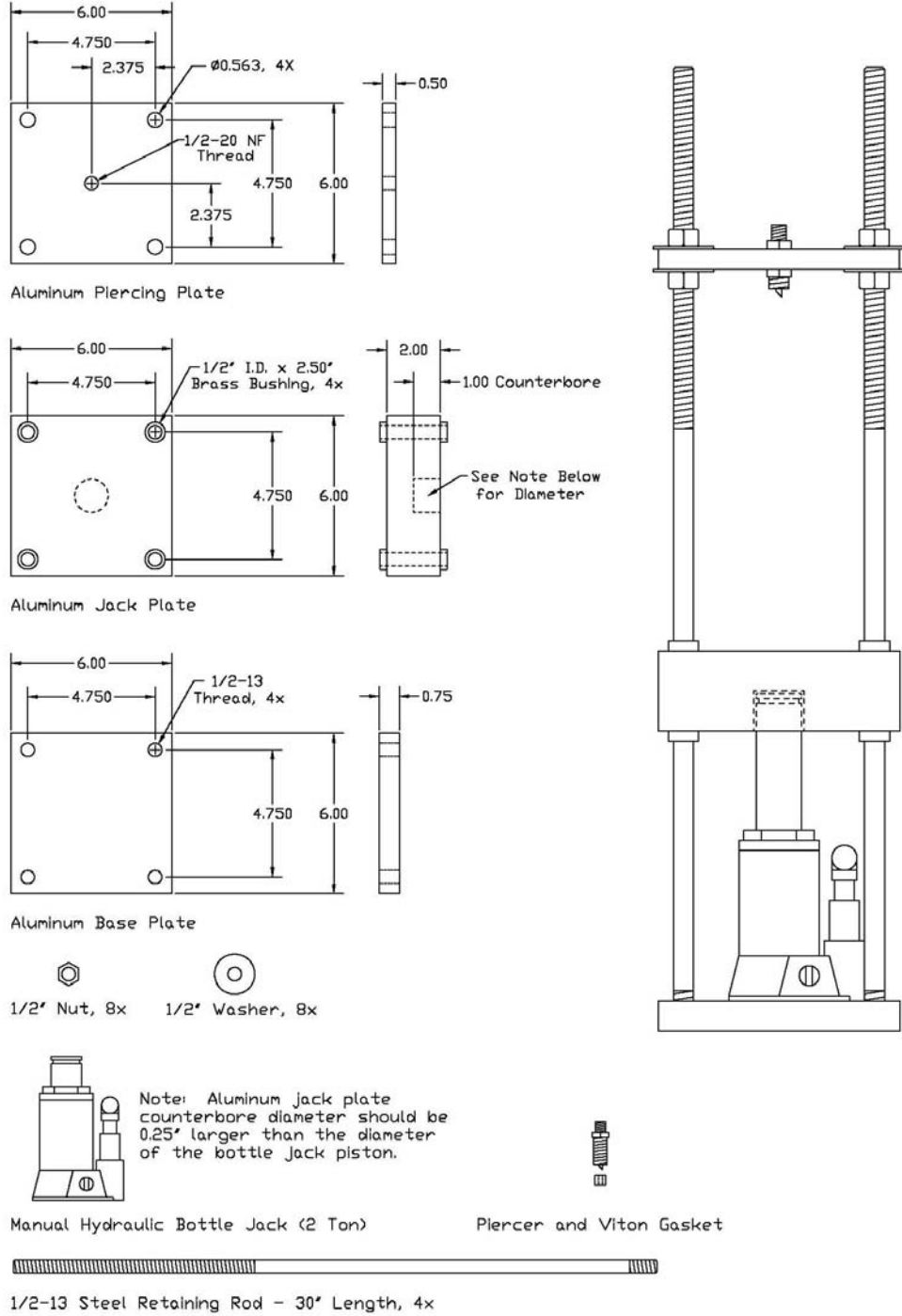


Figure 3
SAMPLE VENTING PLATFORM PIERCER
METAL AEROSOL CONTAINER

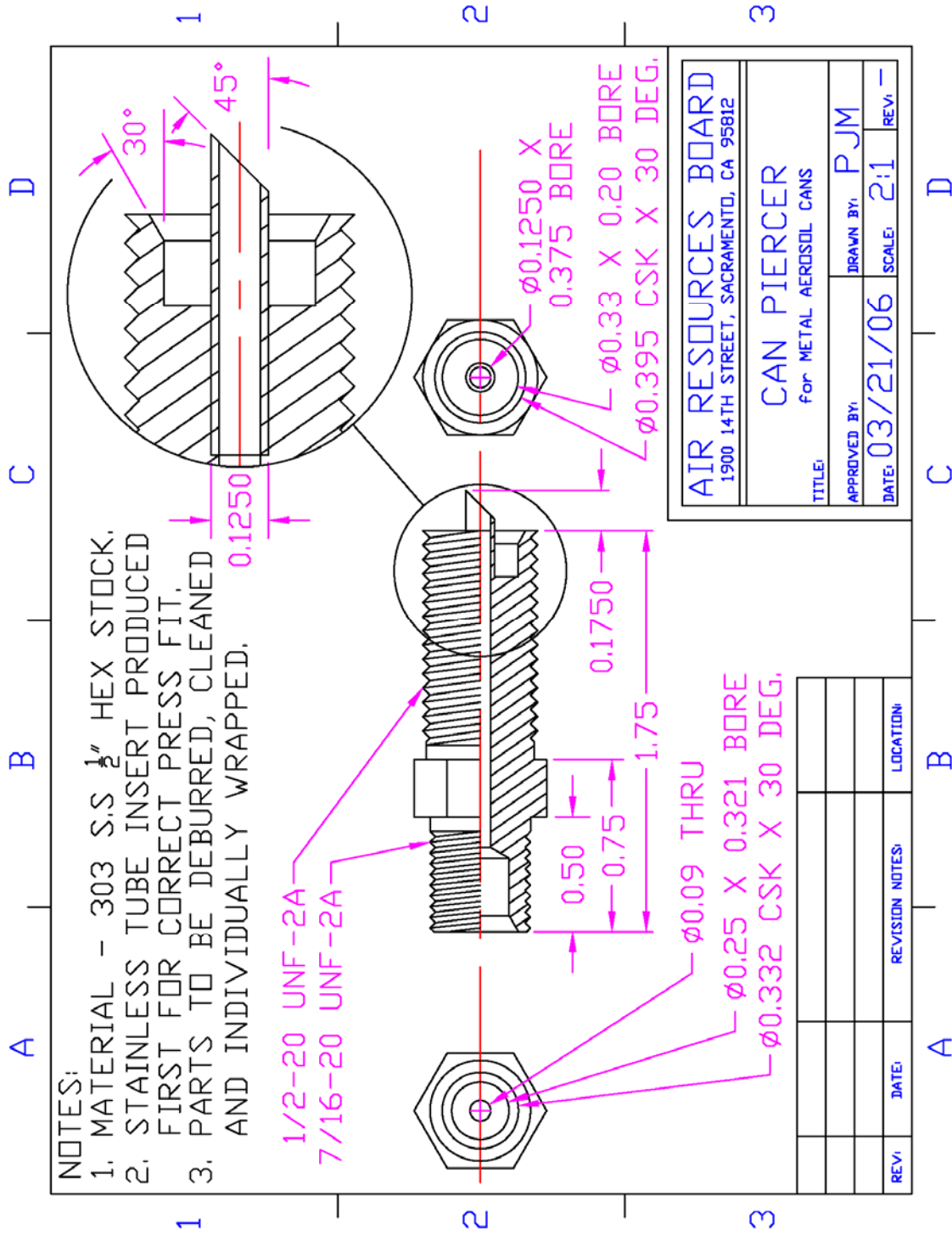


