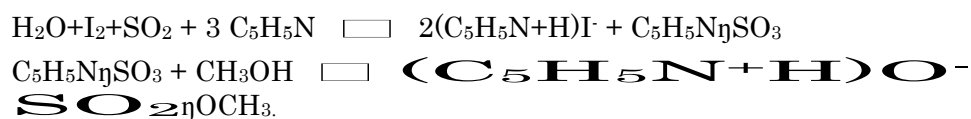


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Water Determination

(Karl Fischer Method)

The Water Determination Test (Karl Fischer Method) is designed to determine water content in substances, utilizing the quantitative reaction of water with iodine and sulfur dioxide in the presence of a lower alcohol such as methanol and an organic base such as pyridine, as shown in the following formulae:



There are two determination methods different in iodine-providing principle: the volumetric titration method and the coulometric titration method.

In the volumetric titration method, iodine required for reaction with water is previously dissolved in water determination TS, and water content is determined by measuring the amount of iodine consumed as a result of reaction with water in a sample.

In the coulometric titration method, first, iodine is produced by electrolysis of the reagent containing iodide ion, and then, the water content in a sample is determined by measuring the quantity of electricity which is required for the electrolysis (i.e., for the production of iodine), based on the quantitative reaction of the generated iodine with water.

Hereinafter in the Monographs, such a specification **■** not more than 4.0% (0.5 g, back titration) **≧** indicates that when determined by weighing about 0.5 g of the sample accurately and performing back titration, the water content is not more than 4.0% of the weight of the sample.

Method Volumetric titration

Apparatus Generally, the apparatus consists of an automatic burette, a back-titration flask, a stirrer, and an equipment for amperometric titration at constant voltage or potentiometric titration at constant current.

Because water determination TS is extremely hygroscopic, the titration apparatus should be protected from atmospheric moisture. Silica gel or calcium chloride for water determination is usually used for moisture protection.

Procedure As a rule, the titration of the sample with water determination TS should be performed at the same temperature as that at the standardization of the TS, while protecting from moisture.

The apparatus is equipped with a variable resistor in the circuit, and the resistor is adjusted to apply a definite voltage (mV) between a pair of platinum electrodes

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immersed in the solution to be titrated. The change in current (μA) is measured during the dropping of water determination TS (Amperometric titration at constant voltage). As titration continues, the abrupt change in current in the circuit occurs, but returns to the original state within several seconds. At the end of a titration, the change in current persists for a certain time (usually, longer than 30 seconds). The end point of titration is determined at this electric state.

Otherwise, by adjusting the resistor, a definite current is passed between the two platinum electrodes, and the change in potential (mV) is measured during dropping water determination TS (Potentiometric titration at constant current). With the progress of titration, the value indicated by the potentiometer in the circuit decreases suddenly from a polarization state of several hundreds (mV) to the nonpolarization state, but it returns to the original state within several seconds. At the end of titration, the non-polarization state persists for a certain time (usually, longer than 30 seconds). The end point of titration is determined when this electric state attains.

In the case of back titration, when the amperometric titration method is used at constant voltage, the needle of microammeter is out of scale while an excessive quantity of water determination TS remains. It returns rapidly to the original position when the titration reaches the end point. Similarly, when the potentiometric titration method at constant current is used, the needle of the millivoltmeter is at the original position while an excessive quantity of water determination TS remains. A definite voltage is applied when the titration reaches the end point.

Unless otherwise specified, the titration of water with water determination TS is performed by either of the methods below. Usually, the end point of the titration can be observed more clearly in the back titration method than in the direct titration method.

(1) Direct titration Unless otherwise specified, proceed as directed below.

Take 25ml of methanol for water determination in a dried titration flask, and titrate with water determination TS to the end point. Unless otherwise specified, weigh accurately a quantity of the sample containing 10 to 50 mg of water, transfer it quickly into the titration flask, and dissolve by stirring. Titrate the solution with water determination TS to the end point under vigorous stirring.

When the sample is insoluble in the solvent, powder the sample quickly, weigh a suitable amount of the sample accurately, and transfer it quickly into the titration vessel, stir the mixture for 30 minutes while protecting it from moisture. Perform a titration under vigorous stirring.

When the sample interferes with the Karl Fisher reaction, water in the sample can be removed by heating and under a stream of nitrogen gas, and introduced into the titration vessel by using a water-evaporation device.

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$$\text{Water(H}_2\text{O)} = \frac{\text{Volume(ml) of TS for Water Determination consumed} \times f \text{ (mg/mL)}}{\text{Weight of the sample(mg)}} \times 100(\%)$$

(2) Back titration Unless otherwise specified, proceed as directed below.

Take 20ml of methanol for water determination in the dried titration vessel, and titrate with water determination TS. Weigh accurately a suitable quantity of the sample containing 10–50 mg of water, transfer the sample quickly into the titration vessel, add an excessive and definite volume of water determination TS, stir for 30 min, protecting from atmospheric moisture, and then titrate the solution with Water–Methanol Standard Solution under vigorous stirring.

Water(H₂O)

$$= \frac{\left[\begin{array}{c} \text{Volume of water determination} \\ \text{TS added (ml)} \end{array} \right] \times f - \left[\begin{array}{c} \text{Volume of Water–Methanol Standards} \\ \text{Solution consumed (ml)} \end{array} \right] \times f'}{\text{Weight of sample (mg)}} \times 100 (\%),$$

Where f = the number of mg of water (H₂O) corresponding to 1 ml of water determination TS,

f' = the number of mg of water (H₂O) in 1 ml of Water–Methanol Standard Solution.

Method 2. Coulometric titration

Apparatus Usually, the apparatus is comprised of an electrolytic cell for iodine production, a stirrer, a titration flask, and a potentiometric titration system at constant current. The iodine production device is composed of an anode and a cathode, separated by a diaphragm. The anode is immersed in the anolyte solution for water determination and the cathode is immersed in the catholyte solution for water determination. Both electrodes are usually made of platinum-mesh.

Because water determination TS is extremely hygroscopic, the titration apparatus should be protected from atmospheric moisture. For this purpose, silica gel or calcium chloride for water determination is usually used.

Procedure Take a suitable volume of an anolyte for water determination in a titration vessel, immerse in this solution a pair of platinum electrodes for potentiometric titration at constant current. Then, immerse the iodide production system filled with a catholyte for water determination in the anolyte solution.

Switch on the electrolytic system and make the content of the titration vessel anhydrous. Next, take an accurately weighed amount of the sample containing 1–5 mg of water, add it quickly to the vessel, and dissolve by stirring. Perform the

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titration to the end point under vigorous stirring. When the sample is insoluble in the anolyte, powder it quickly, and add an accurately weighed amount of the sample to the vessel. After stirring the mixture for 5–30 minutes, while protecting from atmospheric moisture, perform the titration with vigorous stirring.

Determine the quantity of electricity (C) [electric current (A) \times time (s)] required for the production of iodine during the titration, and calculate the content (%) of the water in the sample by the formula below.

When the sample interferes with the Karl Fisher reaction, water in the sample can be removed by heating under a stream of nitrogen gas, and introduced into the titration vessel by using a water-evaporation device.