



A Honeywell Company

## **Water in Liquid Hydrocarbons, and Heavy Hydrocarbons by Vaporizer, using Coulometric Titration**

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### **UOP Method 481-10**

#### **Scope**

This method is for determining the water content of liquid hydrocarbons (naphtha, gasoline, kerosene, diesel), or other petroleum products (sulfolane and other solvents) that are liquid at room temperature using coulometric Karl Fisher titration. The lower limit of quantitation for the titrator is 10 µg of water. This results in an applicable concentration range for a sample of 10 mg/kg (mass-ppm) to 2 mass-% water.

Heavy hydrocarbons (insoluble oils and waxes) and other hydrocarbons that are viscous or solid at room temperature can be accommodated using a vaporizer for determining dissolved trace water and is applicable to samples over a concentration range of 20 mg/kg to 2 mass-% water.

Samples containing less than 500 mg/kg of water can be collected in prepared dry bottles or syringes as described in the Appendix.

Other applications for moisture and common interferences are discussed in Notes 1 and 2.

#### **References**

ASTM Method D1364, "Water in Volatile Solvents (Karl Fischer Reagent Titration Method)," [www.astm.org](http://www.astm.org)

ASTM Method D6304, "Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration," [www.astm.org](http://www.astm.org)

UOP Method 163, "Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration," [www.astm.org](http://www.astm.org)

UOP Method 344, "Moisture in Hydrocarbon Streams Using an On-Line Analyzer," [www.astm.org](http://www.astm.org)

UOP Method 999, "Precision Statements in UOP Methods," [www.astm.org](http://www.astm.org)

#### **Outline of Method**

For liquid hydrocarbon samples, the sample is injected directly into a coulometric Karl Fischer titrator that determines micrograms of water. No standardization is required since 96,000 coulombs is

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| <p>IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).</p> |
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equivalent to 1/2 mole of water. Once prepared, the instrument can be used for repeated sample titrations without additional reagents. The concentration of water in the sample is calculated using the mass of the sample injected. This technique is described in *Procedure, Part A*.

For heavy hydrocarbon samples, a head-space analysis that carries volatilized water from a sample in a dry nitrogen stream to a Karl Fischer titration cell is used. The titration of the water in the nitrogen carrier gas operates as described in Part A. This technique is described in *Procedure, Part B*.

Samples containing less than 500 mg/kg water can be collected in prepared dry bottles or syringes. Dry bottle sampling is recommended since there is less opportunity for moisture contamination from the environment, and the integrity of the sample is preserved for a longer period of time. Syringe sampling, although more convenient, can only be used if the analysis is to be completed within two hours. These techniques are described in the *Appendix*.

## Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

*Balance*, readability 0.1-mg

*Beaker*, 150-mL, VWR, Cat. No. 89000-202

*Crimper*, Cosa Instruments, Cat. No. VABH06

*Desiccator*, plastic, VWR, Cat. No. 24987-026

*Hot plate / magnetic stirrer*, VWR, Cat. No. 12365-452, includes PTFE-coated stir bar

*Pipets*, volumetric transfer, Class A, 100-mL, VWR, Cat. No. 89045-088

*Pipet filler*, VWR, Cat. No. 53497-055

*Regulator*, nitrogen, two-stage, high purity, delivery pressure range 15-200 kPa (2-30 psi), Matheson, Model 3121-580

*Syringe*, glass, with PTFE plunger tip, 100- $\mu$ L, VWR, Cat. No. 60376-252

*Titration*, coulometric-amperometric, designed to perform titrations to pre-set endpoints with a polarizing current capable of maintaining approximately 1 V across two platinum electrodes and a sensitivity capable of indicating an endpoint based on a 50 mV change. The Mitsubishi, Model CA-200 with fritless cathode is satisfactory, Cosa Instruments, Cat. Nos. MC64917 and MC74917.

*Tweezers*, VWR, Cat. No. 63042-970

*Vaporizer*, Model VA-230, Cosa Instruments Cat. No. MC64930

## Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean double deionized or triple distilled, unless otherwise specified.

