MOISTURE (Karl Fischer)

PRINCIPLE

Whole corn is ground to a viscous paste in the presence of methanol in a sealed ball mill. An aliquot of the corn-methanol-water mixture is weighed and titrated with standardized Karl Fischer reagent. The titration end point is detected electrically, and the corn moisture value is calculated from the titer and the water equivalent of the reagent.

SCOPE

This method is applicable to corn of the various types and moisture contents found in commercial channels (Note 1).

SPECIAL APPARATUS

1. Titrator: An automatic volumetric Karl Fischer titrator including a 20 mL buret

2. Mill: A grinding mill equipped with a hardened steel grinding vial and three steel balls. A suitable type would be the MIXER-MILL Model 8000, equipped with hardened steel grinding vial Model 8001, and three steel balls (one 0.5 inch and two 0.25 inch), Spex Industries, Inc., 3880 Park Avenue, Metuchen, NJ 08841.

3. Syringe: 100 mL, glass

4. Transfer pipets: disposable, polyethylene, 3.5 mL draw

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

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)

MOISTURE (Karl Fischer) — continued

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, 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.

Prepare the titrator for use as outlined under Instrument Preparation. Remove 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. Weigh accurately 16-18 g of well mixed whole corn and transfer to a clean dry milling vial containing three steel balls (Note 6). 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 7). 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,

MOISTURE (Karl Fischer) — continued

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 (Note 8). 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.

CALCULATIONS

Water Equivalent (WE) of Karl Fischer Reagent (mg H_2)/mL)

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

$$\text{Sample Moisture, \%} = WE \times [\frac{T \times (C + M) - (A \times B)}{10 \times C \times A}]$$

where : WE = Reagent Water Equivalent, mg/mL

T = Sample Paste Titer, mL

C = Corn Sample Wt., g

M = Methanol Blank Wt., g

A = Sample Paste Aliquot Wt., g

B = Methanol Blank Titer, mL

NOTES AND PRECAUTIONS

1. If the sample moisture content is above 20%, it is necessary to predry prior to grinding. Fill previously dried and tared moisture dishes (with covers) with about 100 g of moist grain and weigh to the nearest 0.1 g. Place dishes (covers removed) in a warm well ventilated place (on top of a heated oven) protected from dust so that the grain dries reasonably fast and reaches

MOISTURE (Karl Fischer) — continued

an approximate air-dried condition in 14 to 24 hours. Reweigh the dishes and calculate the weight of moisture lost.

When moist corn samples are predried prior to Karl Fischer moisture measurement, calculating the moisture content of the original sample must include compensation for the predrying moisture loss.

2. Care should be taken not to splash solvent on the sides of the titration vessel. 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.

5. The water equivalent may also be calculated using sodium tartrate dihydrate as the standard. Grind sodium tartrate dihydrate ($Na_2C_4H_4O_6$ $2H_2O$) 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.

MOISTURE (Karl Fischer) — continued

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

7. 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.

8. While minimized by this procedure, exposure of grain or solvent to atmospheric moisture is not eliminated. All manipulations during such exposure should be performed with speed and care. Vials, balls and syringes should be thoroughly dried before use. Analysis of a second corn-methanol-water paste aliquot from a vial which has once been opened will give a higher moisture value unless the vial was closed immediately after removing the first aliquot. When all these precautions have been observed, at least three consecutive samples may be taken from one vial and titrated with excellent reproducibility.