Figure 4
SAMPLE VENTING PLATFORM VITON GASKET
METAL AEROSOL CONTAINER

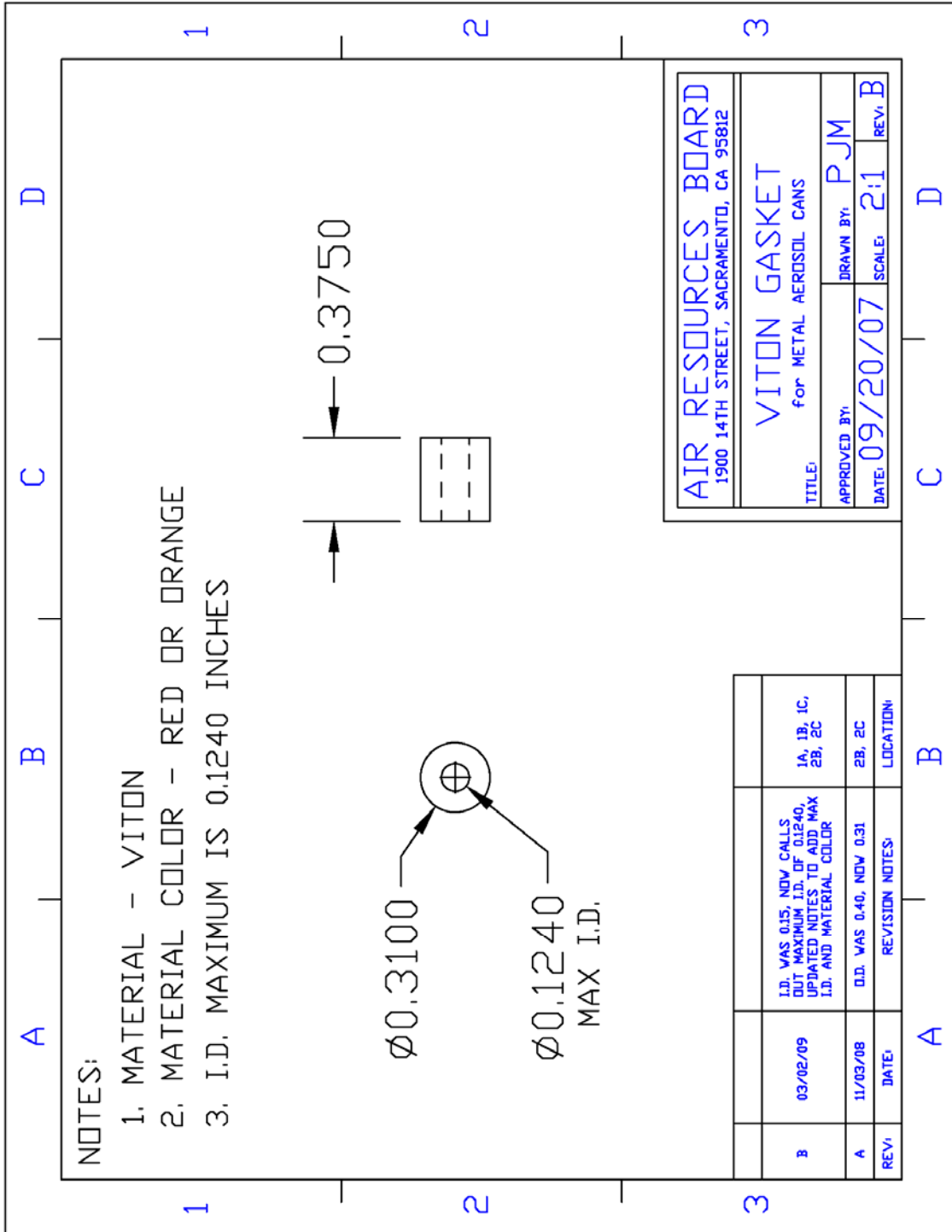


Figure 5
