





Standard Operating Procedure for the Total Volatile Measurement of Consumer Products

SAS 01
Revision 1.7

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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Standard Operating Procedure for the Total Volatile Measurement of Consumer Products

1 Introduction

This standard operating procedure (SOP) describes a procedure for the measurement of the total volatile material in a non-aerosol sample or the non-propellant portion of an aerosol sample, following Method 310 as required by the Consumer Products Regulations. This SOP is based on U.S. EPA Method 24/24A and ASTM D2369-97.

2 Summary of Method

Gravimetric analysis is for the determination of total volatile material in a sample. This procedure details the process for weighing a portion of the sample aliquot into an aluminum weighing dish and heating it in a forced-air oven at $110\pm 5^{\circ}\text{C}$ for one hour. The total volatile material is the difference in weight of the sample before and after heating.

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.
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)
LVP	Low Vapor Pressure
NLB	Northern Laboratory Branch
QC	Quality Control
QCM	Quality Control Manual

replicate	An additional analysis of the same sample aliquot or sample dilution.
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 set	See <i>sample batch</i>
SOP	Standard Operating Procedure
VOC	Volatile Organic Compound(s)

4 Interferences

- 4.1 Certain consumer products may react with the aluminum weighing dishes. Observation of change in the appearance of the aluminum weighing dish or sample effervescence can be an indication of a reaction. In these cases, substitute with Teflon weighing dishes.
 - 4.1.1 Sodium hydroxide reacts with aluminum weighing dishes.
 - 4.1.1.1 Sodium hydroxide is a common ingredient in oven cleaners.
 - 4.1.1.2 Review ingredients on product labels for presence of sodium hydroxide.
- 4.2 Samples with entrained propellant can forcibly eject residues in the oven. If this occurs, follow the procedure in APPENDIX A.

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 Use heat resistant gloves when handling hot items (e.g. removing items from the oven).

7 Hazardous Waste

There is no generation of hazardous waste by this method.

8 Equipment, Supplies, and Chemicals

- 8.1 Oven, forced draft, able to maintain a temperature of $110\pm5^{\circ}\text{C}$ (ASTM Type II A or Type II B recommended)
- 8.2 Laboratory vented enclosure
- 8.3 Analytical Balance, capacity of at least 200g x 0.00001g readability (e.g. Mettler XP205 or Sartorius Genius)
- 8.4 Balance weighing basket or small beaker (e.g. 50mL)
- 8.5 1.0g Mass, ASTM class 1 or better
- 8.6 System Computer for analytical balance
- 8.7 Software for data transfer and collection (e.g. BalanceTalk, Excel, LabX)
- 8.8 Laboratory Information Management System (LIMS)
- 8.9 Weighing Dishes
 - 8.9.1 Aluminum Weighing Dishes w/ a smooth (planar) bottom surface (e.g. Aluminum Crinkle Dish w/Tab, 57mm)
 - 8.9.2 Teflon Weighing Dishes, approximately 50mm x 15mm w/ a smooth (planar) bottom surface
- 8.10 Syringe, disposable, 3-5mL, w/ caps
- 8.11 Transfer Tubes, disposable, 3-5mL capacity
- 8.12 Task wipes (e.g. Kimwipes)
- 8.13 Desiccator with hygrometer and desiccant
- 8.14 Vortex mixer (e.g. Vortex Genie 2)

- 8.15 Gloves, non-powdered nitrile or suitable alternative
- 8.16 Forceps
- 8.17 Tray, low-rimmed metal (e.g. "cookie sheet")
- 8.18 Heat Resistant Gloves (e.g. oven mitt)
- 8.19 Clock or timer
- 8.20 Reagents and Samples
 - 8.20.1 Acetone, ACS grade or better
 - 8.20.2 Methanol, ACS grade or better
 - 8.20.3 Batch Sample – 90% VOC (SAS14)
 - 8.20.4 Sample Aliquots (SAS14)
 - 8.20.5 Oven Control, ASTM Type I water

9 Procedure

Note: For the analysis of dryer sheets, see APPENDIX B. Samples containing sodium hydroxide require the use of Teflon weighing dishes.