*Acetone* (2-propanone), 99.5% minimum purity, VWR, Cat. No. VW0330-3

*Cleaning pad*, synthetic, mild abrasive, Scotch-Brite™, Runco Office Supply, Cat. No. MMM-96

*Cleanser*, mild abrasive, Comet™, Runco Office Supply, Cat. No. PAG-02255

*Crimp cap with septum*, Cosa Instruments, Cat. No. VABH04 and VABH05, respectively

*Desiccant*, 8-mesh, indicating, VWR, Cat. No. 22891-040

*Hydrogen peroxide*, 30%, VWR, Cat. No. VW3742-1

*Karl Fischer reagent*, Aquamicon FLS, Cosa Instrument, Cat. No. MC02032 (see *Note 1*)

*Nitrogen*, 99.999% minimum purity

*Pipets*, disposable transfer, VWR, Cat. No. 16001-188

*Reference Standard (Part A)*, Hydranal Water Standard 0.10, Aldrich, Cat. No. 34847-40ML

*Reference Standard (Part B)*, Reference Material 8507 Mineral Oil, NIST

*Silicone rubber*, nominally 10 x 10 x 5 mm blocks, Cosa Instrument, Cat. No. 02170, to stopper syringe needle tips

*Sulfuric acid*, concentrated, 95-98%, VWR, Cat. No. VW6840-3

*Syringes*, disposable, all PP/PE, 3-, 5-, 10-, 20-, and 50-mL, VWR, Cat. Nos. 53548-002, -004, -006, -008, and -010, respectively, with needle, VWR, Cat. No. BD305187

*Tissue*, Kimwipes™, VWR, Cat. No. 21905-026

*Vials*, Cosa Instruments, Cat No. VABH03

*Water*, double deionized or triple distilled

*Water*, tap, warm

## Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of titration, and the equipment being used.

### Instrument Setup

The instrument should be set up as per manufacturer's specifications. General guidelines for operating conditions for the instrument referred to under *Apparatus* are shown in Tables 1 and 2. However, these conditions may be optimized to meet the user's specific needs/requirements.

### Sampling

Samples containing greater than 500 mg/kg water can be collected in glass screw-cap containers without special precautions. If a liquid hydrocarbon sample is expected to contain less than 500 mg/kg, collect the sample as described in the *Appendix*.

### Electrode Preparation and Cell Conditioning

Clean the double platinum electrode, initially and when the drift continues to exceed 0.15 µg/s with fresh titration solvent using the following procedure:

1. Use a mild abrasive cleanser to prepare a "paste" with warm tap water.
2. Load a wiper or a cleaning pad with the paste. Polish the platinum tips of the detector electrode with the paste and wiper or cleaning pad.
3. Rinse the residue off the electrode with warm tap water, then with deionized water.
  - If required sensitivity is not achieved with cleaning, the electrode tip can be immersed in a solution of equal parts of concentrated sulfuric acid and hydrogen peroxide in a small beaker and

stirred for approximately one hour or more to remove any residual organic coating on the platinum. Safety Caution: Great care should be taken with this acidic solution; work in a hood and use appropriate personal protection equipment.

4. Place the electrode in the titration cell. Pipet 100 mL of the coulometric titration solvent (Karl Fisher reagent) into the 250-mL titration cell. Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center. Condition the titration cell using the 100- $\mu$ L syringe to titrate a 10- $\mu$ L injection of water.
5. Allow the drift to stabilize to less than 0.15  $\mu$ g/s.
  - The electrode and titration cell must be properly conditioned to obtain reproducible and noise-free titration curves.
  - Condition the cell at the beginning of each day that samples are analyzed, as well as each time the titration solvent is replaced.
  - Replace the titration solvent when the solution becomes cloudy or the drift exceeds 0.15  $\mu$ g/s.

