CALIFORNIA
AIR RESOURCES BOARD

Standard Operating Procedure for Consumer Product Sample Preparation

SAS14
Revision 0.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
Manisha Singh, Ph.D., Chief Quality Management Branch	8/5/19
Michael Werst, Chief Northern Laboratory Branch	8/5/19

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 for Consumer Product Sample Preparation

1 Introduction

This procedure describes how to prepare a non-aerosol sample or the non-propellant portion of an aerosol sample for analysis under Method 310 as required by the Consumer Products Regulations.

2 Summary of Method

This procedure describes the aliquotting of non-aerosol samples or the non-propellant portion of aerosol samples into archive and sample aliquot vials. This procedure further outlines preparing dilutions from the aliquot vial contents for further analysis. A laboratory sample of known concentration is also prepared for analysis.

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.
archive aliquot	An aliquot of the sample retained per the sample retention policy for archival and re-test purposes.
Batch Sample (BS)	A laboratory prepared sample aliquot of known concentration for QC evaluation under Method 310.
CARB	California Air Resources Board
duplicate	A second analysis of a sample submitted for analysis under Method 310.
duplicate aliquot	An additional sample aliquot from the same sample carried through all steps of the sampling and analytical procedures of Method 310 in an identical manner.
ID	Identification
LIMS	Laboratory Information Management System
LIMS Manual	Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)
MPA	1-methoxy-2-propanol
NLB	Northern Laboratory Branch
QC	Quality Control
QCM	Quality Control Manual
sample	The sample submitted for analysis under Method 310.

sample aliquot	The sample aliquot is any aliquot used for analysis, and includes the duplicate aliquot, the Batch Sample, or any archive aliquot undergoing a re-test.
sample batch	A set of samples analyzed together under Method 310.
sample dilution	Dilution made from the sample aliquot.
SOP	Standard Operating Procedure
VOC	Volatile Organic Compound(s)

4 Interferences

4.1 Consumer product packaging may prevent separation of the product from the delivery system. In these cases, only qualitative data will be included on the report.

4.2 Samples may not dissolve in solution. In these cases, record this in LIMS and on the report. Additionally, Karl Fischer tartrate data may be the only water data reported at the analyst's discretion.

4.3 Samples may be non-homogenous and not yield a representative aliquot. In these cases, record this in LIMS and on the report.

4.4 Highly volatile samples can evaporate quickly. To minimize this effect, limit the amount of time the vials and containers are open. Add a small amount of solvent to the volumetric flask, then tare the volumetric flask prior to sample introduction.

4.5 Entrained propellant can present challenges in obtaining a dilution weight as it off-gasses. Limit the amount to time the vials and containers are open.

5 Personnel Qualifications

5.1 Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program's requirements per any applicable state and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the 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 Ensure engineering controls are in place and operating (i.e. adequate ventilation).

6.4 Walk-in refrigerators are equipped with safety releases on the doors to prevent locking persons inside. Personnel should wear appropriate clothing for a low temperature environment, and non-slip footwear as moisture can create a slick floor.

7 Hazardous Waste

7.1 For any sample container with product remaining after all required analyses, evaluate the sample container for proper disposal instructions, and consult the Chemical Hygiene Plan as necessary. Store empty sample containers in a secure location until release of custody.

7.2 Archive aliquots are to be disposed of in accordance with the hazardous waste contract upon management approval.

7.3 Contents of sample aliquot vials are to be disposed of in the same manner as excess sample once analysis under Method 310 is complete.

7.4 Sample dilutions are to be disposed of in the consumer products waste container in the satellite hazardous waste accumulation area once analysis under Method 310 is complete.