- 9.1 Label weighing dishes with unique identifiers using a permanent marker - two dishes are required per each sample and oven control. Gloves shall be worn during all steps of this procedure to prevent weighing errors due to handling.
- 9.2 Place weighing dishes on the tray, and place in the oven for one hour at $110 \pm 5^{\circ}\text{C}$.
- 9.3 Using heat resistant gloves remove the tray from the oven and place weighing dishes in desiccator to cool to room temperature. Ensure the hygrometer reads "Low Humidity."
 - 9.3.1 If the desiccator hygrometer reads "High Humidity", do not use. Recheck the hygrometer the following day and if it continues to read, "High Humidity", replace the desiccant.
- 9.4 Remove the weighing dishes from desiccator and place on the tray.
- 9.5 Ensure the accuracy of the analytical balance.
 - 9.5.1 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 $\pm 2sd$ of the target value.

- 9.5.2 Using forceps, 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.
- 9.6 Ensure data transfer software is open on the system computer.
- 9.7 Open the data collection software located on the system computer desktop (see LIMS Manual: Gravimetric Analysis for setting up this spreadsheet). Save spreadsheet under a naming system that includes the sample ID numbers.
- 9.8 Weigh and record the empty weighing dish weight.
- 9.8.1 Place the cursor in the "Weight Pan (g)" column for the first sample.
- 9.8.2 Weigh the corresponding empty weighing dish to 0.00001g and transfer the weight value to the worksheet by pushing the appropriate transfer button on the analytical balance. The highlighted data input area should advance automatically to the next field. Alternatively, use the arrow keys to move to the next sample.
- 9.8.3 Repeat for all remaining samples and oven control in the analytical batch.
- 9.9 Weigh and record the sample aliquot and/or oven control.
- Viscous samples or other materials such as creams, pastes, gels, and semi-solids, may require the use of a transfer tube in place of a syringe, or dispensing into the weighing dish directly from the sample container. This should be done in as thin a film as practicable to maximize surface area. As a final remedy, a small amount of methanol or acetone can assist in evenly distributing the sample over the bottom of the weigh dish; however, use this technique sparingly to minimize unintended chemical reactions that could affect the overall volatility of the neat sample.
- 9.9.1 Tare a clean beaker or balance weighing basket.
- 9.9.2 For each sample aliquot, mix to ensure homogeneity, vortexing if needed.
- 9.9.3 Using a syringe, draw up approximately 1-2mL. Wipe the sides of the syringe with a task wipe to remove any residual sample.
- 9.9.4 Cap and weigh the syringe with sample by placing it in the tared beaker or

balance weighing basket. Transfer the weight to the column marked, "Syringe Weight (g) – Initial weight."

- 9.9.5 Dispense approximately 1mL into the appropriately labeled weighing dish.
- 9.9.6 Cap and reweigh the syringe. Transfer the weight to the column marked, "Syringe Weight (g) – Final weight." The difference, as computed on the "Grav Calc" worksheet, is the actual amount of the sample placed in the weighing dish.
- 9.9.7 Repeat this process from the same sample aliquot for the replicate, or use the remainder of the sample in the syringe.
- 9.9.8 Repeat sections 9.9 for all samples and oven control in the analytical batch.
- 9.10 Place the weighing dishes with samples on the tray in the oven at $110 \pm 5^{\circ}\text{C}$ for one hour.
- 9.11 Using heat resistant gloves, remove the tray with weighing dishes from the oven and place weighing dishes in the desiccator to cool to room temperature for a minimum of five minutes.
- 9.12 Weigh and record the weighing dish with residue weight to the nearest 0.00001g and transfer the weight to the "Weight Pan + Residue" column for each sample and oven control on "Grav Calc" worksheet. If the sample appears to be reacting with the aluminum weighing dish (i.e. effervescence, discoloration, etc.), repeat the analysis using a Teflon weighing dish. Even when using Teflon weighing dishes, some samples can forcibly eject residue out of the dish. If there is evidence that this has occurred, utilize APPENDIX A for the samples that ejected residue, and reanalyze the entire analytical batch.
- 9.13 The workbook will calculate the total weight percent of volatile material in the sample or oven control in accordance with section 12. If the two sample replicate weights differ by more than one percent ($>1\%$) volatile material, repeat section 9 for the affected samples and include an oven control.
- 9.14 Report gravimetric results as the average of the two replicates.
- 9.15 If the oven control results are not within acceptable values ($\pm 3\text{sd}$ of the target value as established per the QCM or more than one percent VOC difference between replicates), check the balance and/or oven conditions and reanalyze the analytical batch.
- 9.16 Perform a Balance Check after all weighing is complete
 - 9.16.1 Using forceps place the 1.0g mass on the analytical balance. When the reading becomes stable as indicated by the analytical balance, record the weight on the "Grav Calc" worksheet (see LIMS Manual Gravimetric

Analysis).

