MOISTURE (Karl Fischer, Buffered)

PRINCIPLE

The 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 to citric acid final product samples, both liquids and solids. 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 10 mL burette, or equivalent (Note 1).

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

3. Glassine weigh paper: reweigh the paper to perfect the transfer of the weight correctly; or use weighing funnels capable of holding up to six grams of sample. Funnels with long stems (5 cm) help to 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. Reagents formulated to consume 5 mg H_2O/mL of KFR are commonly used, but for samples with very low moisture content, reagents formulated to consume 1 or 2 mg H_2O/mL of KFR should be considered.

2. HYDRANAL® Buffer, or equivalent, recommended.

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3. Methanol and Formamide: Reagent grade, suitable for Karl Fischer analysis (<0.1% water). Mix equal volumes of low water 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.

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/formamide (Note 2) 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 3). 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 30-second period, and then refill the buret (Note 4).

Standardization (Notes 5 and 6): Place 0.030-0.040 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 several times on the standardization with water until reproducible results (99-101% water recovery) are obtained, insuring stability of the system. If reproducible results are not achieved within 2-3 attempts, modifications should be made.

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

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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.

Add solvent to the titration vessel (Note 7). Next add a quantity of HYDRANAL® buffer in mL approximately equal to the amount of citric acid sample to be added in grams (Note 8). For example, if a 4-g sample of citric acid is to be tested, then 4-5 mL of the buffer would be added to the solvent. Then blank the solvent-buffer solution. Place a quantity of sample calculated to consume between 2 and 10 mL of KFR (Note 9) in weigh paper or 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. Pour the sample into the titration vessel and replace the stopper. Reweigh the weigh paper or 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 crystals, heat the closed sample container in hot water to dissolve the crystals, taking precautions to prevent any change in moisture content, and cool to room temperature. Blend all liquid samples thoroughly to insure homogeneity.

Add solvent to the titration vessel. Next add a quantity of HYDRANAL® buffer in mL approximately equal to the amount of citric acid sample to be added in grams. For example, if a 4-g sample of citric acid solution is to be tested, then 4-5 mL of the buffer would be added to the solvent. Then blank the solvent-buffer solution. Draw a quantity of sample calculated to consume between 2 and 10 mL of KFR (Note 10) into a clean plastic transfer pipet. 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. Re-weigh the empty transfer pipet and plastic bulb, and calculate the weight of the

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sample delivered. When the titration is complete, note and record the titer. Refill the burette for the next titration.

CALCULATIONS

$$\text{Water Equivalent (WE) of Karl Fischer Reagent (mg } H_2O\text{/mL KFR)} = \frac{\text{Water Weight (mg)}}{\text{Water Titer (mL)}}$$

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

NOTES AND PRECAUTIONS

1. A Coulometric Karl Fischer Titrator might be more suitable for certain products.

2. Straight methanol may also be used as the solvent.

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

4. 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.

5. 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.

6. 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

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mortar to pass 48 mesh and blend unless grinding is not required by reagent manufacturer. 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 certified moisture content is available commercially.

Place 0.15-0.35 g 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)

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

7. For anhydrous citric acid samples, 50-60 mL of total solvent should be added to allow larger amounts of sample to dissolve.

8. The HYDRANAL® buffer may be used by itself as the solvent for the titration in place of either methanol/formamide or methanol for increased buffering capacity. This will add considerably, however, to the cost since HYDRANAL® buffer is more expensive than methanol or formamide.

9. For low moisture samples (500-1000 ppm H_2O), it is not possible to put enough sample into the titration vessel to consume between 2 and 10 mL of

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KFR. For such samples, the maximum amount of sample that can dissolve easily in the solvent system should be used.

10. The water equivalent of the KFR is typically about 5 mg water per mL of reagent. Therefore 10 mL of reagent is equivalent to about 50 mg of water. The recommended sample size for a sample containing 25% water would be about 0.20 g.

REFERENCE

Scholz, E., Karl Fischer Titration: Determination of Water, Springer-Verlag Publishers, Berlin, 1984.

METHOD HISTORY

Citric Acid, Moisture (Karl Fisher) (L-6), Date of Acceptance 9-08-2006.