8 Equipment and Supplies

8.1 40mL Amber Vials, screw top with caps

8.2 20mL Vials, screw top with caps

8.3 8mL Vials, screw top with caps

8.4 2mL Autosampler Vials with caps

8.5 16mL Vials, screw top with caps

8.6 Autosampler vial cap crimper

8.7 Autosampler vial cap decrimper

8.8 Vial racks, various sizes

8.9 Volumetric Flasks, 1mL, 5mL, 10mL, and 500mL

8.10 Analytical Balance, capacity of at least 200g x 0.00001g readability (e.g. Mettler XP205 or Sartorius Genius)

8.11 System Computer for analytical balance

8.12 Software for data transfer and collection (e.g. BalanceTalk, Excel, LabX)

8.13 Top-Loader Balance, capacity of at least 1000g x 0.001g readability

8.14 1.0g Mass, ASTM class 1 or better

8.15 Laboratory Information Management System (LIMS)

8.16 Laboratory vented enclosure

8.17 Pipettors, 1000µL and 5000µL with tips

8.18 Transfer Tubes, disposable, 3-5mL capacity

8.19 Transfer Pipettes, disposable

8.20 Pasteur Pipettes, disposable with bulbs

8.21 Stirring rods

8.22 Scoopulas/spatulas

8.23 Syringes, disposable, 3mL, 20mL, and 60mL

8.24 Pliers

8.25 Can openers

8.26 Screwdrivers

8.27 Cutting tools, various (e.g. snips, scissors, etc.)

8.28 Forceps

8.29 Pipe cutters

8.30 Beakers and Tri-Pours

8.31 Task wipes (e.g. Kimwipes)

8.32 Vortex mixer (e.g. Vortex Genie 2)

8.33 Homogenizer (e.g. IKA T8.01 S1)

8.34 Sonicator (e.g. Bransonic Ultrasonic Cleaner 2510R-MT)

8.35 Syringe Filter (e.g. 25mm GD/X Disposable Filters, Glass Microfiber GMF with Polypropylene Housing, pore size 0.45µL)

8.36 Gloves, non-powdered nitrile or suitable alternative

8.37 Solvent squeeze bottles

8.38 Desiccant

8.39 Sample and Archive Refrigerator(s), capable of maintaining temperature >0^{o}C and ≤10^{o}C, and capable of being secured with access limited to approved staff.

8.40 Standards Refrigerator(s)

8.41 Reagents and Samples

8.41.1 Samples from sample batch

8.41.2 Batch Sample (may be prepared from pure standard materials or purchased as certified solution)

8.41.2.1 Deionized Water, ASTM Type I

8.41.2.2 Acetone, pure (99.9%), or as pure as can be reasonably obtained

8.41.2.3 Methanol, pure (99.8+%), or as pure as can be reasonably obtained

8.41.2.4 Ethanol, 200 proof

8.41.2.5 Sodium chloride, ACS, 99% minimum

8.41.3 1-Methoxy-2-Propanol (MPA), 99+%, dry

8.41.3.1 To prepare MPA place approximately an inch of desiccant in solvent squeeze bottle and add MPA.

8.41.4 Hexane, anhydrous, 95% n-hexane or better

8.41.5 Acetone, ACS grade or better

8.41.6 Methanol, ACS grade or better

8.41.7 Isopropanol, ACS grade or better

9 Procedure

9.1 Aliquotting samples

9.1.1 Labeling vials

9.1.1.1 Label a 40mL amber vial with the laboratory ID number for each sample. This vial is for the archive aliquot.

9.1.1.2 Label a 20mL vial with the laboratory ID number for each sample and duplicate. This vial is for the sample aliquot.

9.1.1.3 Label an 8mL vial and a 2mL autosampler vial with the laboratory ID number for each sample aliquot. These vials are for the sample dilution. Include vials for a solvent blank.

9.1.2 Ensure samples are at room temperature, with the exception of shaving gels.

9.1.2.1 Shaving gels must remain refrigerated prior to and immediately after use.

9.1.3 For an aerosol sample be sure to follow procedures outlined in SAS05 for propellant collection and can weights prior to aliquotting the non-propellant portion.

9.1.4 Mix sample as much as possible to ensure homogeneity.

9.1.5 Open sample container using tools or implements, as necessary.

9.1.6 Some samples may require additional processing to extract the non-aerosol sample or the non-propellant portion of an aerosol sample from the delivery system.

9.1.6.1 Dryer Sheets

9.1.6.1.1 For the handling of dryer sheets, see APPENDIX A.

9.1.6.2 Wipes

9.1.6.2.1 Wring out heavily saturated wipes over a beaker or dish to collect the sample. Ensure the beaker or dish is of adequate size.

9.1.6.2.2 Wipes that are not heavily saturated may require the use of a syringe to facilitate sample collection. Put wipes into a 20mL or 60mL syringe to press out the sample. Repeat as necessary.

9.1.6.2.2.1 At times it may be necessary to use compressed gas to assist in the pressing (see APPENDIX B).

9.1.6.2.3 Sampled and un-sampled wipes shall be stored with empty sample containers and packaging until release of custody.

