California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

MLD SOP SAS04

STANDARD OPERATING PROCEDURE FOR WATER DETERMINATION IN CONSUMER PRODUCTS USING GAS CHROMATOGRAPHY

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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. Any functionally equivalent instrumentation can be used.

1 INTRODUCTION

This procedure is used for the measurement of water in consumer products and is based on U.S. EPA Method 24/24A, Part 60, Title 40, CFR, Appendix A and ASTM D3792-91. Product samples are diluted with solvent and analyzed by gas chromatography. Any mention of brand names or commercial products is included as example only, and any equivalent product can be used.

2 SUMMARY OF METHOD

The samples of consumer products are prepared as a 1:10 wt./volume dilution in 1-Methoxy-2-propanol (MPA). After thorough mixing, the solution may require filtering to remove insoluble material. Some samples, particularly gels will require using the homogenizer unit to obtain sufficient surface area to determine the water. If under special circumstances another solvent is required, then all standards and controls are to be made with the same solvent and analyzed with those samples.

The diluted sample is then analyzed on a gas chromatograph equipped with a thermal conductivity detector to determine the water concentration in the sample. The data are reported as weight fraction of water in the product.

3 INTERFERENCES/LIMITATIONS

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

4 APPARATUS

4.1 Glass vials, 8 mL, with Teflon-lined screw caps (8 mL vial).

4.2 Volumetric Flasks, 10 mL.

4.3 Analytical Balance, capacity of 100 g x 0.00001 g (readability).

4.4 Rainin pipettors, 2.5 mL and 1.0 mL with pipette tips.

4.5 Small disposable pasteur pipettes with bulbs.

4.6 GC vials and caps.

4.7 Stainless steel column, 6’ X 1/8" o.d., packed with HayeSep C, 80/100 mesh, or any

analytical column capable of separating water from all possible interferences and showing a sharp, clean peak that will allow the analyst to achieve a desired detection limit.

4.8 Agilent or HP Gas Chromatograph (GC) configured with a Thermal Conductivity Detector (TCD).

4.8a. GC Parameters are as follows:

Initial Temperature:	80 °C
Initial Time:	1.20 min
Rate:	20.0 °C/min
Final Temperature:	210 °C
Final Time:	6.15 min
Injector Temperature:	250 °C
TCD Detector Temperature:	250 °C
TCD Polarity:	+
Column Flow Rate:	30 mL/min

5 REAGENTS AND MATERIALS

5.1 1-Methoxy-2-propanol, 99.5% (MPA).

5.2 Water: ASTM Type I.

5.3 Calibration standards: Five calibration standards are prepared by diluting 0.010, 0.100, 0.200, 0.500, and 1.00 g ASTM type I water to 10 mL with MPA.

5.4 Helium: Grade 5.

5.5 HPLC Grade Acetone.

5.6 Check Sample: stock solution is prepared by weighing 50 g each of acetone (99.9%) and water into a 200 mL volumetric flask and bringing to volume with MPA.

5.7 Trip Sample: stock solution is prepared by weighing 300 g of water, and 50 g each of NaCl (99.0%), acetone (99.9%), methanol (99.9%), and ethanol (200 proof) into a 500 mL volumetric flask.

6 PROCEDURE

6.1 The samples are prepared as 1:10 dilutions in MPA. Using a 1.0 mL pipette, weigh

to the nearest 0.00001 g a well mixed 1.0 mL aliquot of the product into the 10 mL volumetric flask. Record the weight in the dilution weight logbook. Bring to volume with MPA, mix well, homogenizing if necessary, and transfer to an appropriately labeled 8 mL vial and GC vial and cap both. A check sample and a trip sample are also prepared as 1:10 dilutions in MPA.

6.2 Calibration: A five-point linear regression calibration is made (See 5.3).

6.3 Transfer an aliquot of each standard into appropriately labeled GC vials and cap.

6.4 Transfer an aliquot of each sample, check, and trip sample into appropriately labeled GC vials and cap.

6.5 Aliquot MPA into an appropriately labeled GC vial and cap (MPA blank).

6.6 Place the vials in the autosampler in the following order: MPA blank, calibration standards, check sample, trip sample, and diluted samples. The check sample is run every tenth sample and at the end of the run.