**Table 1**

**Typical Operating Conditions (Part A – Liquid Hydrocarbons)**

|                               | <b><u>Coulometric Titration</u></b> |
|-------------------------------|-------------------------------------|
| <b>Delay</b>                  | <b>10 seconds</b>                   |
| <b>Minimum titration time</b> | <b>1 minute</b>                     |
| <b>End sensitivity</b>        | <b>0.1 <math>\mu</math>g/s</b>      |

**Table 2**

**Typical Operating Conditions (Part B – Heavy Hydrocarbons)**

|                               | <b><u>Coulometric Titration</u></b> |
|-------------------------------|-------------------------------------|
| <b>Delay</b>                  | <b>1 minute</b>                     |
| <b>Minimum titration time</b> | <b>12 minutes</b>                   |
| <b>End sensitivity</b>        | <b>0.1 <math>\mu</math>g/s</b>      |
| <b>Vaporizer temperature</b>  | <b>180 °C</b>                       |
| <b>Nitrogen flow rate</b>     | <b>250 mL/min</b>                   |

**Instrument Performance Verification**

1. Verify the performance of the iodine generation (direct injection coulometric titration) by following the Part A procedure and titrating 1 gram of the *Reference Standard (Part A)*.
2. Verify the performance of the vaporizer by following the Part B procedure and titrating 3 grams of the *Reference Standard (Part B)*.
  - If the determined water concentration is not within 3% of the calculated theoretical value for either reference standard, replace electrolyte/titration solutions or adjust the titration parameters based on manufacturer recommendations.
  - The generating current for coulometric electrodes can vary. Experience gained in the titration of water reference standards will provide guidance in the choice of optimal settings for titration.

**Part A: Liquid Hydrocarbon Samples**

1. If not already filled, pipet 100 mL of the coulometric titration solvent (Karl Fisher reagent) into the 250-mL titration cell.
  - Replace the titration solvent when the solution becomes cloudy, or the drift (Step 2 below) exceeds 0.15  $\mu$ g/s. After replacing the titration solvent, condition the cell as described in *Electrode Preparation*.

2. Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center. Allow the drift reading of the solution to stabilize to less than 0.15  $\mu\text{g/s}$ .
3. Flush a disposable syringe (with needle) at least three times and draw an aliquot of sample for analysis. Quickly remove any liquid adhering to the outside of the needle with a tissue and stopper the tip of the needle with a small piece of silicone rubber.
  - The sample size needed is dependent on the expected water concentration. The optimum sample amount contains approximately 100  $\mu\text{g}$  of water. Use Table 3 as a guide in determining the sample amount needed.

**Table 3**  
**Sample Sizes Guidelines for Expected Water Content**

| <u>Expected Water<br/>Concentration, mg/kg</u> | <u>Sample Amount, g</u> |
|------------------------------------------------|-------------------------|
| 1 to 100                                       | 2 to 10                 |
| 100 to 500                                     | 1                       |
| 500 to 1000                                    | 0.5                     |
| 1000 to 2000                                   | 0.2                     |

4. Weigh the stoppered syringe plus sample to the nearest 0.1 mg.
5. Remove the silicone rubber stopper and inject the sample aliquot into the coulometric Karl Fischer titrator according to the manufacturer's instructions.
  - The needle tip is inserted directly above the level of the Karl Fischer reagent to ensure that the entire sample dissolves in the solution and does not adhere to the cell walls.
6. Replace the stopper and reweigh the stoppered syringe to the nearest 0.1 mg. Calculate the mass of the sample injected by difference and record.
7. Record the  $\mu\text{g}$  water present in the sample as indicated by the coulometric Karl Fischer titrator.
8. Calculate the water content (see *Calculations*).

### Part B: Heavy Hydrocarbon Samples

1. Place an empty vial on the balance and tare.
2. Transfer sample by disposable pipet into the vial using Table 4 as a guide and record the weight to the nearest 0.1 mg.
  - If the sample is solid or viscous at room temperature, warm the sample on a hot plate until fluid.
  - If an expected water concentration is not known, add approximately three grams of sample to the vial. After an approximate water concentration is determined, a more appropriate sample size is selected and the sample is reanalyzed to obtain a precise result.

