Standard Operating Procedure for the Measurement of Ammonium Ion in Aqueous Consumer Products Using Ion Chromatography

SAS02
Revision 3.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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1 Introduction

This standard operating procedure (SOP) is used for the determination of ammonium ion (NH_4^+) in consumer products, following Method 310 as required by the Consumer Products Regulations. Method 310 is used for the determination of volatile organic compounds (VOCs) in consumer products. Ammonia (NH_3) is an inorganic gas that is present as ammonium hydroxide (NH_4OH) in some aqueous consumer products, such as glass cleaners. Ammonium hydroxide is volatile so it can potentially cause an overestimation in the VOC determination if not accounted for. This SOP is based on US EPA Method 300.7.

2 Summary of Method

The sample dilution of the consumer product is further diluted in water and analyzed by ion chromatography using a system comprised of an autosampler, guard column, analytical column, self-regenerating suppressor, eluent generator, and conductivity detector (CD). In the presence of methanesulfonic acid, the ammonia completely dissolves into ammonium ion and is equal to the concentration of ammonia. The following procedure is designed to quantify ammonia, as ammonium ion, at concentrations equal to or greater than 0.1% by weight in consumer products. Results are generated in µg/mL and subsequently converted and reported as a weight fraction of ammonia in the non-aerosol or the non-propellant portion of an aerosol consumer product.

3 Acronyms and Definitions

Acronym or Term	Definition
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.
ASTM	American Standards for Testing and Materials
batch sample	A laboratory prepared sample aliquot of known concentration for QC evaluation under Method 310.
CARB	California Air Resources Board
CD	Conductivity Detector
Chromeleon Console	The home page for the Chromeleon software.

Acronym or Term	Definition
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.
eluent	The liquid mobile phase used to transport the sample through the chromatograph.
HPIC	High Pressure Ion Chromatography
isocratic	A technique used in chromatography involving a mobile phase whose composition is kept constant and uniform.
LIMS	Laboratory Information Management System
LIMS Manual	Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)
MDL	Method Detection Limit
MLD	Monitoring and Laboratory Division
MSA	Methanesulfonic Acid
NH_4^+	Ammonium ion
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).
SAS	Special Analysis Section
SOP	Standard Operating Procedure
US EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
water blank	A blank consisting of ASTM Type I deionized water.
water dilution	A second dilution of the sample dilution made with ASTM Type I deionized water as the solvent.

4 Interferences

4.1 Interferences can be caused by analytes with retention times that overlap that of the cation of interest. Large amounts of any given cation could interfere with the peak resolution of an ion. Dilution of sample may address interference problems of this nature.

4.2 Interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that could lead to detectable concentrations of ions or an elevated baseline. A water blank is run at the beginning of each analytical batch to ascertain any possible contamination from reagents or sample vials used.

4.3 Losses in retention and resolution are symptoms of column deterioration. Refer to manufacturer troubleshooting guidelines to determine if a guard column or analytical column may need to be replaced.

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 and operational (i.e., adequate ventilation).

7 Hazardous Waste

Eluent generator cartridges contain methane sulfonic acid (MSA) and should be disposed of properly. Contact the NLB hazardous waste coordinator as needed.

8 Equipment, Supplies, and Chemicals

8.1 Dionex Integrion HPIC System with CD or equivalent

8.1.1 Laboratory workstation with Chromeleon Chromatography software

8.1.2 Autosampler, Dionex AS-AP

8.1.3 Guard column, Dionex IonPac CG12A – 8 µm (4 x 50 mm)

8.1.4 Analytical column, Dionex IonPac CS12A – 8 µm (4 x 250 mm)

8.1.5 Suppressor, Dionex CDRS 600 (4 mm)

8.1.6 Eluent generator cartridge, Dionex EGC 500 MSA

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

8.3 Laboratory Information Management Systems (LIMS)

8.4 Laboratory vented enclosure or fume hood

8.5 Standards refrigerator(s)

8.6 Volumetric flasks, 100 mL

8.7 Pipettor(s), ranging 100 µL – 1000 µL with tips

8.8 Transfer pipettes, disposable

8.9 Disposable syringes

8.10 Syringe filter (e.g., 25 mm GD/X Disposable Filters, Glass Microfiber GMF with polypropylene housing, pore size 0.45 µL)

