

KARL FISCHER ELECTROMETRIC TITRATION METHOD FOR DETERMINATION OF WATER CONTENT

Method WHO/M/7.R1
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1. Introduction

This method takes into consideration new types of Karl Fischer reagent, free of pyridine, and a two-component titration technique. The apparent pH of the pyridine-free KF reagent is adjusted to such a value that the titration endpoint is reached very quickly avoiding side reaction of the KF reagent leading to a poor end point

Usually, it is possible to determine water also in most samples containing carbonyl groups. But, if reactive carbonyl groups undergo side reactions even with the new KF reagent, then special reagents and titration procedures are available¹.

2. Outline of method

The sample is dispersed in an appropriate solvent and titrated with Karl Fischer reagent of known water equivalent.

3. Apparatus

Karl Fischer titration apparatus is available in various forms of equipment ranging from simple devices used for manually performed titration (see Fig. 2) to fully automated titration apparatus.

4. Reagents

*Karl Fischer reagent*² (KF reagent free of pyridine). This reagent is available in various forms:

- one-component system
- two-component system (separate solvent and titrating solutions)

¹ For additional information, consult the book "Karl Fischer Titration" by Eugen Scholz. (Springer-Verlag, Berlin 1984. English Edition ISBN 3-540-13734-3) or alternatively the free-of-charge publications from companies producing new KF reagents (free of pyridine).

² Karl Fischer reagents are nowadays prepared commercially and despite their high costs, are cheaper than making the solutions oneself, as this requires a lot of experience for obtaining reliable results.

For the determination of water in samples containing reactive carbonyl compounds, special two-component systems are available.

Sodium tartrate dihydrate. Water content 15.66%, for calibration of the KF reagent titre.

Methanol, anhydrous. If the methanol is not already anhydrous, dry it by distillation over magnesium turnings and a little iodine, or by fractionation through a 1.5 m rectifying column, and distil into a receiver protected from atmospheric moisture by a guard-tube. Methanol dried in this manner will contain not more than 0.3 mL water/L methanol. **Warning: dry methanol is very hygroscopic.**

*Standard solution of water*³. Alternatively, for calibration of the KF reagent titre, a standard solution of water in methanol (or in any other dry suitable solvent) could be used and prepared as follows:

Dry thoroughly in an oven a 100 mL volumetric flask and allow to cool in a desiccator. Fill the flask partly with anhydrous methanol (or any other suitable solvent). Add about 0.5 g of distilled water, weighed to the nearest 0.1 mg (m g) from a weighing pipette, make up to the mark with methanol (or any other suitable solvent) and mix thoroughly by shaking. This solution should be prepared immediately before use.

Nitrogen, dry. Supplied from a cylinder under pressure and dried by passing through a guard-tube filled with activated molecular sieve, or freshly activated silica gel or any other suitable desiccant, and then through a wash-bottle containing Karl Fischer reagent (equal volumes of solvent and titration solution in the case of a two-component system).

5. Procedure

5.1 Calibration of the Karl Fischer reagent or the titrating solution

5.1.1 Using sodium tartrate dihydrate

Turn on a slow stream of dry nitrogen, rinse the titration vessel by removing the stopper of the delivery port for a short time and transfer enough (10 to 25 mL depending on the size of the titration vessel) of dry methanol or any other suitable solvent or solvent solution in case of applying the two-component technique, to the vessel by means of either a pipette or a piston burette, so that the ends of the electrodes are covered.

The amount of solvent solution of a two-component system containing sulfur dioxide and a base should not be too small in order to obtain a high speed of reaction. Titrate with the Karl Fischer reagent or the titrating solution until a stable endpoint is obtained.

³ At present, standard solutions of water are commercially available. They contain a defined amount of water in such a solvent that the vapour pressures of water and solvent are equal to each other. So, these standard solutions may be used without a change of the water content during the multiple openings of the bottle.

Ignore the volume of the reagent used because this operation is intended to remove any moisture from the reaction vessel.

Transfer a sample of about 100-200 mg weighed to the nearest 0.1 mg (m mg) of sodium tartrate dihydrate **in a finely powdered form** to the titration vessel and dissolve by stirring. Then, titrate the solution with the Karl Fischer reagent or the titrating solution until a stable endpoint is obtained (V_t mL).

Calculate the water equivalent (WE) of the titrant (Karl Fischer reagent or titrating solution).

$$WE \text{ (mg water/mL titrant)} = \frac{\underline{m} \times 0.1500}{\underline{V}_t}$$

where m = mass (mg) of sodium tartrate dihydrate used
V_t = volume (mL) of titrant used for the titration.

Repeat the calibration procedure at least two times. Use the mean of the results as WE.

5.1.2 *Using a solution of water in a suitable solvent*

Transfer a volume of the anhydrous methanol or any other suitable solvent or solvent solution (10 to 25 mL depending on the size of the titration vessel) into the titration vessel by means of a pipette. Turn on a slow stream of nitrogen and titrate with the KF reagent or the titrating solution until a stable end point is obtained.

