Standard Operating Procedure for Water Determination in Consumer Products Using Gas Chromatography

SAS04
Revision 1.7

Northern Laboratory Branch
Monitoring and Laboratory Division

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

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1 Introduction

This standard operating procedure (SOP) is used for the measurement of water in a non-aerosol or the non-propellant portion of an aerosol consumer product, following Method 310 as required by the Consumer Products Regulations. Development of this SOP was aided by procedures specified in US EPA Method 24/24A, Part 60, Title 40, CFR, Appendix A and ASTM D3792-91.

2 Summary of Method

Sample dilutions are analyzed on a gas chromatograph equipped with a thermal conductivity detector to determine the water concentration. Results are generated in mg/mL, and subsequently converted and reported as a weight fraction of water in the non-aerosol or the non-propellant portion of an aerosol consumer product.

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.
ALS	Automatic Liquid Sampler
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
Control/Check standard	A quality control standard prepared from a source different from the calibration standards. This QC standard is also separately identified as a control standard and a check standard.
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.
GC/TCD	Gas Chromatograph with Thermal Conductivity Detector
ID	Identification
LIMS	Laboratory Information Management System

Acronym or Term	Definition
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
Replicate	An additional analysis of the same sample aliquot or sample dilution.
RL	Reporting Limit
RPD	Relative Percent Difference
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 (prepared per SAS14).
solvent blank	A blank consisting of the reagent used in the sample dilutions, without the target compound(s), analyzed to determine interferences or contamination during analysis.
SOP	Standard Operating Procedure
TCD	Thermal Conductivity Detector
VOC	Volatile Organic Compound

4 Interferences

Compounds with retention times similar to water can interfere with this procedure. These can include dissolved aerosol propellant components.

5 Personnel Qualifications and Training

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 Plans.

6.2 Ensure engineering controls are in place (i.e., adequate ventilation).

6.3 Follow safe handling practices for compressed gas cylinders.

6.4 The GC/TCD has heated areas and parts that can exceed 250˚C. Use caution when operating the instrument.

7 Hazardous Waste

7.1 Discard used autosampler vials in the satellite hazardous waste accumulation area in the “Consumer Product GC Vial Waste” container, and dispose of in accordance with the NLB Chemical Hygiene Plan.

7.2 Dispose of ALS rinse waste in the hazardous waste bottle in the satellite hazardous waste accumulation area, and dispose of contents in accordance with the NLB’s Chemical Hygiene Plan.

8 Equipment, Supplies, and Chemicals

8.1 GC configured with a TCD and ALS (e.g., Agilent 6890/7890)

8.1.1 Laboratory work station with software for data processing (e.g., ChemStation, OpenLab)

8.1.2 Stainless steel column, 6’ x 1/8" o.d., packed with HayeSep C, 80/100 mesh, or equivalent

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

8.3 Software for data collection (e.g., Excel, LabX)

8.4 Laboratory Information Management Systems (LIMS)

8.5 Laboratory vented enclosure

8.6 Standards refrigerator(s)

8.7 Volumetric flasks, Class A, various sizes

8.8 Pipettors, ranging 10 µL – 5000 µL with tips

8.9 Volumetric pipettes, Class A, various sizes with bulb

8.10 Pasteur pipettes, disposable with bulbs

8.11 Transfer pipettes, disposable

8.12 4 mL screw top vials with caps

8.13 2 mL autosampler vials with caps

8.14 Autosampler vial cap crimper

8.15 Autosampler vial cap decrimper

8.16 Vial inserts

8.17 Solvent squeeze bottles

8.18 Desiccant

8.19 Reagents and Samples

8.19.1 1-methoxy-2-propanol (MPA), 99+%, dry

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

8.19.2 Deionized Water, ASTM Type I

8.19.3 Calibration Standards

Pipette deionized water into 10 mL volumetric flasks, and bring to volume with solvent as follows:

Volume of water	Calibration Standard Concentration
10 µL	1 mg/mL
100 µL	10 mg/mL
200 µL	20 mg/mL
500 µL	50 mg/mL
1000 µL	100 mg/mL

Alternative volumes may be prepared with the same final concentration.