PROPELLANT COLLECTION SYSTEM
GLASS AEROSOL CONTAINER

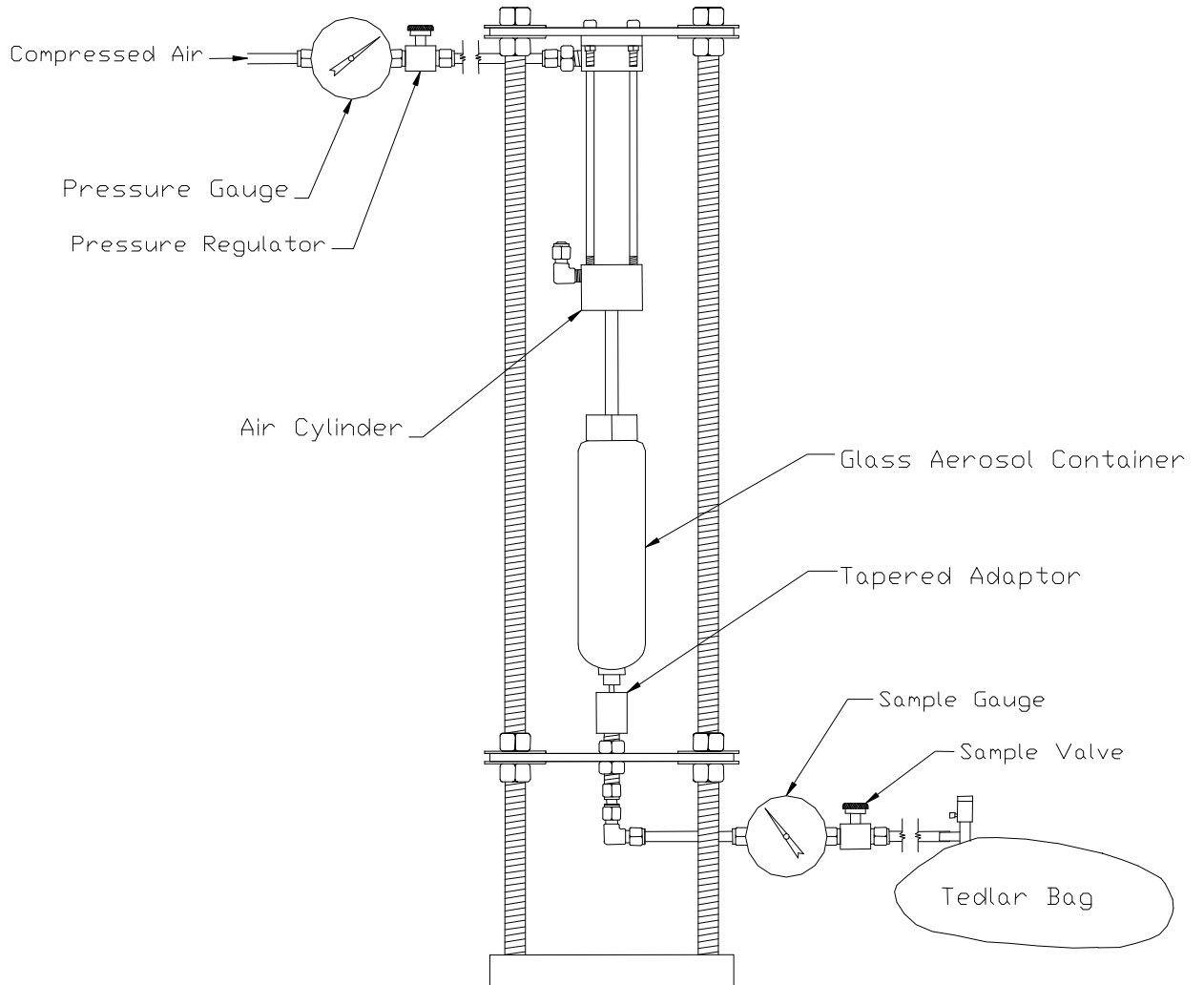
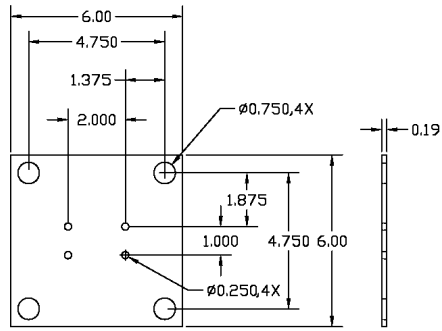
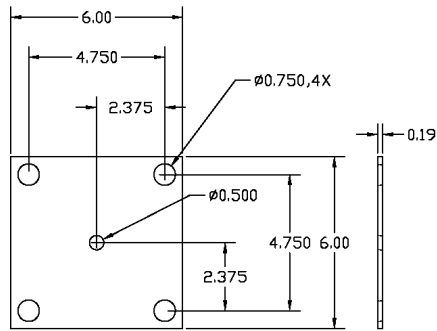


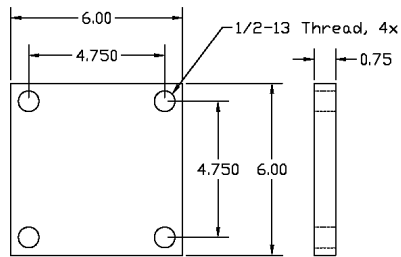
Figure 6 SAMPLE VENTING PLATFORM GLASS AEROSOL CONTAINER



