

## MOISTURE (Karl Fischer)

### PRINCIPLE

The starch sample is dispersed in methanol, stirred to extract water, and then titrated with standardized Karl Fischer reagent. The titration end point is detected electrically, and the water content of the sample is calculated from the titer and the water equivalent of the reagent.

### SCOPE

The procedure described here applies specifically to unmodified corn starch. With only minor modification, however, the method can be applied to modified and derivatized starches, syrups and sugars. Karl Fischer moisture data are precise, and agreement with oven results is within 1% relative (95% confidence limits).

### SPECIAL APPARATUS

1. Titrator: An automatic volumetric Karl Fischer titrator including a 20 mL buret
2. Weighing Funnels: Weighing funnels capable of holding up to three grams of starch. Weighing funnels with long stems (5 cm) help avoid getting sample on the walls of the titration vessel during sample insertion.

### REAGENTS

1. Karl Fischer Reagent (KFR): Single stabilized solution, preferably non-pyridine based. Pyridine-based reagents may also be used.
2. Methanol: Reagent grade, suitable for Karl Fischer analysis (<0.05% water)

### PROCEDURE

Instrument Preparation: Assemble and adjust the instrument as directed in the manufacturer's instruction manual. Fill the buret with Karl Fischer reagent. Add sufficient methanol to the titration vessel so that the electrode is immersed, taking

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care not to splash the sides of the vessel and start the stirrer (Note 1). Adjust the titration rate, end point adjustment and polarizing voltage according to the instrument manufacturer's instructions.

Start the titration and continue blanking the solvent until the titration vessel is anhydrous as indicated by little or no drift in the end point for a 60 second period, and then refill the buret (Note 2).

Standardization (Notes 3 and 4): Place 30-40 mL of purified water in a glass syringe and weigh the syringe and contents to the nearest 0.1 mg.

Prepare the titrator for use as outlined under Instrument Preparation. Remove the stopper from the titration vessel and insert the syringe into the opening. Inject the water into the titration vessel, taking care not to get water on the side walls of the titration vessel, and replace the stopper. Immediately reweigh the syringe to determine the amount of water delivered into the titration vessel. Start the titration, and when complete, note and record the titer. Refill the buret for the next titration.

Repeat the preceding procedure on the standardization with water until reproducible results (99-101% water recovery) are obtained, insuring stability of the system.

Calculate the water equivalent of the Karl Fischer reagent (see CALCULATIONS).

Sample Analysis: If necessary, grind sample completely through a laboratory cutting mill to 20 mesh or finer, taking precautions to prevent significant loss or gain of moisture, and mix thoroughly.

Perform all the following operations with dispatch. Place a quantity of sample calculated to consume between 6 and 15 mL of KFR (Note 5) in a dried weighing funnel with the aid of a small scoop or spatula and weigh to the nearest 0.1 mg. Remove the stopper from the titration vessel and insert the small end of the weighing funnel into the opening. Pour the sample into the titration vessel and replace the stopper. Reweigh the weighing funnel to determine the amount of

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sample delivered to the titration vessel. Start the titration, and when complete, note and record the titer. Refill the buret for the next titration.

**CALCULATIONS**

Water Equivalent (WE) of Karl Fischer Reagent (mg H<sub>2</sub>O/mL KFR)

$$= \frac{\text{Water Weight (mg)}}{\text{Water Titer (mL)}}$$

$$\text{Sample Moisture, \%} = \frac{\text{Sample Titer (mL)} \times \text{WE} \times 100}{\text{Sample Wt., (mg)}}$$

**NOTES AND PRECAUTIONS**

1. The electrode probe should be positioned so that it is not struck by the rotating stirring bar.
2. When the titration vessel becomes full, the vessel's contents should be removed and replaced according to the manufacturer's instructions. If new solvent is added, the titration vessel must again be rendered anhydrous.
3. Most Karl Fischer reagents are very stable. Nevertheless, standardization must be performed on each new lot of reagent, and daily thereafter, purging the buret with fresh reagent. If a problem occurs in obtaining a stable (reagent) water equivalent, moisture may be leaking into the system. Check the tubing and titration vessel seals.

The first titration or two after a prolonged shutdown (e.g., overnight) may be in error because of a change in the water equivalent of reagent standing in the buret. If the first value differs from subsequent values, it should be ignored.

4. The water equivalent may also be calculated using sodium tartrate dihydrate as the standard. Grind sodium tartrate dihydrate (Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>•2H<sub>2</sub>O) in a mortar to pass 48 mesh and blend. Determine the exact moisture content of each lot by drying 5 g for four hours in a vacuum oven at 150 °C (Theoretical value = 15.66%). Primary standard with a certified moisture content is available commercially.

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Place 900-1000 mg of sodium tartrate dihydrate (standard) into a dried weighing tube with the aid of a small scoop or spatula. Weigh the tube and contents accurately to the nearest 0.1 mg.

Prepare titrator for use as outlined under Instrument Preparation. Remove stopper from the titration vessel and insert the small end of the weighing tube in the opening. Pour the tartrate standard into the titration vessel and replace the stopper. Reweigh the weighing tube to determine the amount of tartrate standard delivered to the titration vessel. Start the titration, and when complete, note and record the titer. Refill the buret for the next titration.

Repeat the preceding procedure on the tartrate standard until reproducible results (Theoretical value =  $15.66 \pm 0.15\%$ ) are obtained, insuring stability of the system.

Water Equivalent (WE) of Karl Fischer Reagent (mg H<sub>2</sub>O/mL KFR)

$$= \frac{\text{Tartrate Wt. (mg)} \times \text{Tartrate Moisture (\%)}}{\text{Tartrate Titer (mL)} \times 100}$$

5. The water equivalent of the KFR is typically about 5 mg water per mL of reagent. Therefore 15 mL of reagent is equivalent to about 75 mg of water. The recommended sample size for starch containing about 10% water would be 0.75 g. Sample sizes exceeding 2.0 g are not recommended.