8.19.4 Helium: Grade 5

8.19.5 Acetone, ACS grade or better

8.19.6 Control/Check Standard dilution prepared using SAS14 from a stock solution of 25% each acetone and water. Stock solutions may be purchased as certified solutions or prepared as follows:

The control/check standard stock solution (0.25 g/mL) is prepared by weighing 25.00 g each of acetone and deionized water into a 100 mL volumetric flask and brought to volume with solvent. Mix by inversion. An

alternative volume may be prepared with the same final concentration.

Fill 4 mL screw top vials with no less than 1.5 mL, and no more than 3.0 mL each of the control/check standard stock and cap.

Label each vial with “Acetone/Water Control/Check” and the concentration level, preparation date, expiration date, and the preparer's initials.

The expiration date shall be three years from the date of preparation or the expiration date of the reagents or stock solution from which they are prepared, whichever is sooner.

Store the Control/Check standard aliquots under refrigeration (stored aliquots may be used, it is not necessary to prepare a new stock each analysis).

8.19.7 Sample dilutions prepared using SAS14

8.19.8 Solvent blank prepared using SAS14

9 Procedure

9.1 Analysis Preparation

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

9.1.2 Prepare the analytical batch for analysis either using 2 mL autosampler vials prepared in SAS14 or by transferring sample dilutions, control/check standard dilutions, and solvent blank(s) prepared in SAS14 to new 2 mL autosampler vials and cap.

9.1.3 Transfer Calibration Standards prepared in section 8 to appropriately labeled 2 mL autosampler vials and cap.

9.2 Instrument Preparation

9.2.1 Ensure there is sufficient He for the analytical sequence.

9.2.1.1 Change the tank when the pressure regulator indicates 500 psi or less.

9.2.1.2 Ensure the output pressure of He leaving the tank is sufficient to maintain the flows required for the method.

9.2.2 Prepare the ALS: Fill solvent rinse vials with appropriate solvent required for analysis and ensure that the waste vials are empty.

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

ALS	
Syringe size	10 µL
Injection volume	1 µL
Inlet	
Control mode	Flow
Heater	250°C
Column	
Control mode	Constant Flow
Flow	30 mL/min
Oven	
Initial Temperature	80°C
Hold time	1.20 min
Ramp 1	20.0°C/min
Final Temperature	210°C
Hold Time	6.15 min
Run Time	13.85 min
Maximum oven temperature	250°C
Equilibration	0.3 min
Detector/TCD	
Heater Temperature	250°C
Reference Flow	15 mL/min
Data rate	10.00 Hz
Peak width	0.02 min

9.2.4 Create a sequence

9.2.4.1 The following sequence should be followed with a maximum of ten samples between control and checks, ending with a check:

Solvent Blank
Calibration standards
Solvent Blank
Control Standard
Sample dilutions
Solvent Blank
Check Standard

9.2.4.2 Repeat sample dilutions, Solvent Blank, Check Standard as necessary

9.2.5 Verify or input the following parameters in the sequence:

Sample location
Sample names
Method name

Injector location
Injection source
Number of injections (2 for the sample assigned as the replicate, 1 for all others)
Sample type (i.e., calibration for calibrators, sample for samples)
For the calibration standards:
Calibration levels
Response factors will be replaced
Retention times will be averaged

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

9.2.7 Verify analyst initials are associated with the analytical sequence.

9.2.8 Save and print the sequence.

9.3 Water Analysis

9.3.1 Place the vials in the ALS, matching the sample location in the sequence. It is not necessary to prepare a separate vial for each solvent blank and control/check standard.

9.3.2 Run the sequence.

9.3.3 Print and review the chromatograms and the calibration curve.

9.3.4 Verify the data has met the QC criteria in section 10.1.

9.3.5 Any anomalies occurring during the analysis that affect the data shall be documented and all affected samples shall be reanalyzed. If anomalies continue, notify management and proceed under their direction.

9.3.6 Any instrument issues or maintenance shall be documented in the instrument logbook.

9.3.7 Upload to LIMS (refer to LIMS Manual: GC Analysis).

9.3.7.1 LIMS will average results of replicate pairs for reporting purposes.

9.3.8 Upon completion of analyses remove 2 mL autosampler vials from the ALS, and verify the instrument is in standby mode.