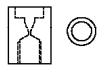
Air Cylinder Mounting Plate



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

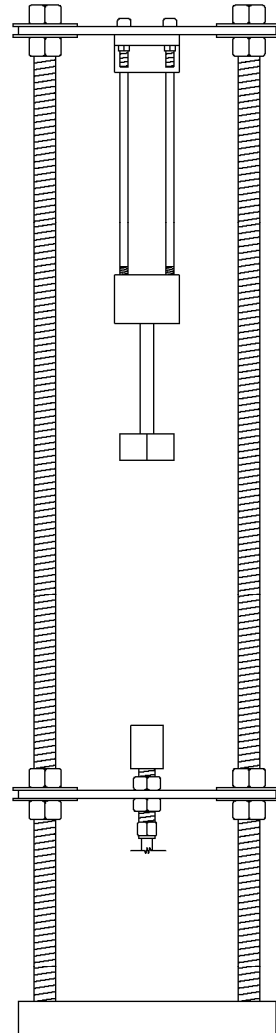
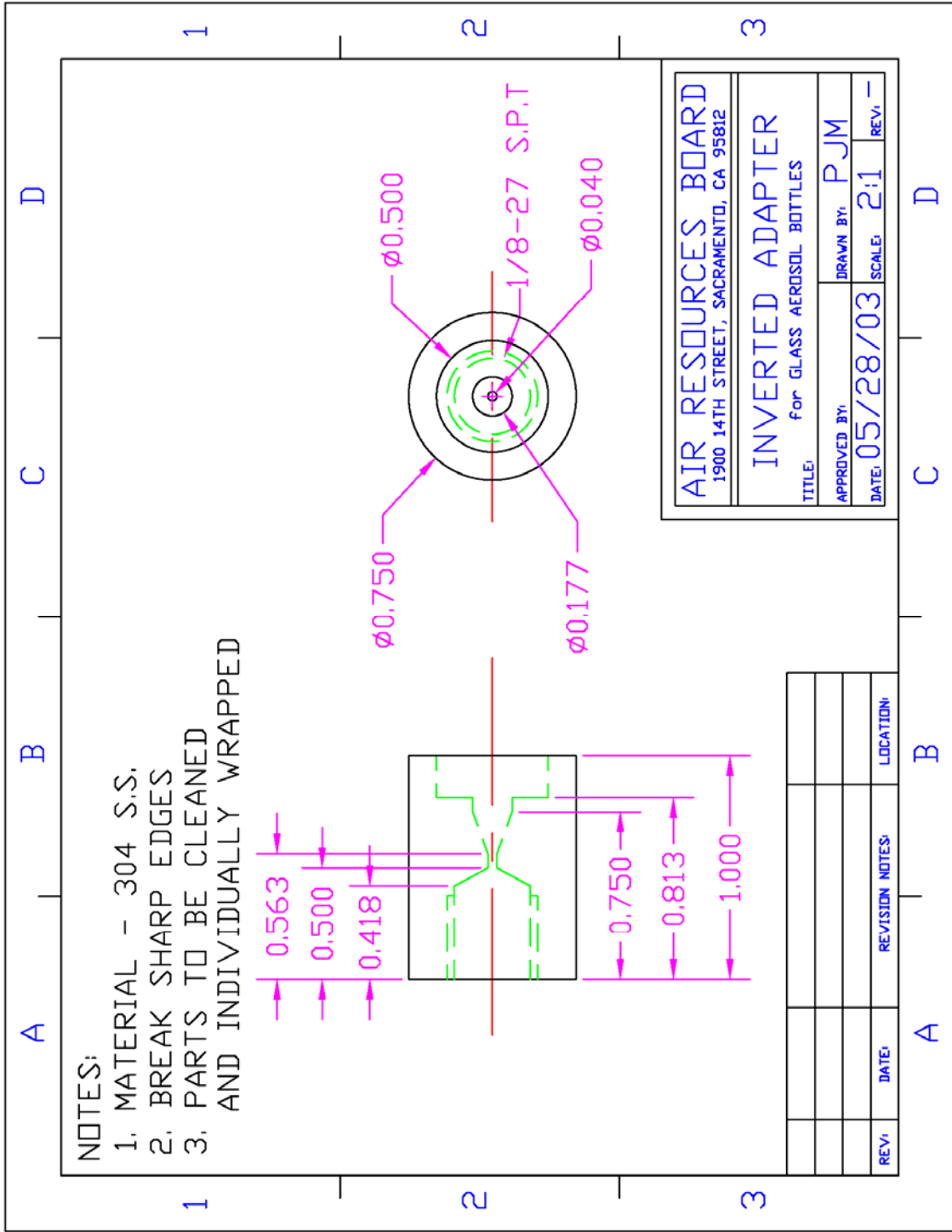


