**[[1]](#footnote-1)MT 30.6 Water determination by Karl Fischer Method**

**SCOPE**

This method is intended for measuring the water content of plant protection products. Water determination by Karl Fischer method can be carried out by two different procedures:

* Volumetric titration ( section A )
* Coulometric titration ( section B )

Volumetric titration is preferably used for samples having a water content > 0.1 % (m/m). The coulometric titration is much more sensitive to water and can be used in a range of 0.001 % to 1 % water content. The coulometric method is recommended for water contents below 0.5 %.

These methods are applicable to all solid and liquid formulation types and materials compatible with the Karl Fischer reagents. Components interfering with the Karl Fischer reaction lead to false results and in most cases to higher values.

The methods are based on the use of automated titration systems.

**REASON FOR REVISION**

The method was editorially revised, the procedure for coulometric titration was included, a definition of ranges for sample weight was included and the description of equipment was revised.

MT 30.6 supersedes MT 30.5.

**A Volumetric titration**

**OUTLINE OF METHOD**

The volumetric determination of water described in this method is based on a titration of the sample in a water free solvent with an iodine containing titrant. The water of the sample is consumed by reacting with the reagents (Karl Fischer reaction). The endpoint of the titration is detected electro-potentiometrically. Interferences by side reactions consuming Karl Fischer reagent lead to higher results (Note 1).

The sample is dissolved or dispersed in a suitable solvent and titrated with an iodine containing solution, titrant, of known titer (water equivalent).

The optimum pH range for the volumetric Karl Fischer titration is weakly acidic (pH 5 - 7). Samples with pH values outside of this range should be buffered or neutralized using acid or base.

**REAGENTS**

Two types of Karl Fischer reagents are available:

*One-component systems:*

* Solvent: a suitable alcohol, e.g. methanol (Note 2)
* Titrant (titration solution): solution of sulfur dioxide, iodine and a base (e.g. imidazole) in a suitable alcohol

*Two-component systems:*

* Solvent: suitable alcohol containing sulfur dioxide and a base (e.g. imidazole) (Note 2)
* Titrant (titration solution): solution of iodine in a suitable alcohol

In addition, special reagents may be required in case of samples interfering with the Karl Fischer reagents, e.g. to prevent the formation of water during titration (Note 1).

**APPARATUS**

*Automated titration system for Karl Fischer titration*

*Burettes*, e.g. 10 ml

*Analytical balance,* with an accuracy of at least 0.1 mg

**PROCEDURE**

Ensure that the titration vessel is thoroughly protected against moisture from the air by using a drying tube containing fresh molecular sieve (Note 3). Carefully wipe clean the rim and the rubber seal of the opening where the sample is introduced. Condensation of solvent vapor at this position from the previous titration acts as trap for humidity and can slow down equilibration of the system during conditioning considerably. Introduce liquid samples using a syringe.

***(a) Pre-titration/Conditioning***

Operate the automatic titrator according to the instructions of the manufacturer.

Choose the suitable titration solution according to the expected water content of the sample (see table in section (c) below). Maximize the distance between the burette tip and the electrode.

To prepare the system for titration, fill a sufficient amount of the solvent (Notes 2 & 4) into an empty titration cell (approx. 40 ml for a 90 ml cell) to cover the platinum tips of the electrodes completely, close the vessel and start conditioning. Within this process, the titrant is added by the titrator system to consume any water present in the titration vessel and from the reagents until stable equilibrium conditions are achieved. Instable readings (e.g. caused by drift) may indicate high water residues in the vessel and / or penetration of atmospheric moisture.

Pre-titration/conditioning is required before each titration of a water standard (cf. section (b)) or titration of a sample (cf. section (c)).

In case the automated system works with blank subtraction rather than pre conditioning a blank determination is carried out and result obtained for the blank is subtracted from the value obtained for the test sample as described in section B Coulumetric titration.

***(b) Determination of the water equivalent of the titration solution***

Calibration is performed to determine the titer of the titrant and to ensure the tightness of the titration system. It should be performed on a regular basis and after changing the titrant or the electrode.

