Method 8.3 – Refined sugar: moisture by Karl Fischer titration

1. Rationale

This method is applicable to refined sugar and speciality sugars and determines the total moisture content of the sample.

2. Principle

The moisture in sugar is present in three forms:

- free moisture contained on the surface of the crystal leaving the centrifugals, which is easily and quickly removed on drying,
- bound moisture contained in the glassy layer on the surface and in the re-entrant angles, and which is released slowly as the glass crystallizes, and
- inherent moisture included within the crystal structure and released only, in general, by grinding.

This method determines the total moisture electrochemically by titrating with two Karl Fischer 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 formamide. 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. Apparatus

3.1 Karl Fischer titrating apparatus

3.2 Micro-syringe: 25 μl

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

3.4 Sample tube

The tube should be 82 mm long and 23 mm ϕ with a rubber stopper through which there is fitted a thin long glass tube with a stopper. The capacity is such that the tube will hold a sample of 20 - 30 g.

3.5 Analytical balance readable to 0.0001 g

4. Reagents

4.1 Hydranal-Composite 5 (Karl Fisher titrant)

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

4.2 Formamide

Formamide is a flammable solvent, is toxic and corrosive to the eyes and respiratory tract. Only open in a fume cupboard while wearing gloves and safety glasses.

4.3 Methanol

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

4.4 Formamide:Methanol solvent

Prepare a sufficient quantity of a 1:1 mixture of formamide and methanol. This mixture is also available commercially.

4.5 Distilled water

5. Procedure

5.1 Drying of the reaction jar

Introduce 60 cm^3 of formamide: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 formamide: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.

5.2 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 6.1. The duplicate determinations of the water equivalent should agree to within 0.05 units.

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

5.3 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.

5.4 Analysis

Introduce 60 cm^3 of fresh formamide:methanol solvent to the reaction jar and dry according to the procedure indicated in 5.1. Weigh the sample tube containing the sugar to 0.001 g. Introduce the sugar to the jar (± 5 g), close and stir for 30 minutes. Reweigh the empty tube and record the mass. Clear the volume reading. Titrate to dryness, record the volume of titrant used and empty the jar. For subsequent samples only do steps 5.1 and 5.4.

6. Calculations

6.1 Standardisation of the Karl Fischer Titrant (water equivalent)

mass of water = $M_1 - M_2$

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

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

6.2 Moisture in sample

mass of sugar = $M_3 - M_4$

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

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

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

Report results in percentage to 3 decimal places.

7. Example

7.1 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 mg/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

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

= $4.307\ \text{mg/cm}^3$

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

= $4.326\ \text{mg/cm}^3$

blank volume = $0.21\ \text{cm}^3$

7.2 Determination of the sample moisture

mass of tube before sample introduction = 51.5512 g
mass of tube after sample introduction = 31.9704 g
mass of sugar = 19.5808 g

titre of Karl Fischer titrant = $1.42\ \text{cm}^3$
corrected titre = $(1.42 - 0.21)\ \text{cm}^3$
= $1.21\ \text{cm}^3$

moisture in sample = $\frac{1.21\ \text{cm}^3 \times 4.326\ \text{mg/cm}^3}{19.5808\ \text{g} \times 1000} \times 100$

= 0.027%

8. Precision

The tolerance associated with the analysis is ± 0.005 unit.

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 white sugar using Karl Fischer titration method. *SMRI Test Methods,* TM031.