Figure 7
SAMPLE VENTING PLATFORM INVERTED ADAPTOR
GLASS AEROSOL CONTAINER



Appendix A

COLLECTION OF PROPELLANT FROM METAL AEROSOL CONTAINERS

DAY 1

1. Attach sample venting platform to the propellant collection system (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.
 - 3.1 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 (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. Note the pressure of the container 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 is confirmed from output 1, attach an appropriate sized prepared Tedlar bag.
11. Open the Tedlar bag valve just short of 2 turns to collect the propellant.
 - 11.1 Monitor any non-propellant sample that appears in the PTFE tube. See step 12.2 if the non-propellant portion of the sample advances towards the end of the PTFE tube, where it connects to the venting station.
12. Close the Tedlar bag valve and disconnect the Tedlar bag when either:

- 12.1 the Tedlar bag is full, or
- 12.2 the non-propellant portion of the sample advances to within the last loop of the PTFE tube. Should this happen:
 - 12.2.1 Close off valve 1.
 - 12.2.2 Close the Tedlar bag valve.
 - 12.2.3 Disconnect the PTFE tube at the panel.
 - 12.2.4 Secure the end of the PTFE tube in a tared bottle 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.
 - 12.2.5 Disconnect the Tedlar bag.
 - 12.2.6 When the non-propellant sample is no longer coming through the PTFE tubing, advance to step 16.
13. The Tedlar bag is now ready for GC analysis (see Appendix E).
14. Open vent output on the propellant collection system.
15. Periodic adjustments to the pressure regulator knob will be necessary, until the full open position is reached.
16. 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.
17. Turn the hydraulic jack valve open, and carefully lower the sample container. Close the hydraulic jack valve.
18. Remove the sample container and transfer it to the platform shaker. Set platform shaker to around 85 rpm and allow the sample can to agitate overnight.
19. 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.

DAY 2

20. Remove the sample container from the platform shaker.
21. Weigh the container, to the nearest 0.01 g. Record this as the “vented” weight.
22. Open sample container. Mix and transfer the non-propellant portion to both a 20 mL and 40 mL vial. Properly dispose of any remaining non-propellant portion.
23. 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.
24. Rinse sample container to remove any residues. Allow the container to dry completely.
25. Weigh sample container, to the nearest 0.01 g. Record this as the “empty” weight.

Appendix B

COLLECTION OF PROPELLANT FROM GLASS AEROSOL CONTAINERS

PART 1

1. Attach propellant collection system (Figure 5) to compressed 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 appropriate sized, prepared Tedlar bag.
10. Open Tedlar bag valve just short of 2 turns.
11. Open sample valve to collect propellant.
12. Close the Tedlar bag valve, close the sample valve and disconnect the Tedlar bag when either:
 - 12.1 the Tedlar bag is full, or
 - 12.2 the non-propellant portion of the sample reaches to within 12" of the end of the sampling tube.
13. The Tedlar bag is now ready for GC analysis (see Appendix E).

14. 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.
- 14.1 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

15. When venting ceases:
 - 15.1 Close sample valve. Decrease pressure on air cylinder. Remove the sample container from the venting platform. Turn sample container to its upright orientation.
 - 15.2 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.
16. Sampling tube. 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.
17. Sampling assembly. 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.
18. Punch a very small hole into the top of the crimp, just next to the actuator valve.
19. 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.
20. Place the sample container into a tared 400 mL beaker, on the platform shaker. Set platform shaker to around 85 rpm.
21. When there is minimal or no foaming when the sample container is swirled, remove vacutainer assembly from shaker.
22. 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

23. Remove the sample container and tared beaker from the platform shaker.
24. Weigh the sample container to the nearest 0.01 g. Record this as the “vented” weight.
25. 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.
26. Retrieve sampling jar from walk-in.
27. 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.
 - 27.1 When opening the sampling jar do so slowly, as there may be pressure from any residual entrained propellant
28. Rinse sample container to remove any residues. Allow the container to dry completely.
29. Weigh sample container, to the nearest 0.01 g. Record this as the “empty” weight.