As calibration substance either water, a water standard solution in a suitable alcohol or crystalline sodium tartrate dihydrate can be used. The following masses are recommended to be weighed into the titration cell to the nearest 0.1 mg:

*(i) Water* distilled or de-ionised: 30 to 40 mg

*(ii) Water standard solution* (e.g. 1 %): 3 to 4 g

*(iii) Sodium tartrate dihydrate*: 0.20 to 0.25 g
 (water content: 15.66 ± 0.05 %)

Carry out the titration (bin [ml])

Calculate the amount of water (W) titrated.

For *(i)* $W = m\_{1}$

For *(ii)* $W =0.01 ∙ m\_{2}$ (Note 5)

For *(iii)* $W= \frac{15.66 ∙ m\_{3}}{100}$

Water equivalent of the titration solution: $c\_{E} = \frac{W ∙1000}{b}$

where:

*m1* = mass of water taken for the calibration

*m2* = mass of water standard solution taken for the calibration[g]

*m3* = mass of sodium tartrate dihydrate taken for the calibration [g]

*W* = mass of water in amount of calibration substance used [g]

cE = water equivalent of the titration solution [g/l]

*b* = volume required for the calibration [ml]

***(c) Determination***

Weigh (to the nearest 0.1 mg) at least the amount of the sample (ms in [g]) given below (Note 6) into the titration cell.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Expected water content of the sample [g/kg] | Mass of sample [g] | Expected mass of water [mg] | Titer of titrant [mg/ml] | Expected consumption of titrant [ml] |
|  |  |  |  |  |
| 0.5 | 2 | 1 | 2 | 0.5 |
| 1 | 1 | 1 | 2 | 0.5 |
| 2 | 0.5 | 1 | 2 | 0.5 |
| 5 | 0.2 | 1 | 2 | 0.5 |
| 10 | 1 | 10 | 5 | 2 |
| 20 | 0.5 | 10 | 5 | 2 |
| 50 | 0.25 | 12.5 | 5 | 2.5 |
| 100 | 0.25 | 25 | 5 | 5 |
| 200 | 0.25 | 50 | 5 | 10 |

Allow the sample to be dissolved or dispersed (Note 2) and carry out the titration (Vt in [ml]).

 ***(d) Calculation***

Calculate the amount of water in the sample by:

Water content = $\frac{V\_{t} ∙ c\_{E}}{m\_{s}} g/kg$

where:

cE = water equivalent of the titration solution [g/l]

Vt = volume required for the sample determination [ml]

*ms* = mass of sample taken [g]

(e) ***Calculation using blank subtraction***

Calculate the amount of water in the sample by:

Water content = $\frac{(V\_{t} - V\_{b}) ∙ c\_{E}}{m\_{s}} g/kg$

where:

cE = water equivalent of the titration solution [g/l]

Vt = volume required for the sample determination [ml]

Vb = volume required for the blank determination [ml]

*ms* = mass of sample taken [g]

**B Coulometric titration**

**OUTLINE OF METHOD**

The coulometric determination of water described is based on the *in-situ* electrolytic generation of the iodine needed for the Karl Fischer reaction. The iodine is continuously generated in the titration cell by electrochemical oxidation of iodide until a trace level of unreacted iodine is detected. The amount of iodine generated is calculated from the consumed amount of electricity in Coulomb.

Samples are injected through a septum into the system, whether directly or dissolved in a suitable solvent. There are also systems commercially available which use an oven to release the water from the sample and transfer it through a stream of dried gas (e.g. nitrogen) into the reaction vessel.

The titration cell consists of two compartments (anode and cathode) separated by an ion-permeable membrane. Two reagent solutions are required for the analysis. Anolyte and catholyte solutions are loaded into the separate compartments. The main compartment contains the anolyte solution containing an alcohol (e.g. methanol), base (imidazole), sulphur dioxide and iodine.

**REAGENTS**

*Karl Fischer anolyte reagent*

*Karl Fischer catholyte reagent*

**APPARATUS**

*Automatic titrator for Karl Fischer titration*

*Oven sampler (optional)*

*Analytical balance,* with an accuracy of at least 0.1 mg

**PROCEDURE**

***(a) Pre-titration***

Operate the coulometric titrator according to the instructions of the manufacturer.

Dispense enough reaction solution into the empty titration cell so that the platinum tips of the electrodes are completely immersed. Changing the reaction solution after each determination is not necessary.

***(b) Blank samples***

If the sample is dissolved in a suitable solvent the consumption of the solvent has to be determined before the analysis.