9.1.6.3 Liquid or Gel Beads, Solid gels

9.1.6.3.1 Transfer some of the beads/gel to a 20mL or 60mL syringe, and break apart by pressing them through the tip of the syringe. Repeat as necessary.

9.1.6.4 In instances not addressed by section 9.1.6, where separation of the non-aerosol sample or the non-propellant portion of an aerosol sample from the delivery system is not possible, no dilution is prepared. Report only qualitative data from SAS13, SAS05 and SAS06.

9.1.7 Ensure sample is mixed thoroughly, if not, mix.

9.1.8 Aliquot into 40mL vial for archive aliquot.

9.1.8.1 Store archive aliquots in sample and archive refrigerator.

9.1.8.2 Retain archive aliquots for three years from completed analysis and then dispose of as hazardous waste.

9.1.9 Ensure sample is mixed thoroughly, if not, mix. Aliquot into 20mL vial for sample aliquot.

9.1.10 Dispose of excess sample appropriately. Utilize any information on the product label, and the chemical hygiene plan for proper disposal procedures.

9.1.11 For aerosol samples, follow SAS05 to obtain empty weight.

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

9.2 Preparing Batch Sample (May be prepared from pure standard materials or purchased as certified solution.)

9.2.1 A Batch Sample stock solution is prepared by weighing 300g of deionized water and 50g each of sodium chloride, acetone, methanol, and ethanol into a 500mL volumetric flask. Mix by inversion.

9.2.1.1 Dissolve sodium chloride completely in the deionized water prior to adding the acetone, methanol, and ethanol.

9.2.2 Fill 16mL vials with approximately 4.5mL aliquots of the Batch Sample stock solution and cap.

9.2.3 Label each Batch Sample vial with “Batch Sample”, preparation date, expiration date, and the preparer's initials.

9.2.4 Store Batch Sample aliquots in standards refrigerator (stored aliquots may be used, it is not necessary to prepare a new Batch Sample stock).

9.3 Prepare Dilutions for analysis under Method 310.

9.3.1 Dilutions are prepared using MPA as the solvent.

9.3.1.1 There are some instances where another solvent may be required for a particular analysis as MPA may interfere with the compound of interest (e.g. trichloroethylene). In these cases, all blanks, controls, calibrators, and sample are to be prepared using this same alternate solvent, in addition to the MPA dilutions.

9.3.2 Prepare solvent blank by filling the appropriately labeled 8mL vial and 2mL autosampler vial with the same solvent used to make the dilutions. Cap the vials.

9.3.3 For each sample aliquot, weigh 1.0mL into a 10mL volumetric flask and record the value in LIMS.

9.3.3.1 For procedure details related to dilutions prepared from dryer sheets, see APPENDIX A.

9.3.3.2 Ensure the accuracy of the analytical balance.

9.3.3.2.1 Check the LIMS balance control record (see LIMS Manual: Balance Controls). If no record for the current day exists, perform a balance control on the analytical balance prior to use, using a 1.0g mass, and record the value in LIMS. The 1.0g mass should be within ±2sd of the target value.

9.3.3.2.2 Using the forceps included with the weight set, place the 1.0g mass on the analytical balance. When the reading becomes stable, as indicated by the analytical balance, record the weight in LIMS (see LIMS Manual: Balance Controls). If the weight is not within the control limits, manually recalibrate the analytical balance per the manufacturer's instructions. After the calibration, re-weigh the mass and record in LIMS. If the weight is still outside the control limits, there may be a problem with the analytical balance or the mass. Contact appropriate personnel for service.

9.3.3.3 Ensure data transfer software is open on the system computer.

9.3.3.4 Open the data collection software located on the system computer desktop (see LIMS Manual: Dilution Weights, Dryer Sheet Weights and Hexane Dilution Weights, for setting up this spreadsheet). Save spreadsheet under a naming system that includes the sample ID numbers.

9.3.3.5 For each sample dilution, tare a 10mL volumetric flask on the analytical balance (it is acceptable to add a small amount of MPA to the flask prior to this step). Pipette approximately 1mL of sample into the tared flask.

9.3.3.5.1 An equally proportioned dilution of less volume may be necessary if

sample size is limited. In these cases note the volumes used and be sure to adjust the dilution weight entered into LIMS to account for the amount used.

