Method 6.3 – C-molasses: moisture by Karl Fisher titration

1. Rationale

This method is applicable to C-molasses and is used to determine the dry solids or moisture content of a molasses sample as an alternative to the vacuum oven drying method (Method 6.2).

2. Principle

This method determines the total moisture in a sample electrochemically by titrating with two Karl Fischer (KF) reagents in the presence of a double platinum electrode to which a constant DC voltage is applied. The first reagent is Hydranal-Composite 5 which consists of iodine, sulphur dioxide and imidazole dissolved in diethylene glycol monoethyl ethter (DEGEE). The second acts as the solvent and is a mixture of formamide and methanol. In the presence of water, the sulphur dioxide is oxidised by the iodine to sulphuric acid, in accordance with the following equation.

$$SO_2 + I_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

The reaction is irreversible due to the presence of the solvent. When no more water is left in the reaction mixture, the free iodine acts as a depolariser to cause a measurable change in the electrode voltage.

3. Definitions

3.1 Moisture

Water represents the primary heat-volatile liquid in molasses and is referred to as moisture or water content.

3.2 Dry substance

Dry solids are the material remaining after drying a product to constant mass or for a specific period. The mass of dry solids can also be found by deducting the mass of the moisture as determined in a specific manner from the mass of the product.

4. Apparatus

4.1 Karl Fischer titrating apparatus

4.2 Micro-syringe: 25 µl

4.3 Self-indicating silica gel in a glass tube with cotton wool

4.4 Syringe: 5 cm^3

4.5 Analytical balance readable to 0.1 mg

5. Reagents

5.1 Hydranal-Composite 5 (Karl Fisher titrant)

The Hydranal-Composite 5 titrant is harmful to human health. Wear gloves and safety glasses during use.

5.2 Methanol

Methanol (CH_3OH) is a flammable solvent and is toxic to humans. Wear safety glasses to avoid contact with the eyes.

5.3 Distilled water

6. Procedure

6.1 Drying of the reaction jar

Introduce 60 cm^3 of methanol mixture to the jar and titrate to dryness. The solution must be stirred at a constant rate. This reading is determined when the pulse, which changes because of the reaction, lies between 90-100%. Stop the stirrer and swirl the jar to make sure that all the drops of methanol mixture on the sides of the jar are mixed into the bulk of the solution. Start the stirrer and titrate once again to dryness. Repeat this until the jar is completely dry.

6.2 Standardisation of the Karl Fischer Titrant

Fill a 25 µl syringe with distilled water and record the mass. Introduce approximately 0.025 g of distilled water into the reaction jar and reweigh the syringe. The difference in weight is recorded. Titrate to dryness and record the volume of Karl Fischer titrant used. Repeat with another portion of water. Calculate the water equivalent as indicated in 7.1. The duplicate determinations of the water equivalent should agree to within 0.05 unit.

The methanol solvent should not be used more than twice for the determination of the water equivalent

6.3 Blank

Open the dry reaction jar for 25 seconds, close and stir for 30 minutes to simulate the introduction and dissolution of a sample. Clear the volume reading. Titrate to dryness and record the volume of the titrant used. This is the blank volume.

6.4 Analysis

Weigh the sample syringe containing the well-mixed final molasses. Introduce approximately 0.1 - 0.2 g carefully into the titration jar, close and stir for 4 minutes. Reweigh the syringe and record the mass. Titrate to dryness and record the volume of titrant used. Duplicate samples may be introduced into the reagent jar without first emptying it. Duplicate determinations should agree within 0.25%.

7. Calculations

7.1 Standardisation of the Karl Fischer Titrant (water equivalent)

$$\text{mass of water} = M_1 - M_2$$

where M_1 ≡ mass of syringe before addition (g)
M_2 ≡ mass of syringe after addition (g)

$$\text{water equivalent} = \frac{\text{mass of water (g)} \times 1000}{\text{volume of reagent (cm}^3\text{)}}$$

7.2 Moisture in sample

mass of sample = $M_3 - M_4$

where M_3 ≡ mass of syringe before sample introduction (g)
M_4 ≡ mass of syringe after sample introduction (g)

corrected titre = volume KF titrant (cm^3) - blank volume (cm^3)

$$\text{moisture \% sample} = \frac{\text{titre (cm}^3\text{)} \times \text{water equivalent(factor, mg/cm}^3\text{)}}{\text{mass of sample (g)} \times 1000} \times 100$$

Express results as percentage to 2 decimal places.

8. Example

8.1 Determination of the water equivalent (factor)

mass of syringe before addition = 12.5031 g
mass of syringe after addition = 12.4786 g
mass of water = (12.5031 - 12.4786) g
= 0.0245 g

titre of Karl Fischer titrant = 5.64 cm^3

$$\text{water equivalent (factor)} = \frac{0.0245 \text{ g} \times 1000}{5.64 \text{ cm}^3}$$

= 4.344 g/cm^3

Repeat

mass of syringe before addition = 12.5012 g
mass of syringe after addition = 12.4785 g
mass of water = (12.5012 - 12.4785) g
= 0.0227 g

titre of Karl Fischer titrant = 5.27 cm^3

$$\text{water equivalent (factor)} = \frac{0.0227 \text{ g} \times 1000}{5.27 \text{ cm}^3}$$

= 4.307 g/cm^3

$$\text{average of the two factors} = \frac{(4.344 + 4.307) \text{ mg/cm}^3}{2}$$

= 4.326 g/cm^3

blank volume = 0.210 cm^3

8.2 Determination of the sample moisture

mass of syringe before sample introduction = 12.5946 g
mass of syringe after sample introduction = 12.4676 g
mass of sample = 0.1270 g

titre of Karl Fischer titrant = 3.874 cm^3
corrected titre = (3.874 - 0.210) cm^3
= 3.664 cm^3

moisture in sample = $\frac{3.664\ cm^3 \times 4.307\ mg/cm^3}{0.1270\ g \times 1000} \times 100$

= 12.43 %

9. References

ICUMSA (1994). Moisture in speciality sugars, molasses, cane raw sugars and syrups by the Karl Fischer procedure. *ICUMSA Methods Book*, GS4/7/3-12.

SMRI (2000). Determination of the moisture in final molasses using Karl Fischer titration method. *SMRI Test Methods,* TM030.