**Table 4**  
**Sample Sizes Guidelines for Expected Water Content**

| <u>Expected Water<br/>Concentration, mg/kg</u> | <u>Sample Amount, g</u> |
|------------------------------------------------|-------------------------|
| 20 to 100                                      | 3                       |
| 100 to 500                                     | 1 to 2                  |
| 500 to 1000                                    | 0.5                     |
| >1000                                          | 0.1 to 0.2              |

3. Crimp cap tightly onto the vial.
4. Also prepare two “conditioning blank” vials, empty vials with crimped septum caps that are prepared the same day as the samples.
5. Turn on vaporizer and nitrogen gas and allow the temperature to stabilize with nitrogen flowing through the vaporizers warming chamber.
  - An empty vial with a crimped septum cap should be kept in the vaporizer when a sample is not present. The dual needle should be inserted in the vial to allow dry nitrogen to flow through the titration cell at all times.
6. If not already filled, pipet 100 mL of the coulometric titration solvent into the 250-mL titration cell.
  - Replace the titration solvent when the solution becomes cloudy, or the drift (Step 7 below) exceeds 0.15 µg/s. After replacing the titration solvent, condition the cell as described in *Electrode Preparation and Cell Conditioning*.
7. Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center. Allow the drift reading of the solution to stabilize to less than 0.15 µg/s with nitrogen flowing through the titration cell prior to starting any analysis.
8. Remove the empty vial from the vaporizer using tweezers and insert a conditioning blank.
  - The blank is performed in duplicate. The blank value should be within the range of 30-120 µg of water and duplicate values should agree within 5%.
9. Insert the sample vial into the vaporizer and puncture the septum with the dual needle.
10. Record the µg water generated for the sample as indicated by the coulometric titrator.
11. Calculate the water content (see *Calculations*).

## Calculations

Calculate the water concentration to the nearest mg/kg using Equation 1:

$$\text{Water, mg/kg} = \frac{A}{B} \quad (1)$$

where:

**A** = instrument reading, µg H<sub>2</sub>O

**B** = mass of sample, g

When the water concentration is greater than 2000 mg/kg (0.2 mass-%), calculate the water concentration to the nearest 0.01 mass-%, using Equation 2:

$$\text{Water, mass-\%} = \frac{A}{10^4 B} \quad (2)$$

where:

**A, B** = previously defined, Equation 1

**10<sup>4</sup>** = factor to convert mass-ppm to mass-%

## Notes

1. Common interferences include: aldehydes, ketones and mercaptans. Special Karl Fischer reagents may be purchased to allow for water determination in the presence of ketones and aldehydes. Such reagents include Aquamicon AU and Aquamicon CK, Cosa Instrument, Cat. Nos. MC02012 and MC02016, respectively.

Mercaptans oxidize to disulfides concurrently with the water determination. This gives a false high water content. The measured water concentration can be mathematically corrected for mercaptan if the mercaptan concentration is first determined by a separate method such as UOP Method 163, "Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration." Calculate the water, corrected for mercaptan interference, using Equation 3:

$$\text{Corrected water, mass-ppm} = \text{water, from Equation 1} - 0.281 S \quad (3)$$

where:

$S$  = mercaptan sulfur

$$0.281 = \frac{18}{(32)(2)} \quad (3a)$$

where:

$2$  = correction for the  $2 e^-$  oxidation of water,  
 $1 e^-$  oxidation of RSH

$18$  = molecular weight of water

$32$  = atomic mass of sulfur

Other interferences and their corrections are beyond the scope of this method, but may be available in the literature.

- ASTM Method D1364, "Water in Volatile Solvents (Karl Fischer Reagent Titration Method)," a volumetric Karl Fischer method, is generally used for samples containing greater than 2 mass-% water. Additional information on coulometric titration for water is available in ASTM Method D6304, "Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration." Since accurate measurement of water content in liquid hydrocarbons is primarily dependent on the ability to obtain and keep representative samples, the on-line technique described in UOP Method 344 is recommended, when applicable.