9.16.2 If the weight is not within the control limits, repeat the gravimetric analysis for the analytical batch.

9.17 Upload the data to LIMS (see LIMS Manual: Gravimetric Analysis).

10 Quality Control

10.1 Table of Quality Controls

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Balance Control	Daily prior to use	$\pm 2sd$ 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	$\pm 2sd$ 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. Reanalyze the analytical batch.
Oven Control	one pair of replicates per analytical batch	One percent VOC difference or less between replicates, and Total weight percent VOC within $\pm 3sd$ of the target value	Perform a Balance Check. If the balance check is outside the control limits, perform corrective action for the balance check. If balance check is within control limits, check the oven conditions. Bring the system back into control, contacting appropriate personnel for service if necessary. Reanalyze the analytical batch.

Replicate	All samples and controls	One percent VOC difference or less between replicates.	Reanalyze the affected sample and its replicate: include an oven control and its replicate. If still outside criteria, note this on the report to the client.
Duplicate	one pair of replicates per ten or fewer sample replicate pairs in the sample batch	No QC criteria for this SOP. Evaluate duplicate results after calculating total VOC under Method 310 per SAS13.	Not applicable.
Batch Sample	one pair of replicates per sample batch	No QC criteria for this SOP. Evaluate Batch Sample results after calculating total VOC under Method 310 per SAS13.	Not applicable.

10.2 Equipment Requirements

- 10.2.1 The analytical balance requires calibration by an outside source annually.
- 10.2.2 The 1.0g mass is calibrated by an outside source annually.
- 10.2.3 The Oven requires verification by an outside source using NIST traceable test equipment 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. Additional SOPs that cover sample and data management as they pertain to sample preparation and data reporting under Method 310 include SAS13 and SAS14.
- 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

Note: Refer to APPENDIX B for calculations related to the analysis of dryer sheets.

- 12.1 Weight fraction of total volatile material in a non-aerosol sample or the non-propellant portion of an aerosol sample (per weighing dish)

$$TV_n = \frac{(B - C) - (D - A)}{(B - C)}$$

Where:

- TV = Weight fraction of total volatile material in a non-aerosol sample or the non-propellant portion of an aerosol sample
- n = Sample/control (X) or replicate (Y)
- A = weight of empty weighing dish to the nearest 0.00001g
- B = Weight of syringe w/ sample to the nearest 0.00001g
- C = Weight of syringe after dispensing sample to the nearest 0.00001g
- D = Weight of cooled weighing dish with sample residue to the nearest 0.00001g

- 12.2 Weight fraction of total volatile material in a non-aerosol sample or the non-propellant portion of an aerosol sample

$$TV = \frac{(TV_x - TV_y)}{2}$$

- 12.3 Percent Total Volatile = $TV \times 100$

- 12.4 Percent total volatile of sample and/or control: $X = TV_x \times 100$

- 12.5 Percent total volatile of replicate: $Y = TV_y \times 100$

- 12.6 Percent VOC Difference = $|Y - X|$

13 References

- 13.1 METHOD 310 DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS AND REACTIVE ORGANIC COMPOUNDS (ROC) IN AEROSOL COATING PRODUCTS, August 1, 2014
- 13.2 U.S. EPA Method 24 Determination of Volatile Matter Content, Water Content, Volume Solids, and Weight Solids of Surface Coatings
- 13.3 U.S. EPA Method 24a Determination of Volatile Matter Content and Density of Printing Inks and Related Coatings
- 13.4 ASTM D2369-97 Volatile Content of Coatings
- 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
- 13.8 Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)
- 13.9 SAS13 Standard Operating Procedure for Sample Batch Management and Reporting
- 13.10 SAS14 Standard Operating Procedure for Sample Preparation

14 Revision History

	Date	Updated Revision	Original Procedure
1	Description: Revision 1.0		
	October 10, 1996	Additions to the QC section the addition of the trip sample and clarify the calibration of the balance.	Unknown
2	Description: Revision 2.0		
	March 10, 1998	Adjusted document font to Times New Roman 12. Inserted appendix A formerly a stand-alone document.	Unknown
3	Description: Revision 3.0		
	October 26, 2000	Renumbered to new Section Number, Change Font to Arial 12.	Unknown