9.3.3.5.2 For samples that cannot be pipetted (such as viscous liquids, creams, pastes, gels, and semi-solids), a transfer tube may be used in place of a pipettor, or the sample may be dispensed into the flask directly from the sample container.

9.3.3.6 Weigh and transfer the weight value to the dilution spreadsheet in the appropriate cell.

9.3.4 Dilute to 10mL with MPA. Invert or vortex to mix (a homogenizer or sonicator may also be used). Samples may require filtering/settling. Make note of any samples that do not dissolve well.

9.3.4.1 Indications of dilutions requiring filtering or settling include cloudiness, floating particles, undissolved solids, and gel like appearance.

9.3.4.2 Attach a syringe filter to the tip of a 3mL disposable syringe and pass the sample dilution through the filter into appropriately labeled 8mL vial and 2mL autosampler vials and cap.

9.3.4.3 If the sample becomes turbid, repeat filtering.

9.3.5 Perform a Balance Check after all weighing is complete.

9.3.5.1 Using the forceps included with the weight set, remove the 1.0g mass and place it on the analytical balance. When the reading becomes stable as indicated by the analytical balance, record the weight on the dilution spreadsheet.

9.3.5.2 If the weight is not within the control limits, the dilutions must be prepared again and bracketed between a successful balance control and check.

9.3.6 Upload dilution data for samples to the LIMS (see LIMS Manual: Dilution Weights, Dryer Sheet Weights and Hexane Dilution Weights).

9.3.7 Transfer the sample dilutions into appropriately labeled 8mL vial and 2mL autosampler vials and cap.

10 Quality Control

10.1 Table of Quality Controls

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Balance Control	Daily prior to use	±2sd of the target value	If outside control criteria, recalibrate the balance manually per the manufacturer's instructions. After the calibration, re-weigh the mass and record in LIMS. If the weight is still outside the control limits, there may be a problem with the balance or the mass. Contact appropriate personnel for service.
Balance Check	After weighing session	±2sd of the target value	If outside the control criteria, perform a Balance Control using any corrective action necessary to bring the balance back into control. Re-prepare dilutions.

10.2 Equipment Requirements

10.2.1 The balances require calibration by an outside source annually.

10.2.2 The 1.0g mass is calibrated by an outside source annually.

10.2.3 Verify and record refrigerator temperatures weekly.

10.2.3.1 Sample Refrigerator

10.2.3.1.1 Temperature shall be maintained >0^{o}C and ≤10^{o}C.

10.2.3.1.2 Prior to analysis, aerosol samples must be stored in a refrigerator that meets this criterion.

10.2.3.2 Archive Refrigerator

10.2.3.2.1 Temperature shall be maintained >0^{o}C and ≤10^{o}C.

10.2.3.2.2 Exceedance of temperature range for more than one week may compromise the integrity of the archive samples and requires notification to the client.

10.2.4 Pipettors require certification by an outside source annually.

11 Sample and Data Management

11.1 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.

11.2 Sample and data management follow procedures outlined in the QCM. The LIMS Manual describes data management procedures as they pertain to LIMS for this SOP. Additionally, SAS13 and this SOP describe sample and data management as they pertain to Method 310.

11.3 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.

12 Calculations

There are no calculations in this method.

13 References

13.1 Method 310 Determination of Volatile Organic Compounds (VOC) in Consumer Products and Reactive Organic Compounds (ROC) in Aerosol Coating Products, May 25, 2018

13.2 SAS05 Standard Operating Procedure for the Determination of Compounds in Aerosol Consumer Product Propellant by Gas Chromatography

13.3 SAS06 Procedure for the Qualitative Determination of Compounds in Consumer Products by Headspace Gas Chromatography/Mass Spectrometry

13.4 SAS13 Standard Operating Procedure for Consumer Product Sample Batch Management and Reporting

13.5 NLB Laboratory Quality Control Manual, September 17, 2018

13.6 MLD076 Standard Operating Procedure Preparation of Northern Laboratory Branch’s Standard Operating Procedures, Revision 0.0

13.7 NLB Chemical Hygiene Plan, June 2018 (or most current version)

13.8 Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)

14 Revision History

	Date	Updated Revision	Original Procedure
1	**Description:** New SOP for Sample Preparation, Revision 0.0		
	August 5, 2019	Procedures for sample preparation for analysis under Method 310	None

APPENDIX A

Handling of an Atypical Sample Matrix: Dryer Sheets

1 Summary

This document describes a procedure for the sampling and dilution preparation of dryer sheets.