Appendix C

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.
 - 3.1 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 (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. Note the pressure of the container on the pressure gauge.
 - 6.1 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 appropriate sized prepared Tedlar bag.
11. Open the Tedlar bag valve just short of 2 turns 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 Tedlar bag.
13. The Tedlar bag is now ready for GC analysis (see Appendix E).

14. When the pressure gauge indicates zero pressure, the container is fully vented.
15. Turn the hydraulic jack valve open, and carefully lower the sample container. Close the hydraulic jack valve.
16. Remove the container from the sample venting platform.
17. Weigh the container, to the nearest 0.01 g. Record this as the “vented” weight.
18. Open sample container and cut open the inner pouch with scissors.
19. Transfer the non-propellant portion to both a 20 mL and 40 mL vial. Properly dispose of any remaining non-propellant portion.
20. Rinse sample container to remove any residues. Allow the container to dry completely.
21. Weigh sample container, to the nearest 0.01 g. Record this as the “empty” weight.

Appendix D

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 appropriate sized prepared Tedlar bag.
 - 5.1 Monitor if foam enters the Tedlar 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 Tedlar bag. The Tedlar bag is now ready for GC analysis (see Appendix E).
7. Place the sample container on the platform shaker, with the vacutainer needle still inserted, for several 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. Open sample container. Mix and transfer the non-propellant portion to both a 20 mL and 40 mL vial. Properly dispose of any remaining non-propellant portion.
 - 10.1 If the sample is expected to foam, placed the container in the walk-in refrigerator to bring it below room temperature and minimize sample loss.
11. Rinse sample container to remove any residues. Allow the container to dry completely.
12. Weigh sample container, to the nearest 0.01 g. Record this as the “empty” weight.

Appendix E

PROPELLANT ANALYSIS

Instruments are annually calibrated for each compound, using a six-point calibration. 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:

<u>Calibration Level</u>	<u>Split Ratio</u>
5%	47.114:1
10%	22.483:1
20%	10.707:1
50%	3.425:1
75%	1.8:1
100%	1:1

Following the annual calibration or one performed, as indicated in section 7.2, Calibration Controls and Checks provide ongoing verification that the annual calibration remains valid.

- 1 Attach each Tedlar bag sample to a port on the GC autosampler manifold. Make certain to snug the attaching nut $\frac{1}{4}$ turn past finger tight, then turn the bag valve just short of 2 turns. Helium is run as the blank.
- 2 Load Method:
 - 2.1 Under **Method**, select **Load Method**.
 - 2.2 Select **SAS_05**.
 - 2.3 Click **OK**.
- 3 Load Sequence:
 - 3.1 Under **Sequence**, select **Load Sequence**.
 - 3.2 Select **screen.s**.
 - 3.3 Click **OK**.
- 4 Sequence:
 - 4.1 Under **Sequence**, select **Sequence Parameters**.
 - 4.1.1 Enter analyst initials under **Operator Name**.

- 4.1.2 Verify Correct **Data File Path**.
- 4.1.2.1 Should read: C:\CHEM32\1\DATA\xxxx, where xxxx equals current year.
- 4.1.3 Enter **Subdirectory** using two decimals each for month, day and year (i.e. June 12, 2008 would be entered as **061208**); a letter can be put at the end to distinguish specific analyses run on the same day.
- 4.1.4 Click **OK**.
- 4.2 Under **Sequence**, select **Sequence Table**.
- 4.2.1 Under **Vial**, enter the number that corresponds to the position of the sample Tedlar bag.
- 4.2.2 **Sample Name**. Enter sample names in the following order: **Helium Blank, Propellant Standard #1, Propellant Standard #2, Helium Blank, all samples being analyzed, Helium Blank, Propellant Standard #1, and Propellant Standard #2**.
- 4.2.2.1 The last line has no **Vial** or **Sample Name**.
- 4.2.3 **Method Name**. Enter **SAS_05** for all lines except the last. For the last line, enter **Standby**.
- 4.2.4 **Inj/Vial**. Enter “**1**” for all lines.
- 4.2.5 **Sample Type**. Enter “**Sample**” for all lines.
- 4.2.6 Click **OK**.
- 5 Print Sequence List:
 - 5.1 Under **Sequence**, select **Print Sequence**.
 - 5.2 Check both **Sequence Parameters & Method** and **Injection Ports** boxes.
 - 5.3 Click **Print**.
 - 5.4 Verify that all of the information on your Sequence List is correct.
- 6 Run Sequence:
 - 6.1 Under **RunControl**, select **Run Sequence**.
- 7 After the conclusion of analysis, review all data.