4	Description: Revision 1.4		
	June 27, 2003	Added procedure for use of Network LimsLink V2.1 software into Appendix A. Corrected version enumeration.	Unknown
5	Description: Revision 1.5		
	June 22, 2007	Reviewed for grammar and content. Miscellaneous additions/deletions made. Revised Appendix A to reflect use of BalanceTalk (v4.0) software instead of LimsLink v2.1 software.	Unknown
6	Description: Revision 1.6		
	August 17, 2010	Reviewed for grammar and content. Miscellaneous additions/deletions made. Added Appendix B to describe handling of atypical sample matrix.	Unknown
7	Description: Revision 1.7		
	October 24, 2018	Reviewed for grammar and content, and compliance with the most recent versions of the QC Manual and MLD076 Revision 0.0. Miscellaneous additions/deletions made. Replaced the "Trip Sample" with "Batch Sample". Incorporated APPENDIX A into body of SOP. APPENDIX B became APPENDIX A. Added APPENDIX B to describe handling of dryer sheets. Added additional QC: balance check after weighing.	Editorial and administrative changes. Original procedure did not have a balance check after weighing session.

APPENDIX A

Handling of an Atypical Sample Matrix: Viscous Oven Cleaner Containing Sodium Hydroxide and/or Entrained Propellant

1 Summary

Gravimetric results for the total weight percent VOCs can be problematic to obtain from certain sample matrices. Thick oven cleaners containing sodium hydroxide and/or entrained propellant are examples of such sample matrices. Even when using Teflon weighing dishes, the sample can forcibly eject residue during the one-hour oven drying process, and likely contaminate other nearby weighing dishes and the interior oven walls with residue. To mitigate contamination and retain the ejected residue for obtaining meaningful gravimetric results, the following handling procedures may be used.

2 Equipment and Supplies

- 2.1 In addition to the supplies listed in section 8 of SAS01, the following are necessary for this appendix.
 - 2.1.1 Teflon Petri Dish, 100mm x 15mm w/ a flat bottom surface
 - 2.1.2 Teflon Bowl, 98mm x 40mm deep with 5 equally spaced ~1/4-inch holes drilled in the center of the bowl's bottom

3 Procedure

- 3.1 The Teflon Petri dish will hold a smaller Teflon weighing dish containing the sample; and the Teflon bowl will cover the sample and contain the potential ejected sample residue.
 - 3.1.1 Place the smaller Teflon weighing dish facing up, in the middle of the large Teflon petri dish and cover with bowl (applying the sample to the smaller Teflon dish within the containment unit). This sample system of Teflon dishes and bowl comprise one sample container and containment unit.
- 3.2 Follow section 9 of SAS01 using this sample system in place of a weighing dish.

APPENDIX B

Handling of an Atypical Sample Matrix: Dryer Sheets

1 Summary

This appendix describes a procedure for the measurement of the total percent VOC in a dryer sheet, where the separation of the sample from the delivery system is not possible. The total grams volatile material per dryer sheet is the difference in weight of the sample before and after heating multiplied by the weight in grams of a single dryer sheet.

2 Equipment and Supplies

2.1 In addition to the supplies listed in section 8 of SAS01, the following are necessary for this appendix.

2.1.1 Weighing Dishes, 70mm w/ a smooth (planar) bottom surface

2.1.2 Scissors

2.1.3 Circular Template, 60mm diameter

3 Procedure

3.1 Begin by following sections 9.1 – 9.7 of SAS01.

3.2 Using the circular template cut a section out of the center of the folded dryer sheet.

3.3 Place the circular piece of sample into the appropriately labeled and tared weighing dish and weigh to the nearest 0.00001g. Record the weight in the column marked, "Syringe Initial Weight (g)".

3.4 Manually enter "0" in the column marked "Syringe Final Weight (g)".

3.5 The difference, as computed on the "Grav Calc" worksheet, is the actual amount of the product placed in the weighing dish.

3.6 Repeat this step with the other piece from the center of the dryer sheet. This sample is two semicircular pieces from the template cut.

3.7 Continue following SAS01 at section 9.10.

4 Calculations

4.1 Weight fraction of total volatile material in a non-aerosol sample or the non-

propellant portion of an aerosol sample

$$TV = \left[\frac{S - (D - A)}{S} \right]$$

Where:

- TV = Weight fraction of total volatile material in a non-aerosol sample or the non-propellant portion of an aerosol sample
- S = Mass of the dryer sheet sample to the nearest 0.00001g
- A = Weight of empty weighing dish to the nearest 0.00001g
- D = Weight of cooled weighing dish with sample residue to the nearest 0.00001g