## Precision

Precision statements were determined using UOP Method 999.

### Repeatability and Site Precision, Liquid Hydrocarbons and Solvents

Samples containing less than 500 mg/kg of water were collected in dry bottles as described in the *Appendix*.

A nested design was carried out for determining water in three samples with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests on each sample each day. For Sample C, three tests were performed each day. The total number of tests was 28. The precision data are summarized in Table 5. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

### Repeatability and Site Precision, Heavy Hydrocarbons

A nested design was carried out for determining water in two samples with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests (for sample E) or three tests (for sample F) on each sample each day. The total number of tests was 20. The precision data are summarized in Table 6. Two tests performed by the same analyst on the same day should not

differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

**Table 5**  
**Repeatability and Site Precision, Water, mg/kg (mass-ppm)**

| <u>Sample</u> | <u>Mean</u> | <u>Repeatability</u>  |                             | <u>Site Precision</u> |                             |
|---------------|-------------|-----------------------|-----------------------------|-----------------------|-----------------------------|
|               |             | <u>Within-Day esd</u> | <u>Allowable Difference</u> | <u>Within-Lab esd</u> | <u>Allowable Difference</u> |
| A             | 16          | 0.3                   | 1                           | 0.6                   | 3                           |
| B             | 100         | 0.5                   | 2                           | 0.9                   | 3                           |
| C             | 979         | 4.2                   | 14                          | 4.9                   | 17                          |

**Table 6**  
**Repeatability and Site Precision, Heavy Hydrocarbons, Water, mg/kg (mass-ppm)**

| <u>Sample</u> | <u>Mean</u> | <u>Repeatability</u>  |                             | <u>Site Precision</u> |                             |
|---------------|-------------|-----------------------|-----------------------------|-----------------------|-----------------------------|
|               |             | <u>Within-Day esd</u> | <u>Allowable Difference</u> | <u>Within-Lab esd</u> | <u>Allowable Difference</u> |
| E             | 59          | 2.5                   | 8                           | 2.6                   | 8                           |
| F             | 210         | 3.4                   | 13                          | 5.3                   | 21                          |

The data in Tables 5 and 6 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

### **Reproducibility**

There is insufficient data to calculate the reproducibility of the test at this time.

### **Time for Analysis**

The elapsed time for one analysis is 2 hours. The labor requirement to prepare the coulometric titrator is 1.5 hours. The labor requirement/elapsed time for each analysis is 0.5 hour.

### **Suggested Suppliers**

Aldrich, Milwaukee, WI 53201 (414-438-3850) [www.sigma-aldrich.com](http://www.sigma-aldrich.com)

Cosa Instrument Corporation, 7125 North Loop East, Houston, TX 77028 (713-947-9591)  
[www.cosa-instrument.com](http://www.cosa-instrument.com)

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)  
[www.mathesontrigas.com](http://www.mathesontrigas.com)

NIST (National Institute of Standards and Technology), Office of Standard Reference Materials,  
Chemistry Building, Room B-311, 100 Bureau Drive, Gaithersburg, MD 20899 (301-975-6776)  
[www.nist.gov](http://www.nist.gov)

Runco Office Supply, 1655 Elmhurst Road, Elk Grove Village, IL 60007 (847-437-4300)  
[www.runcoonline.com](http://www.runcoonline.com)

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) [www.vwr.com](http://www.vwr.com)

## Appendix

### Sampling Procedures for Low Water Content Hydrocarbons (<500 mg/kg)

#### Scope

This appendix describes two sampling procedures for low water content samples: “dry bottle” and “syringe.” The procedures are designed to minimize environmental moisture contamination.

The dry bottle procedure is recommended since the integrity of the sample is preserved for a longer period of time. The syringe procedure may be used as long as the analysis will be completed within two hours of sampling. Due to increased opportunities for moisture contamination using the syringe sampling procedure, the dry bottle precision listed in Table 5 may not be achieved.

#### Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

The following apparatus are an addition or substitution to those listed in the body of the method.

*Connectors*, tee, polypropylene, 6.4-mm, VWR, Cat. No. 62860-063

*Drying tube*, for nitrogen stream, Fisher Scientific, Cat. No. 09-206

*Gloves*, thermal protection, VWR, Cat. No. 32932-270

*Needles*, metal hub, 100-mm, non-coring, VWR, Cat. No. 20068-600

*Oven*, drying, capable of operation at  $115 \pm 5^{\circ}\text{C}$

*Tubing*, Tygon™, 6.4-mm ID, VWR, Cat. No. 63009-174

*Wire*, copper, 18-gauge, for fastening rubber tubing to needles, VWR, Cat. No. 66248-040

#### Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

The following reagents and materials are an addition or substitution to those listed in the body of the method.

*Aluminum foil*, VWR, Cat. No. 29952-029

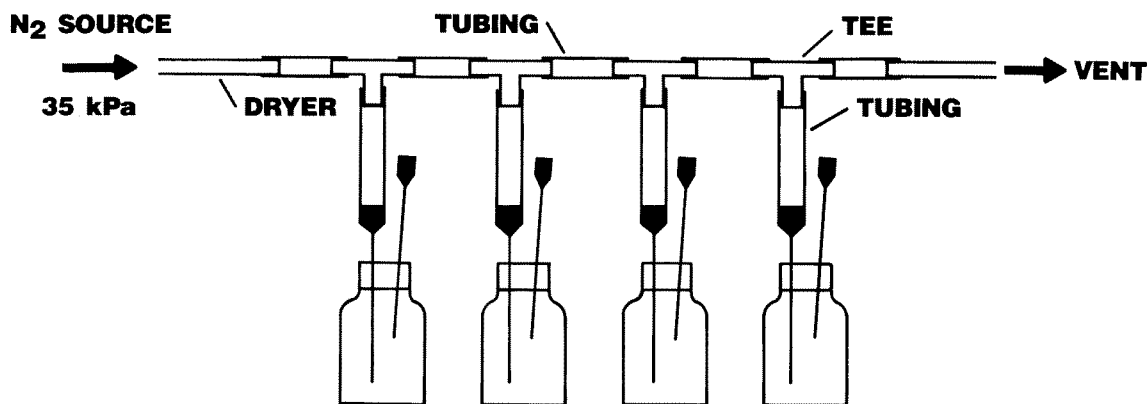
*Bottles*, serum, 60-mL, Wheaton, VWR, Cat. No. 16171-374, with rubber stoppers, VWR, Cat. No. 16171-660

*Nitrogen*, 99.999% minimum purity

#### Procedure, Dry Bottle

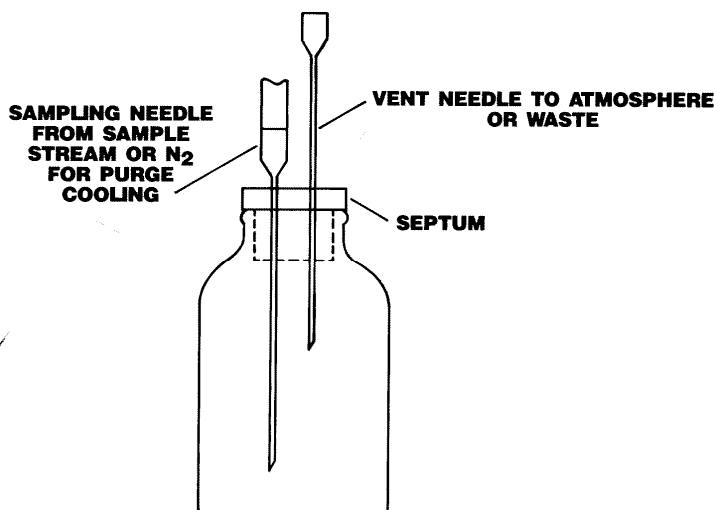
##### Bottle Preparation

1. Assemble the manifold for cooling the stoppered bottles under flowing dry nitrogen as shown in Figure A1.
2. Rinse the 60-mL serum bottles and needles with acetone. Dry them by purging with nitrogen.