6.7 In the GC ChemStation software, edit the SEQUENCE parameters appropriately.

6.8 Run the sequence.

7 QUALITY CONTROL

7.1 An MPA solvent blank must be analyzed for each batch of samples. The water concentration in the solvent blank must be less than 0.1% wt./volume.

7.2 A check sample (25% wt./vol. water) is run after the calibration, after every ten samples and at the end of the run. The result must fall within ± 3s of the control limits.

7.3 A trip sample of known concentration (60% water ±3%) is also analyzed.

7.4 LIMS assigns at least one duplicate sample for every sample set. Duplicate analysis should not have an absolute difference greater than ±3%.

7.4 The five-point calibration curve must have a correlation coefficient of greater than 0.98.

7.5 The LOD for the water analysis should be determined annually. The 1.0 mg/mL standard is used to determine the LOD for this method.

8 CALCULATIONS

The weight fraction of water in the product is calculated as follows:

$$\text{Weight Fraction Water} = \frac{\text{mg/ml } H_2O}{\text{dilution weight (g)}} \times 10^{-2}$$

9 REFERENCES

9.1 ASTM Method D3792-91, "Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" (EPA Method 24).

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

APPENDIX A

GC WATER PROCEDURE: OPERATION OF THE GC

1. GC/Water analysis is run on either a HP 5890 (5890) or an Agilent 7890 (7890) using injector A (front) and detector A (the TCD) or an Agilent 6890 (6890) using injector A (front) and detector B (TCD).

2. Preparation of Calibration Standards:

   Weigh into 10 mL volumetric flasks ASTM Type 1 water (from the Nanopure system) as follows:

1 mg/mL	0.01 g
10 mg/mL	0.10 g
20 mg/mL	0.20 g
50 mg/mL	0.50 g
100 mg/mL	1.00 g

   Bring to volume with MPA and store the individual standards in an appropriately labeled GC vial and 8 mL vial each.

3. Check Sample:

   A check sample of 25 mg/mL water is analyzed after the calibration, after every ten samples, and at the end of the run. A stock solution of 25% acetone/water in MPA is kept in the refrigerator. The check is prepared as a 1:10 dilution of the stock. Pipette 1.0 mL of the stock solution into a 10 mL volumetric and bring to volume with MPA. Store the check sample in an appropriately labeled GC vial and 8 mL vial. The water check stock solution is prepared by weighing 50 g each of acetone and water into a 200 mL volumetric flask and bringing to volume with MPA. Note: the water and acetone were weighed out in the preparation of the stock, so the concentration is already g/mL.

4. Trip Sample:

   A trip sample of known concentration is carried out with the procedure. The trip sample stock standard is stored in 20 mL vials and kept in the refrigerator. One is taken with the sample set. The trip sample is prepared as a 1:10 dilution of the stock. Pipette 1.0 mL of the stock solution into a 10 mL volumetric flask and bring to volume with MPA. The trip sample stock solution is prepared by weighing 300 g of water, and 50 g each of NaCl, acetone, methanol, and ethanol into a 500 mL volumetric flask.

5. Samples:

   Weigh a 1 mL aliquot of the sample into a 10 mL volumetric flask and bring to volume with MPA. Record the weight in the dilution weight logbook. If the sample does not dissolve, a vortexer or a homogenizer may be used to aid in the mixing of the sample dilution. If the dilution is not clear it may be filtered. Transfer the diluted sample into appropriately labeled GC vial and 8 mL vial and cap. These same dilutions are used for the Karl Fischer, Acetone/Alcohol, DCM, Siloxane, MEK, and Glycol analyses.

6. Using disposable pipettes transfer the MPA blank, standards, check, trip, and samples into appropriately labeled GC vials and cap if not already done.

7. Check that there is sufficient He (the carrier gas) for the run. The tank should be changed when the pressure regulator indicates 500 psi or less.

