

MOISTURE (Karl Fischer)

PRINCIPLE

The syrup sample is dissolved in a mixture of methanol and formamide (50:50 v/v) 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 corn syrup. With only minor modification, however, the method can be applied to sugars, starches, feedstuffs and other corn products. 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. Transfer pipets: disposable, polyethylene, 3.5 mL draw

REAGENTS

1. Karl Fischer Reagent (KFR): Single stabilized solution, preferably non-pyridine based. Pyridine-based reagents may also be used.
2. Methanol and Formamide: Reagent grade, suitable for Karl Fischer analysis (<0.1% water). Mix equal volumes of methanol and formamide in quantities suitable for the number of analyses anticipated. Avoid prolonged storage of the mixed solvent system (more than one day) because the formamide begins to break down and release ammonia.

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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/formamide to the titration vessel so that the electrode is immersed, taking 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: Perform all the following operations with dispatch. Draw a quantity of sample calculated to consume between 6 and 15 mL of KFR (Note 5) into a clean disposable transfer pipet. If the syrup is extremely viscous, the end of the plastic transfer pipet may be cut off to give a bigger opening for drawing up the syrup (Note 6). Quickly dry the outside of the transfer pipet. The bulb end of a second plastic transfer pipet should be cut off and placed on the open end of the

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transfer pipet containing the syrup to prevent moisture contamination. Weigh the filled transfer pipet to the nearest 0.1 mg, transfer the contents directly to the titration vessel, and start the titration. Reweigh the empty transfer pipet and plastic bulb, and calculate the weight of the syrup delivered. When the titration is complete, note and record the titer. Refill the buret for the next titration.

CALCULATIONS

Water Equivalent (WE) of Karl Fischer Reagent (mg H₂O/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

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($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$) 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.

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_2O /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 a syrup containing about 25% water would be about 0.30 g.
6. For extremely viscous samples that will not go into a transfer pipet at all, use two spatulas to transfer the sample to the titration vessel. Scoop a suitable amount of syrup onto one spatula and tare this, along with a second clean spatula. Then use the second spatula to scrape the sample off the first spatula into the solvent. Reweigh both spatulas to determine the amount of syrup transferred to the titration vessel.