8.11 10 mL autosampler vials with septa and caps

8.12 Disposable gloves

8.13 Task wipes (e.g., Kimwipes)

8.14 Reagents and samples

8.14.1 Methanesulfonic acid contained in the eluent generator cartridge (See Section 8.1.6)

8.14.2 Deionized water, ASTM Type I

8.14.3 Ammonium ion standards in water, two 1000 µg/mL containers from different sources.

8.14.4 Sample dilutions prepared using SAS14

9 Procedure

9.1 Instrument Preparation

9.1.1 Ensure that both eluent reservoirs have sufficient levels of deionized water.

9.1.2 Open the Chromeleon software and select the **Instruments** category from the Chromeleon Console. Select the **Pump** tab in the work area and turn on the pump. Ensure that the pump flow rate reaches 1.0 mL/min before proceeding.

9.1.3 Open the drop-down menu for the **Smart Startup** (Sun icon) in the toolbar above the work area and select the 'Smart Startup using Instrument Method' option. Choose the 'Ammonia IM' instrument method. Startup will take several minutes and is complete when 'End of Startup' is shown in the audit messages.

9.1.4 Verify the following conditions:

Autosampler	
Sample Loop Volume	25 µL
Injection Volume	10 µL
Pump	
Flow Type	Isocratic
Flow Rate	1.0 mL/min
Eluent Concentration	20 mM MSA
Conductivity Detector	
Cell Temperature	35°C
Background	< 1.0 µS
Data Collection Rate	5.0 Hz
Column	
Column Temperature	30°C
Suppressor	
Current	59 mA

9.1.5 Create a sequence.

9.1.5.1 Select the **Data** category from the Chromeleon Console. Follow the path, Chromeleon Local/Methods/Sequences to open a sequence template.

9.1.5.2 The following sequence should be followed with a maximum of ten water dilutions between control and checks, ending with a check:

Water blank
Calibration standards
Water blank
Control standard

Water dilution(s)
Water blank
Check standard

Repeat water dilutions, water blank and check standard as necessary.

9.1.5.3 Verify the following parameters in the sequence:

Injection names
Injection positions
Re-injections
Sample types (i.e., calibration standard for the calibrators and unknown for water dilutions)
Calibration levels
Directory path
Instrument method
Processing method

9.1.6 Save and print the sequence.

9.1.7 Open the drop-down menu next to the **Start** button and select 'Add to Queue.'

9.1.8 Go back to the **Instruments** category. Select the **Queue** tab in the work area and verify that 'run Smart Shutdown' is selected in the drop-down menu next to 'After running the queue' at the bottom of the screen.

9.2 Preparation of Eluent

Eluent is generated online by the Eluent Generator Cartridge and requires no preparation other than ensuring that the reservoir has sufficient Deionized water.

9.3 Preparation of Calibration Standards and Control/Check Standards

9.3.1 The ammonium ion standards must be at ambient temperature prior to the preparation of calibration standards and control/check standard.

9.3.2 Calibration Standards

Prepare 1.0 µg/mL, 5.0 µg/mL, and 10.0 µg/mL calibration standards by adding 100 µL, 500 µL and 1000 µL of the ammonium ion standard into 100 mL volumetric flasks and bring to volume with deionized water. Mix by inversion.

9.3.3 Control/Check Standard

Prepare a 3.0 µg/mL control/check standard by adding 300 µL of the second ammonium stock standard into a 100 mL volumetric flask and bring to volume with deionized water. Mix by inversion.

9.4 Analysis Preparation

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

9.4.2 Prepare a water dilution by adding 1 mL of the sample dilution (i.e., this is a 1:10 dilution from the sample), as prepared using SAS14, into a 100 mL volumetric flask and bring to volume with deionized water. Mix by inversion. This will result in a 1:1000 dilution of the consumer product sample. Repeat for all samples in the analytical batch.

9.4.3 Attach a syringe filter to the tip of a disposable syringe and pass the sample through the filter into appropriately labeled 10 mL autosampler vials, and seal with septum and cap.

9.4.4 Prepare a water blank by adding deionized water to an autosampler vial, and seal with septum and cap.

9.5 Analysis

9.5.1 Place the vials in the autosampler, matching the injection positions in the sequence. It is not necessary to prepare a separate vial for each water blank and control/check.

9.5.2 Change the re-injection number in the sequence from 0 to 1 for the sample assigned as a replicate.

9.5.3 If the background (CD Total) is <1.0 µS, start the sequence: In the **Queue** tab, click on the **Ready Check** button. If the Ready Check result is successful, click on the **Start** button.