8. The GC conditions and settings are as follows:

	5890	**6890**	**7890**
Column:	Hayesep C 80/100 mesh, 6 ft x 1/8th in. o.d. stainless steel packed column		
Initial Oven Temperature:	80 ^{o}C		
Initial Time:	1.20 min		
Rate:	20.0 ^{o}C/min		
Final Temperature:	210 ^{o}C		
Final Time:	6.15 min		
Injector Temperature:	250 ^{o}C		
Detector Temperature:	250 ^{o}C		
TCD Polarity:	[+]	Negative Polarity not checked	
TCD Sensitivity:	Low	not applicable	
Data Rate:	5.00 Hz		20.0 Hz
Peak Width:	0.053 min	0.04 min	0.01 min
Column Flow Rate:	30 mL/min		
TCD Reference Flow Rate:	45 cc/min	15 mL/min	

9. Verify that you have loaded the water method in the system. In GC ChemStation, click on Method; then click on Load Method. The method used is **WATER**, so click on WATER.M to highlight it, and then click on OK.

10. Verify that the **WATER** sequence is loaded. Click on SEQUENCE, then click on WATER.S to highlight it, and then click on OK.

11. First enter your initials and the subdirectory for the data by clicking on Sequence, then Sequence Parameters and entering the information in the appropriate box. Enter in Subdirectory a data file using two digits each for year, month, and day

    e.g. 961016

    You should get a message that the Directory does not exist do you want to create it? Click on the Yes button. If a message does not come up, that directory already exist, so add a letter to the end of the directory name until you get the message

12. To edit the Sequence table, click on Sequence and then Sequence Table.

    Under Sample Name, enter the MPA blank, the five standards, the blank again, the check, the trip, and the samples. An MPA blank followed by the check is run after every ten samples and again at the end of the run. The method is WATER and the vial number corresponds to the position on the autosampler tray. Place sample vials in the autosampler in the following order: MPA blank, calibration standards, check standard, trip sample, and diluted samples.

    Each vial will have its own vial number, but the sequence number is just the line item number in the table. To run the blank and the check multiple times, just insert the vial number, it is not necessary to prepare a separate vial.

    Click on OK when done.

13. Check to be certain everything has been entered correctly by printing the sequence by clicking on Sequence and then Print Sequence. Make sure that vials in autosampler match the vial location in the sequence. If not make the necessary corrections and print out the sequence again. If everything seems correct then save the sequence by clicking on Sequence and then click on Save Sequence.

14. To start running the sequence click on Run Control and then click on Run Sequence.

15. The correlation coefficient for compounds present in the calibration must be greater than 0.98. If the calibration fails, the sequence is stopped and corrective action is implemented. Corrective action can include reanalyzing the calibration curve or making up a new dilution of the calibration curve and then reanalyzing.

16. After the sequence is complete, verify that the check sample recoveries are within control limits. If the check is not within the control limits, re-run the analysis for the affected samples. It may also be necessary to recalibrate the instrument and rerun the affected samples. Also indicate if there is anything detected in the blank. Print out the calibration curve for the standards.

17. Review the chromatograms. Check the MPA peak to be certain it is approximately the same height throughout the analysis. If a sample was misinjected, the problem will most likely show up in the MPA peak. Calculate the value for each analyte found by dividing the amount from the report (mg/mL) by the sample dilution weight.

18. Verify that the trip sample recovery is correct (60% water). The recovery for the trip sample should be within the error of the method (± 3%).

19. Note any problems in the lab notebook.

SOP REVISION HISTORY

DATE	VERSION	NOTES
May 16, 1996	1.0	Addition of trip samples to QC.
March 10, 1998	1.1	Adjusted document font to Times New Roman 12. Inserted appendix A formerly a stand-alone document.
January 4, 2003	1.2	Renumbered to new section number. Adjusted document font to Times New Roman 12. Modified calibration curve concentrations (changed 80ug/ml to 100ug/ml).
September 5, 2003	1.3	Corrected typographical errors. Corrected version enumeration.
June 19, 2007	1.4	Updated and corrected typographical errors.
August 19, 2010	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