Ignore the volume of the reagent used up to this stage. This operation is intended to remove any moisture from the titration vessel. Transfer a further 10.0 mL of the methanol or any other suitable solvent used for the standard solution of water to the titration vessel and titrate as above with the KF reagent or titrating solution, noting the volume used (V_b mL).

Then add to the titration vessel 10.0 mL of the standard solution of water in methanol or in any suitable solvent and titrate again with the KF reagent or the titrating solution (V_t mL).

Calculate the water equivalent (WE) of the titrant (Karl Fischer reagent or titrating solution).

$$WE \text{ (mg water/mL titrant)} = \frac{\underline{m}}{10(\underline{V}_t - \underline{V}_b)}$$

where

m = mass (mg) of distilled water used in preparing 100 mL of standard solution of water in methanol or in any other suitable solvent.

V_t = volume (mL) of titrant used for the titration of the standard solution of water

\underline{V}_b = volume (mL) of titrant used for the titration of the 10 mL solvent.

Repeat the calibration procedure at least two times. Use the mean of the results as WE.

5.1.3 *Using commercially available standard solutions of water*

Proceed as described in section 5.1.2, paragraphs 1 and 2. Transfer an appropriate volume (\underline{V} mL, e.g., 5 mL) of the standard solution of water to the titration vessel and titrate with the KF reagent or titrating solution, noting the volume used (\underline{V}_t mL).

Calculate the water equivalent (WE) of the titrant (Karl Fischer reagent or titrating solution).

$$WE \text{ (mg water / ml titrant)} = \frac{\underline{V} \times C}{\underline{V}_t} \text{ where}$$

\underline{V} = volume (mL) of the standard solution of water

C = mg water/mL of the standard solution of water

\underline{V}_t = volume (mL) of titrant used for the titration.

Repeat the calibration procedure at least two times. Use the mean of the results as WE.

5.2 Analysis of sample

5.2.1 *Liquid samples*

Add a volume of dry methanol or any other suitable solvent or solvent solution (10 to 25 mL depending on the size of the titration vessel) to the titration vessel. Turn on a slow stream of nitrogen, switch on the current and pretitrate as described in section 5.1.1. Ignore the volume of reagent used. Immediately transfer the sample weighed by means of a weighing pipette to the nearest 0.1 mg (\underline{w} g) to the titration vessel.

The mass of sample depends on its expected water content and on the type of apparatus used. Titrate with the Karl Fischer reagent or the titrating solution. (Volume used = V_s).

5.2.2 *Solid samples readily soluble in the working medium*

Solid samples which are readily soluble in the working medium can be titrated immediately using the same procedure as described in section 5.2.1. Stir the sample with the solvent in the titration vessel until it dissolves and titrate with the Karl Fischer reagent or the titrating solution.

5.2.3 *Solid samples requesting a preliminary extraction*

Solid samples which are slightly soluble or insoluble in the working medium are, if appropriate, previously extracted by the following procedure:

Transfer the sample weighed to the nearest 0.1 mg (\underline{w} g) into a volumetric flask. The mass of the sample, the volume of the flask and the aliquot taken after extraction depend on the expected water content of the sample and the type of apparatus used.

Disperse in anhydrous methanol or solvent solution or any other suitable solvent taking all possible precautions to avoid contamination with atmospheric moisture. Make up to volume with the appropriate solvent and mix well.

Remove any moisture in the titration vessel as described in section 5.2.1. By means of a pipette, transfer an aliquot of this suspension containing an appropriate amount of water into the titration vessel and titrate with the Karl Fischer reagent or the titrating solution. (Volume used = V_s). Carry out a blank titration on a volume of the solvent used for extraction equal to that present in the aliquot of the sample solution. (Volume used = V_b).

6. Calculation

6.1 Liquid samples and solid samples readily soluble in the working medium

$$\text{Water content (g / kg)} = \frac{WE \times \underline{V}_s}{\underline{w}}$$

where

WE = water equivalent (mg/mL) (section 5.1)

\underline{V}_s = volume (mL) of KF reagent or titrating solution used (section 5.2.1 for liquid samples or 5.2.2 for solid samples readily soluble in the working medium)

\underline{w} = mass (g) of sample

6.2 Solid samples requesting a preliminary extraction

$$\text{Water content (g/kg)} = \frac{WE \times (\underline{V}_s - \underline{V}_b)}{\underline{w}}$$

where

WE = water equivalent (mg/mL) (section 5.1)

\underline{V}_s = volume (mL) of KF reagent or titrating solution used for titration of the aliquot (section 5.2.3)

\underline{V}_b = volume (mL) of KF reagent or titrating solution used for the blank titration

\underline{w} = mass (g) of sample in the aliquot

7. Successive titration

After one titration is finished another sample of the same kind is added to the same solution which acts as dehydrated working medium for the next determination. Thus several samples can be determined without pretitrating the solvent component each time. However, in the case of applying the two component technique, a deficiency of sulfur dioxide, amine and alcoholic solvent, (the essential ingredients of the solvent component), should be avoided. If necessary, additional solvent component is added which then must be pretitrated.