9.5.4 The correlation coefficient for the calibration must be greater than 0.98. If the calibration fails, corrective action is implemented and can include reanalyzing the calibration curve or making up a new dilution of the calibration curve. Analyze the sample set after a successful calibration.

9.5.5 Print and review the chromatograms and the calibration curve.

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

9.5.7 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.

9.5.8 Any instrument issues, troubleshooting and/or maintenance shall be documented in the instrument logbook.

9.5.9 Upload results to LIMS (refer to LIMS Manual: Ammonia Analysis).

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

9.5.10 Upon completion of analysis, remove the vials from the autosampler, and verify that the instrument components have shutdown.

10 Quality Control

10.1 Table of Quality Controls

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Water 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 a check after every ten or fewer samples and at the end of the 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/checks standards. Three consecutive control standards falling between the warning and control limits require investigation and corrective action as described in the QCM.

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Replicate	One of ten or fewer samples in the analytical batch.	For replicate results ≥ 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.
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 Pipettors require certification by an outside source annually.

10.2.2 The MDL for ammonia 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 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 ammonium ion for each sample as follows:

$$\text{Weight Fraction } NH_4^+ = \frac{\text{concentration of } NH_4^+ \text{ µg/mL}}{\left(\frac{Y}{100 \text{ mL } H_2O}\right)} \text{ X } \frac{1 \text{ g}}{10^6 \text{ µg}}$$

Where:

Y = sample dilution per SAS14 (sample dilution in g/mL of solvent used)

This fractional amount of ammonium ion is reported as ammonia.

12.2 LIMS will automatically calculate the average ammonia of replicate pairs:

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

Where:

X = the sample result

Y = the replicate result

12.3 Relative Percent Difference shall be calculated as follows:

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

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, Revision 0.0, August 5, 2019

13.3 SAS14 Standard Operating Procedure for Consumer Product Sample Preparation, Revision 0.0, August 5, 2019

13.4 ASTM D1426-98 Standard Test Methods for Ammonia Nitrogen in Water (December 10, 1998)

13.5 US EPA Method 300.7, Dissolved Sodium, Ammonium, Potassium, and Calcium in Wet Disposition by Chemically Suppressed Ion Chromatography, EPA Report #600/4-86-024, (March 1, 1986)

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

13.7 MLD076 Standard Operating Procedure Preparation of Northern Laboratory Branch's Standard Operating Procedures, Revision 0.0, July 18, 2017

13.8 NLB Chemical Hygiene Plan, June 2019 (or most current version)

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

13.10 Chromeleon 7 Chromatography Data System Reference Card, Revision 1.8

13.11 Chromeleon 7 Chromatography Data System Quick Start Guide, Revision 1.8

13.12 Dionex Integrion HPIC System Operator's Manual, Revision 04, August 2016

14 Revision History

	Date	Updated Revision	Original Procedure
1	**Description:** Version 1 Revision 1		
	August 20, 1996	MLD 301. The samples will be prepared from the 1:10 dilutions in MPA. The samples are weighed 1.0 mL aliquots to 10 mL in MPA and 1.0 mL of this dilution is prepared for the ammonia analysis.	Unknown
2	**Description:** Version 2 Revision 1		
	March 10, 1998	MLD SOP ES02 Revision 2.2. Adjusted document font to Times New Roman 12. Inserted appendix A formerly a stand-alone document.	MLD 301
3	**Description:** Version 3 Revision 1		
	June 20, 2001	SOP updated to reflect change in instrumentation. Ion Chromatography will now be used for the ammonia analysis. Changed font to Arial 12.	MLD SOP ES02 Revision 2.2
4	**Description:** Version 2 Revision 1		

	Date	Updated Revision	Original Procedure
	July 7, 2003	MLD SOP SAS02 Revision 2.1. Corrected typographical errors. Corrected version enumeration.	Unknown
5	**Description:** Version 2 Revision 2		
	August 18, 2010	SAS02 Revision 2.2. Corrected typographical errors. Added analytical and data analysis instructions to sections 6 and 7. Clarified NH_4 weight fraction calculation. Reviewed document completion and accuracy.	MLD SOP SAS02 Revision 2.1
6	**Description:** Version 3 Revision 0		
	November 17, 2021	SAS02 Revision 3.0. SOP updated to reflect change in instrumentation. Ensured compliance with the most recent versions of the QCM and MLD076 Revision 0.0.	SAS02 Revision 2.2