Inject the corresponding volume of pure solvent (as used for determination) into the system and titrate until the endpoint is reached.

If an oven sampler is used measure the water content of empty sample vials before analysis.

***(c) Determination***

The determination can be carried out by three different procedures depending on the type of the sample.

The mass of water injected into the reaction cell should correspond to 0.01 mg to 10 mg (for (i)) or 0.1 mg to 10 mg (for (ii) and (iii)).

*(i) Without dissolving/dispersing the sample*

Inject directly an amount of sample (ms in [mg]) into the reaction cell and carry out the water determination (Note 7).

*(ii) With dissolving the sample*

Weigh (to the nearest 1 mg) an amount of the sample (ms in [mg]) and dissolve in a suitable solvent. Carry out the water determination until the endpoint is reached.

*(iii) With an oven sampler*

Weigh (to the nearest 1 mg) an amount of sample (ms in [mg]) into the sample vial. The vial is hermetically sealed and placed in the turntable of the oven sampler. The oven temperature should be optimized that the sample releases all of its water without evaporating the sample itself. Carry out the water determination until the endpoint is reached.

 ***(d) Calculation***

The instrument measures the time and the electric current needed to reach the end point of the titration. The product (time multiplied with current) is directly proportional to the generated amount of iodine and so to the water amount present in the sample.

electric charge: $Q=t ∙I$

mass of iodine: $m\_{I} = \frac{M\_{I } ∙ Q}{z\_{I }∙ F}$

mass of water in the sample: $m\_{W}$ = $\frac{m\_{I} ∙ M\_{W}}{M\_{I}}$

where:

*Q* = electric charge (C)

*t* = time [s]

*I* = electric current (A)

*mI* = mass of iodine, generated by electrolysis [µg]

*MI* = molar mass of iodine (253.8 g/mol)

*zI* = equivalence number, number of electrons exchanged per ion (2)

*F* = Faraday constant (96485.33 C/mol)

*mW* = mass of water determined [µg])

*MW* = molecular mass of water (18.0 g/mol)

Calculate the amount of water (W):

For *(i):* W = *mW*

 Water content of the sample = $\frac{W}{m\_{s}} g/kg$

For *(ii)* W = *mW* - mb

 Water content of the sample = $\frac{ W ∙ V\_{D}}{m\_{s} ∙ V\_{I}} g/kg$

For *(iii)* W = *mW* - mb

 Water content of the sample = $\frac{W}{m\_{s}} g/kg$

where:

*mW =* mass of water determined [µg]

*ms =* mass of sample taken [mg]

*mb =* mass of water of blank determination, mean value of three determinations [µg]

*VD =* Volume of the solution [ml]

*VI =* Volume injected [ml]

**REPORTING OF RESULTS**

Report the Water content of the sample in [g/kg]. Report the applied method (volumetric or coulometric determination) and measurement conditions such as type of instrument, reagents, use of oven sampler etc.

*Note 1* Examples of components in the sample which can interfere with the Karl Fischer titration are given in the respective manuals of the suppliers for reagents and instruments.

*Note 2*  Instead of dissolving/dispersing the sample in the pure solvent, a mixture of the solvent with appropriate solubilisers may be used. The content of solvent should be at least 50 % (V/V).

*Note 3* The molecular sieve must be replaced in regular intervals or can be regenerated in an open container, e.g. in a drying oven at 300 °C for at least 4 hours.

*Note 4*Due to the fact that the solvent contains parts of the reaction components (SO2 and base), it has a limited water capacity. Therefore 20 ml of solvent can only titrate maximal 100 mg of water.

*Note 5* The factor 0.01 in this equation represents a water content of the water standard solution of 10 mg/g. Substitute this factor for the correct one, if the water content on the certificate for the specific batch of the water standard solution used is different from 10 mg/g

*Note 6* The given table is applicable to a 10 ml burette.

*Note 7* It is important that the sample is fully dissolved/dispersed in the reaction solution/solvent before starting the analysis. Where a sample is not fully dissolved or dispersed, the entrained portion of the water may not be completely determined due to incomplete extraction.

1. CIPAC method 20XX. Replaces MT 30.5, CIPAC Handbook J, p. 120. [↑](#footnote-ref-1)