8 Shut Down:

8.1 Close and remove all sample bags.

8.2 Cover sampling ports with caps.

Appendix F

PROPELLANT DENSITY ANALYSIS

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.

1 CALIBRATION (monthly):

- 1.1 Inspect the desiccant in the cartridge on top of the instrument to make sure it is satisfactory for analysis. Change the desiccant if the indicator grains have changed to the appropriate 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.
- 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?**” ($\rho_{\text{air}} = 0.00116\text{-}0.00124$)
- 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 Nanopure water (or Mettler Standardized 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 is successful, record value and press **RESET**. If unsuccessful, repeat steps 1.1 through 1.9.
- 1.11 Record value in instrument lab book.
- 1.12 Inject about 3 mL of ethanol 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.

- 1.13 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.
- 1.14 Place purge line into the desiccant port.
- 1.15 Press **PUMP**, allowing air to dry the measuring cell. Press **PUMP** again to shut off.
- 1.16 Replace purge line to the deionized water trap. Replace clear intake tubing in the lower intake port.

2 **SAMPLING (every analysis):**

- 2.1 **Instrument Check** - expected $p_{He} = 0.00018$
 - 2.1.1 Attach helium Tedlar bag, opening valve at least one turn. Purge dry measuring cell with Helium prior to actual measurement by gently pressing on Tedlar bag.
 - 2.1.2 Press **CHECK**.
 - 2.1.3 Lightly press the Tedlar bag to introduce gas into the measuring cell, noting a steady stream of bubbles in the deionized water trap. Close Tedlar bag, leaving it attached.
 - 2.1.4 Press **ENTER**.
 - 2.1.5 The instrument will complete the check and print out a report. The instrument will pass/fail based on ± 0.00002 .
 - 2.1.5.1 If the check value fails, repeat steps 2.1.1 - 2.1.5.
 - 2.1.5.2 If the check still does not pass after step 2.1.5.1, start over at Section 1 (Calibration).
 - 2.1.6 Record value in instrument lab book.
 - 2.1.7 Press **RESET**, and disconnect Tedlar bag.
- 2.2 **Sample Check** - expected $p_{152a} = 0.00270-0.00278$.
 - 2.2.1 Attach 152a Tedlar bag, opening bag valve at least one turn.
 - 2.2.2 Lightly press the Tedlar bag to introduce gas into the measuring cell,

noting a steady stream of bubbles in the deionized water trap. Close Tedlar bag, leaving it attached.

2.2.3 Press **MEASURE**.

2.2.4 The instrument will complete the measurement and print out a report. Record value in instrument lab book.

2.2.5 Press **RESET**, and disconnect Tedlar bag.

2.3 **Samples:**

2.3.1 The instrument is ready to run samples.

2.3.2 Attach sample Tedlar bag, opening bag valve at least one turn.

2.3.3 Repeat steps 2.2.2 through 2.2.5 until all samples are tested.

2.3.4 The instrument check (He) and sample check (HFC-152a) are run again after the last sample by repeating steps 2.1.1 through 2.2.5.

SOP REVISION HISTORY

DATE	VERSION	NOTES
October 16, 1996	1.0	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.
March 10, 1998	1.1	Adjusted document font to Times New Roman 12. Inserted Appendix A and B formerly a stand-alone document.
December 10, 1999	2.0	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.
October 17, 2003	2.1	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.
April 8, 2004	2.2	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.
June 9, 2008	3.0	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.
September 29, 2009	3.1	SOP updated to reflect the various updates and modifications made to the propellant analysis. All Figures updated, including additional detailed drawings of key components.

August 18, 2010	3.2	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.
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