**Figure A1**  
**Bottle Cooling Manifold**

3. Store the needles in a desiccator until needed.
4. Place the clean bottles in the drying oven overnight at  $115 \pm 5^\circ\text{C}$ .
5. Place the rubber septum in the oven thirty minutes before removing the serum bottles.
  - Rubber septums deteriorate rapidly at this temperature. Therefore, the length of time they can be safely left in the oven will vary with each septum batch.
6. Stopper the bottles with the septum while they are both still in the oven.
  - Heat resistant gloves should be worn while handling the hot dry bottles.
7. Remove the stoppered bottles from the oven and connect the bottles to a manifold that is continuously purged with dry nitrogen. Connect the bottles by inserting one of the 100-mm hypodermic needles, which is part of the manifold, through the septum of the bottles. Immediately insert another needle through the septum to serve as a vent.
  - See Figure A2 for bottle and needle configuration.



**Figure A2**  
**Bottle-Needle Configuration**

8. Purge the bottles for approximately 20 minutes, or until cool.
9. Remove the vent needles and allow the serum bottles to attain the manifold pressure of 35 kPa gauge (5 psig).
10. Remove the stoppered bottles from the manifold.
11. Cover the septums by wrapping with aluminum foil and store in a desiccator.
  - The aluminum foil prevents dirt and extraneous water, such as rain or snow, from contaminating the surface of the septum during field sampling. Alternatives such as a plastic bag or a box may be used to keep the bottles dry during transportation before and after sampling.

### **Plant Sampling**

1. Flush the plant sample tap for several minutes.
  - The sample tap must be fitted with an adapter to accept the hypodermic needle.
  - Collect all the flushed sample, Steps 1 through 9, and dispose of it in an environmentally safe manner according to local practices and regulations.
2. Stop the sample flow and attach a 100-mm hypodermic needle to the sample tap. Restart the sample flow at 50 mL/min or less and continue to flush with sample.
  - A minimum flush of one liter is recommended. Where sample is limited, the maximum available volume should be used for flushing.
3. Remove a 100-mm needle from the desiccator and connect a length of tubing to the hub of the needle to be used as the sample vent.
  - The tubing allows excess sample to be collected in a suitable container.
4. Withdraw the bottle from the desiccator and remove the aluminum foil.
  - Steps 5 through 11 must be done in rapid succession.
5. Insert the vent needle, with the tubing attached, through the septum into the bottle.
6. Adjust the position of the vent needle so that the bottle will be about 80% full before the sample flows out the vent.
7. Stop the sample stream momentarily and insert the sampling needle through the septum to a depth near the bottom of the bottle. Restart the sample stream.
  - See Figure A2 for diagram of bottle and needle configuration.
8. Flush the bottle with sample at a rate of approximately 50 mL/min or less.
  - Flushing the bottle with sample establishes an equilibrium between the inner walls of the sample bottle and the sample. A minimum flush of 150 mL is recommended. Where sample is limited, the maximum available volume should be used for flushing.
  - Collect and dispose of the excess sample flushed through the bottle in an environmentally safe manner according to local practices.
9. Stop the sample flow and quickly remove the vent and sampling needles.
10. Cover the septum with dry aluminum foil and store the bottle in a desiccator until time for analysis.
  - The sample must be analyzed as quickly as possible after sampling. Since the rubber septum will allow some water contamination of the sample to occur with time, it is recommended that samples be analyzed within 24 hours.