10 Quality Control

10.1 Table of Quality Controls

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Solvent Blank	At minimum before the control and before each check	< RL	If the blank result is < the RL, no action is taken. If the blank result is ≥ the RL, and the affected samples are at least ten (10) times higher than the blank value, then no action is taken. If the blank is ≥ the RL and the sample result is < than 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 re-prepared and analyzed.
Calibration	Each analytical batch	Must have a correlation coefficient of greater than 0.98.	If criterion is not met, reanalyze the calibration curve or make up a new calibration curve. Reanalyze the analytical batch after a successful calibration.
Control/Check Standard	The control is analyzed after the calibration, and check standard after every ten or fewer samples and at the end of the analytical sequence.	Warning and control limits are set at ±8 and ±10 percent difference respectively from the target value.	If an analysis is out of the control limits, the affected sample result(s) are invalid. Take action to bring the system back into control and reanalyze the control/check standard and any samples 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.
Replicate	One of ten or fewer samples in the analytical batch.	For replicate results ≥ 5 x RL: RPD ≤ 25	If a replicate pair does not meet criteria, the analytical batch should be re-analyzed or invalidated if re-analysis is not possible.

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
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.

10.2 Equipment Requirements

10.2.1 The balances require calibration by an outside source annually.

10.2.2 Pipettors require certification by an outside source annually.

10.2.3 The MDL for the water analysis should be verified annually following procedures outlined in the QCM.

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

12.1 LIMS will automatically calculate the weight fraction of water for each sample as follows:

$$\text{Weight Fraction Water} = \frac{\text{mg/mL } H_2O}{\text{sample dilution weight (g)/10 mL}} \times \frac{1\text{ g}}{1000\text{ mg}}$$

12.2 Percent water:

$$\text{Percent water} = \text{weight fraction water} \times 100$$

12.3 LIMS will automatically calculate the average water of replicate pairs:

$$\text{Average water} = \frac{(Y+X)}{2}$$

12.4 Relative percent difference (RPD) shall be calculated as follows:

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

Where:

X = the sample result

Y = the replicate result

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

13.3 SAS14 Standard Operating Procedure for Consumer Product Sample Preparation

13.4 ASTM D3792-99 Standard Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph (May 10, 1999)

13.5 US EPA Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings, Title 40 Code of Federal Regulations (CFR) Part 60, Appendix A, (July 1, 1996)

13.6 US EPA Method 24A, Determination of Volatile Matter Content and Density of Printing Inks and Related Coatings, Title 40 CFR Part 60, Appendix A, (July 1, 1994)

13.7 "Determination of Volatile Organic Compounds (VOC) in Water Based Aerosol Paints". Bay Area Air Quality Management District Method 36, August 31, 1990

13.8 CARB NLB Laboratory Quality Control Manual, September 17, 2018

13.9 MLD076 Standard Operating Procedure Preparation of Northern Laboratory Branch's Standard Operating Procedures, Revision 0.0

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

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

14 Revision History

	Date	Updated Revision	Original Procedure
1	**Description:** Version 1 Revision 1		
	May 16, 1996	Addition of trip samples to QC.	MLD-303
	Description: Version 1 Revision 2		
	March 10, 1998	MLD SOP ES04 Revision 1. Adjusted document font to Times New Roman 12. Inserted appendix A formerly a stand-alone document.	Unknown
3	**Description:** Version 1 Revision 3		
	January 4, 2003	Renumbered to new section number (MLD SOP SAS04). Adjusted document font to Times New Roman 12. Modified calibration curve concentrations (changed 80ug/ml to 100ug/ml).	MLD SOP ES04 Revision 1
4	**Description:** Version 1 Revision 4		
	September 5, 2003	MLD SOP SAS04 Revision 1.3. Corrected typographical errors. Corrected version enumeration.	Unknown
5	**Description:** Version 1 Revision 5		
	June 19, 2007	Updated and corrected typographical errors.	MLD SOP SAS04 Revision 1.3
6	**Description:** Version 1 Revision 6		
	August 19, 2010	MLD SOP SAS04, Revision 1.5. Modified calibration curve, commands to reflect updated software and additional GC Models. Prior to this revision the font was changed to Arial 12.	Unknown

	Date	Updated Revision	Original Procedure
7	**Description:** Revision 1.7 (Version 1 Revision 7)		
	October 28, 2021	SAS04 Revision 1.7. Reviewed for grammar and content, and compliance with the most recent versions of the QC Manual and MLD076 Revision 0.0. Added new QC measure replicate with criteria and corrective action. Miscellaneous additions/deletions made. Replaced the “Trip Sample” with “Batch Sample”. Added clarification to the revision history.	MLD SOP SAS04 Revision 1.5. Editorial and administrative changes.