2 Equipment and Supplies

2.1 In addition to the supplies listed in section 8 of SAS14, the following are necessary for this appendix.

2.1.1 Platform Shaker

2.1.2 Circular Template, 60mm diameter

3 Procedure

3.1 Label vials

3.1.1 Label a 20mL vial with the laboratory ID number for each dryer sheet sample in the sample batch.

3.1.2 Label an 8mL vial and a 2mL autosampler vial with the laboratory ID number for each dryer sheet sample in the sample batch. Include vials for a solvent blank, Batch Sample, and any control/checks if not already done so for other samples in the sample batch.

3.2 Ensure samples are at room temperature.

3.3 Ensure the accuracy of the analytical balance per section 9.3.3.2 of SAS14.

3.4 Ensure data transfer software is open on the system computer.

3.5 Open the data collection software located on the system computer desktop (see LIMS Manual: Dilution Weights, Dryer Sheet Weights and Hexane Dilution Weights, for setting up this spreadsheet). Save spreadsheet under a naming system that includes the sample ID numbers. Navigate to the “DryerSheet” spreadsheet. Enter the current date, analyst name, and data set information. Enter in the sample ID for each dryer sheet weight under the Sample ID column.

3.6 Take a single dryer sheet from the middle of the box of dryer sheets and weigh to the nearest 0.00001g. Transfer the whole sheet weight in the “Whole Sheet Wt (g)” column.

3.7 Using circular template cut a section from the center of the folded dryer sheet to

create a sample aliquot. Weigh to the nearest 0.00001g. Transfer the sample aliquot weight in the “Aliquot Wt (g)” column.

3.8 Insert the sample aliquot into the 20mL vial, add volumetrically 10mL of MPA, and cap vial.

3.9 Perform a Balance Check after all weighing is complete per section 9.3.5 of SAS14.

3.10 Upload dilution data for dryer sheet samples to the LIMS (see LIMS Manual: Dilution Weights, Dryer Sheet Weights and Hexane Dilution Weights).

3.11 Place the vial on its side on a platform shaker. Shake for 16 to 24 hours at 100 to 150 rpm.

3.12 Transfer each sample dilution into appropriately labeled 8mL and autosampler vials and cap.

3.12.1 Allow any particulates to settle out before transferring, filtering if necessary.

APPENDIX B

Handling of an Atypical Sample Matrix: Wipes

1 Summary

This document describes a procedure for the sampling of wipes using the assistance of compressed gas.

2 Equipment and Supplies

2.1 In addition to the supplies listed in section 8 of SAS14, the following are necessary for this appendix.

2.1.1 Wipe Compression Assembly (Figure 1)

2.1.2 Compressed air

3 Procedure

3.1 Set up the apparatus.

3.1.1 Establish a flow of compressed air to the wipe compression assembly not to exceed 40psi.

3.2 Prepare archive aliquot and sample aliquot.

3.2.1 Remove plunger from 60mL syringe.

3.2.2 Insert 1-3 wipes into syringe.

3.2.2.1 If initial attempt to obtain sample from wipe fails, try a different number of wipes.

3.2.3 Insert plunger into syringe without pressing down on wipes.

3.2.4 Place vial under the platform in the wipe compression assembly.

3.2.5 Place syringe on the platform so the syringe tip is through the center hole and the air cylinder piston is in contact with the plunger, ensuring the syringe tip is over the vial opening.

3.2.6 Actuate the air cylinder piston and adjust pressure to 25-30psi so that the air cylinder piston is activated forcing the plunger down.

3.2.7 Ensure sample collection in vial.

3.2.7.1 Increase pressure as necessary, or use a different number of wipes

placed in the syringe to achieve sample collection.

3.2.8 When sample flow stops, deactivate the air cylinder piston and remove syringe from the platform.

3.2.9 Remove the syringe plunger and use forceps to remove the wipes from the syringe.

3.2.9.1 Wipes shall be stored with empty sample containers and packaging until release of custody.

3.2.10 Repeat as necessary to fill archive aliquot and sample aliquot vials.

3.3 Shutting down the apparatus

3.3.1 Turn off the flow of compressed air.

3.3.2 Ensure the air cylinder plunger is all the way up.

FIGURE 1

WIPE COMPRESSION ASSEMBLY