Emptying of the vessel is carried out by sucking out the content using a plastic bottle with a suction-pipe and whilst a stream of dry nitrogen passes through the vessel to avoid the penetration of atmospheric moisture.

Note 1: Examples for Karl Fischer Titration Systems:

- Fisher Scientific Automatic KF Titrimeter System, USA
- Harvard LTE, Turbotitrator, UK
- Hiranuma Aqv-5 Aquacounter, Japan
- Kyoto MKS-3p, Japan
- Metrohm 633 KF Titrator; 658 KF Processor; 701 KF Titrino, CH
- Mitsubishi CA-06, Japan
- Mettler DL 18 KF Titrator, CH
- Radiometer ETS 850; MTS 855, DK
- Schott TR 151; TR 152, D

Note 2: Examples for Karl Fischer Reagents:

- Baker: Reaquant
- Merck: KF solution pyridin-free
- Riedel de Haen: Hydranal
- etc.

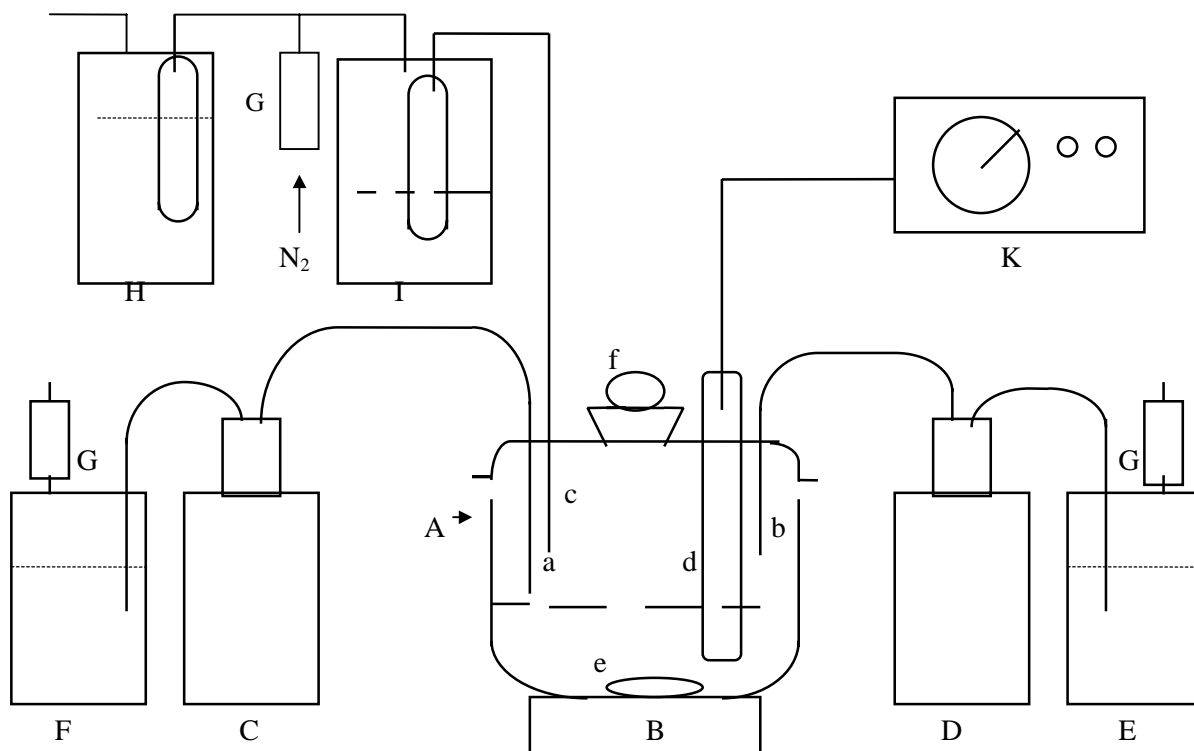


Fig. 2 Karl Fischer Titration System (schematic)

- A Titration vessel consisting of lower part and upper part, the latter fitted with several openings
- B Magnetic stirrer
- C Piston (motor) burette for titrant component
- D Piston (motor) burette for solvent component⁴
- E Reservoir for solvent component
- F Reservoir for titrant component
- G Guard-tube filled with activated molecular sieve or other desiccant
- H Wash bottle with conc. sulphuric acid
- I Wash bottle with Karl Fischer reagent (equal volumes of solvent and titrant component)
- K Electrometric indication circuit (bi-amperometrical indication)
- N₂ Nitrogen / protective gas supply
- a Burette tip of titrant burette
- b Burette tip of solvent burette
- c Inlet tube for nitrogen/protective gas
- d Platinum double-ring or two-pin electrode
- e Stirring bar
- f Delivery port for sample introduction.

⁴ Instead of using a motor burette "D", appropriate volumes of solvent component may be transferred to the titration vessel through the delivery port using a piston pipette