### Analysis

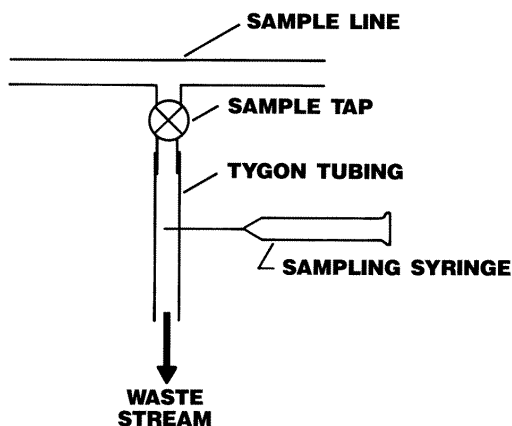
1. Fit a syringe with a 100-mm needle, remove the aluminum foil and insert the needle through the bottle septum.
  - The syringe size is dependent on the sample amount needed.
2. Flush the syringe at least three times and draw an aliquot of sample for analysis. Quickly remove any liquid adhering to the outside of the needle with a tissue and stopper the tip of the needle with a small piece of silicone rubber.
  - The sample size needed is dependent on the expected water concentration. The optimum sample amount contains from 100  $\mu\text{g}$  to 3 mg of water. Use Table 3 as a guide in determining the sample amount needed.
3. Weigh the stoppered syringe plus sample to the nearest 0.1 mg.
4. Remove the silicone rubber stopper and inject the sample aliquot into the coulometric Karl Fischer titrator according to the manufacturer's instructions.
  - The needle tip is inserted directly above the level of the Karl Fischer reagent to ensure that the entire sample dissolves in the solution and does not adhere to the cell walls.
5. Replace the stopper and reweigh the stoppered syringe to the nearest 0.1 mg. Calculate the mass of the sample injected by difference and record.
6. Record the  $\mu\text{g}$  water present in the sample as indicated by the coulometric Karl Fischer titrator.
7. Calculate the water content (see Calculations in the body of the method).

## Procedure, Syringe

### Sampling

1. Rinse sampling needles with acetone. Dry them by purging with nitrogen. Store in a desiccator until needed.
2. Flush the plant sample tap for several minutes.
3. Attach a Tygon sampling tube to the sample tap, and continue to flush with sample.
  - A minimum flush of one liter is recommended. Where sample is limited, the maximum available volume should be used for flushing.
4. Fit a sampling syringe with a 100-mm needle, and insert it into the sampling tubing.
  - The syringe size is dependent on the sample size needed, see Table 3 in the body of the method.
  - See Figure A3 for the sampling tubing and syringe needle arrangement.
5. Flush the syringe at least three times with flowing sample without removing the syringe needle from the sampling tubing, and then draw an aliquot of sample for analysis.
  - The sample size is dependent on the expected water concentration. The optimum sample amount contains from 100  $\mu\text{g}$  to 3 mg of water. Use Table 3 in the body of the method as a guide in determining the sample amount needed.
6. Withdraw the syringe needle from the sampling tubing and quickly stopper the tip of the needle with a small piece of silicone rubber. With a tissue, remove any liquid adhering to the outside of the needle.

- The sample aliquot must be analyzed within two hours of sampling since the silicone rubber-stoppered syringe will allow water contamination of the sample to occur with time.



**Figure A3**  
**Syringe Sampling Arrangement**

### Analysis

1. Weigh the stoppered syringe plus sample to the nearest 0.1 mg.
2. Remove the stopper and inject the sample aliquot into the coulometric Karl Fischer titrator according to the manufacturer's instructions.
  - The needle tip is inserted directly above the level of the Karl Fischer reagent to ensure that the entire sample dissolves in the solution and does not adhere to the cell walls.
3. Replace the stopper and reweigh the stoppered syringe to the nearest 0.1 mg. Calculate the mass of the sample injected by difference and record.
4. Record the  $\mu\text{g}$  water present in the sample as indicated by the coulometric Karl Fischer titrator.
5. Calculate the water content (see *Calculations* in the body of the method).

### Suggested Supplier

The following suggested supplier is an addition or substitution to that listed in the body of the method.

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) [www.fishersci.com](http://www.fishersci.com)