MOISTURE (Karl Fischer)

PRINCIPLE

The sample is dissolved in a solvent 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 to corn, corn starch, corn syrup, corn sugar (Note 1), steepwater and fuel alcohol. With only minor modifications, however, the method can be applied to 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

3. Weighing Funnels: Weighing funnels capable of holding up to six grams of sugar. Weighing funnels with long stems (5 cm) help avoid getting sample on the walls of the titration vessel during sample insertion.

4. Syringe: 100 mL, glass

5. Syringe: 20.0 mL, disposable, polyethylene. A 20 mL volumetric glass pipet is also acceptable.

6. Microliter syringe: 50 to 100 µL capacity

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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.

3. 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 solvent 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 2). 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 3).

Standardization (Notes 4 and 5): Place 30-40 mL of purified water in a glass syringe and weigh the syringe and contents to the nearest 0.1 mg. For fuel alcohol, draw 30-40 µL of purified water into 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

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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, Solids: Perform all the following operations with dispatch. 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.

Place a quantity of sample calculated to consume between 6 and 15 mL of KFR (Note 6) 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 sample delivered to the titration vessel. Start the titration, and when complete, note and record the titer. Refill the buret for the next titration.

Sample Analysis, Liquids: If the sample contains crystalline sugar, heat the closed sample container in hot water to dissolve the sugar, taking precautions to prevent any change in moisture content, and cool to room temperature. Blend all liquid samples thoroughly to insure homogeneity.

Draw a quantity of sample calculated to consume between 6 and 15 mL of KFR (Note 7) into a clean plastic 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. 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 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

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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.

Sample Analysis, Corn: Perform all the following operations with dispatch. Weigh accurately 16-18 g of well mixed whole corn and transfer to a clean dry milling vial containing three steel balls (Note 8). With a syringe, inject 20.0 mL of anhydrous methanol into the vial, cap, and seal the vial immediately. Place vial in mill and grind for 15 minutes. Remove the vial and cool to ambient temperature (Note 9). Remove the cap and fill a plastic transfer pipet immediately with the paste. Quickly dry the outside of the transfer pipet. The bulb end of a second disposable plastic transfer pipet should be cut off and placed on the open end of the transfer pipet containing the paste to prevent methanol evaporation. 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 paste aliquot delivered. When the titration is complete, note and record the titer. Refill the buret for the next titration.

Determine the blank titer of the methanol used in the milling procedure by introducing 20.0 mL of methanol into the syringe. Use the same pipet for all 20.0 mL additions of methanol. Weigh the filled syringe to the nearest 0.1 mg, transfer the contents directly to the titration vessel, and start the titration. Reweigh the empty syringe, and calculate the weight of the methanol delivered. When the titration is complete, note and record the titer. Repeat the procedure several times and use the average values of the weight and titer for the 20.0 mL of methanol added to the milling vial.

Sample Analysis, Fuel Alcohol:

Draw a quantity of sample calculated to consume 6-15 mL of Karl Fischer Reagent (Note 9) in a dry plastic transfer pipet. Quickly dry the outside of the transfer pipet with a dry lint-free wipe and place a cap over the pipet opening (Note 10). Weigh the filled pipet and cap to the nearest 0.1 mg, transfer the contents directly to the titration vessel, and start the titration. Reweigh the empty pipet and bulb, and calculate the weight of the sample delivered. When the titration is complete, note and record the titer. Refill the buret for the next titration. Repeat this process to obtain a replicate analysis

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CALCULATIONS

Water Equivalent (WE) of Karl Fischer Reagent (mg H_2O/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. Crude and refined sugars include crystalline dextrose (anhydrous and hydrate), crystalline fructose, dextrose solutions, partially or completely inverted sucrose, corn sugar liquor and corn sugar molasses (greens and/or hydrol).

2. The electrode probe should be positioned so that it is not struck by the rotating stirring bar.

3. 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.

4. 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.

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5. The water equivalent may also be calculated using sodium tartrate dihydrate as the standard. Grind sodium tartrate dihydrate ($Na_2C_4H_4O_6 \bullet 2H_2O$) 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 ± 0.15%) are obtained, insuring stability of the system.

   Water Equivalent (WE) of Karl Fischer Reagent (mg H_2O/mL KFR)

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

6. 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 sugar containing about 10% water would be about 0.750 grams. If the sugar is anhydrous crystalline dextrose or fructose, it is impossible to use a quantity of sample calculated to consume a large amount of KFR. Because typical moisture levels are so low, KFR with a water equivalent of 2 or 1 mg water per mL of reagent should be used and the sample size should be about 4 g.

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7. 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.

8. Because 16-18 g portions of whole corn may not be representative, duplicate determinations are recommended.

8. The sample may be cooled rapidly in a refrigerator or freezer as long as the sample doesn't become too cold. The sample vial must be at room temperature before opening.

9. The water equivalent of the Karl Fischer Reagent 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 fuel ethanol containing about 1% water would be about 3.0 g.

10. A cap for the disposable plastic pipets may be conveniently made by cutting the bulb end from another of the pipets at such a location as to allow the remaining part of the shaft to fit snugly over the tip end of the pipet being used for the sample. Such a cap could be used indefinitely.

METHOD HISTORY

Combined the Moisture (Karl Fisher) methods for Corn (A-13), Corn Starch (Unmodified) (B-36), Corn Syrup (E-46), Corn Sugar (F-32), Steepwater (J-44) and Fuel Ethanol (K-30) on 11-09-2010.

Corn, Moisture (Karl Fisher) (A-13), Date of Acceptance 10-20-1987, Revised 11-17-1992.

Corn Starch (Unmodified), Moisture (Karl Fisher) (B-36), Date of Acceptance 5-22-1961, Revised 11-17-1992.

Corn Syrup, Moisture (Karl Fisher) (E-46), Date of Acceptance 5-16-1966, Revised 11-17-1992.

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Corn Sugar, Moisture (Karl Fisher) (F-32), Date of Acceptance 5-16-1966, Revised 11-17-1992.

Steepwater, Moisture (Karl Fisher) (J-44), Date of Acceptance 5-16-1966, Revised 11-17-1992.

Fuel Ethanol, Moisture (Karl Fisher) (K-30), Date of Acceptance 4-11-1994.