2.8 Determination of water by the Karl Fischer method

The titrimetric determination of water by the Karl Fischer method depends on the reaction that takes place quantitatively between water and a reagent consisting of sulfur dioxide and iodine in anhydrous pyridine and usually methanol. The reaction is carried out in a suitable solvent such as methanol or acetic acid.

The reagents and solutions used in the determination of water by this method are sensitive to water and precautions must be taken throughout to prevent exposure to atmospheric moisture.

The titration vessel is fitted with two platinum electrodes, a gas inlet tube if needed, a stopper, which accommodates the burette tip, and a vent tube protected by a desiccant. The substance to be titrated is introduced through an inlet tube or side-arm, which can be closed by an airtight stopper. The Karl Fischer reagent TS is protected from light and stored in a bottle into which is fitted an automatic burette. The reagent is pumped into the burette by means of a hand bellows, the access of moisture being prevented by a suitable arrangement of desiccant tubes. Stirring is accomplished magnetically or by means of a stream of suitably dried nitrogen passed through the solution during the titration.

The end-point is obtained by using an electrical circuit composed of a microammeter, platinum electrodes, and a 1.5-V or 2-V battery connected across a variable resistance of about 2000 Ω. The resistance is adjusted so that an initial current passes through the platinum electrodes in series with a microammeter. After each addition of reagent, the pointer of the microammeter is deflected but quickly returns to its original position. At the end of the reaction a deflection is obtained that persists for 10-15 seconds. Alternatively, the end-point can also be determined by a voltametric method. A potential difference of 30-50 mV is applied to the platinum electrodes to serve as a constant polarizing current and the solution is titrated with the reagent. The potential difference is monitored by means of a microvoltmeter. The end-point is reached when the voltmeter indicates a stable decrease of voltage. In the voltametric method the end-point may also be obtained graphically by plotting the voltage versus the volume of the reagent, and establishing the beginning of the drop in potential.

Recommended procedure

Direct titration (Method A)

Add about 20 mL of dehydrated methanol R, unless otherwise specified in the monograph, to the titration vessel and titrate to the end-point with Karl Fischer reagent TS. Quickly transfer the specified quantity of substance, accurately weighed, to the titration vessel. Stir for 1 minute and titrate again to the end-point with Karl Fischer reagent TS.

Backtitration (Method B)

Add about 10 mL of dehydrated methanol R, unless otherwise specified in the monograph, to the titration vessel and titrate to the end-point with Karl Fischer reagent TS. Quickly transfer the specified quantity of substance, accurately weighed, to the titration vessel, followed by an accurately measured amount of Karl Fischer reagent TS, sufficient to give an excess of about 1 mL. Allow to stand protected from light for 1 minute or the time specified in the monograph, stirring from time to time.

Titrate the excess of Karl Fischer reagent TS to the end-point with dehydrated methanol R, to which has been added an accurately known amount of water, usually equivalent to about 2.5 mg/mL.