Volumetric two-component ethanol based Karl Fischer Titration

DOC316.52.93129

1 to 100 mg of water in sample used

This document applies to volumetric Karl Fischer titrations determined with two-component ethanol based reagents. The white cells in the table below show the applicable applications.

		One-component		Two-component	
Methanol-based titrations	Titrant in the syringe	*Composite 5*	*Composite 2*	*Titrant 5*	*Titrant 2*
	Solvent in the beaker	*Methanol rapid*	*Methanol rapid*	*Solvent or Solvent CM*	*Solvent or Solvent CM*
	Available application	***1-component methanol C5***	***1-component methanol C2***	***2-component methanol T5***	***2-component methanol T2***
	Application note	***DOC316.52.93124***		***DOC316.52.93098***	
Methanol-free titrations	Titrant in the syringe	*Composite 5K*		Titrant 5E	Titrant 2E
	Solvent in the beaker	*Medium K or Working Medium K*		Solvent E	Solvent E
	Available application	***1-component C5K****		**2-component ethanol T5E**	**2-component ethanol T2E**
	Application note	***DOC316.52.93125***		**DOC316.52.93129**	

*used specially for samples containing aldehydes and ketones

Refer to the related application note to use other reagents.

Make sure not to mix titrant and solvent reagents of different systems.

1. Introduction

Water analysis is, without doubt, one of the most frequently performed laboratory analyses in various industries such as the oil, pharmaceutical and food industries. For many products, water content needs to be determined at every stage of the manufacturing process from raw materials to finished goods. The quality and/or the preservation of the final product depend on the amount of water present.

Excess levels of moisture will, for example, allow bacterial growth in food, decrease the performance of oils and lubricants, modify the density and the viscosity of paints and inks, disturb the texture of powdered products by forming conglomerates and impede the combustion properties of fuels.

Titrations and settings described in this document have been chosen to cover sample types commonly examined for their water content. They should be used as a starting point for specific samples and, if needed, optimized to suit analysis requirements.

2. Principle

The Karl Fischer technique is the most commonly used for moisture determination because of its rapidity, accuracy and ease of use. The sample is generally injected into the titration cell where an appropriate solvent dissolves it. The cell content is then titrated to complete dryness with a solution containing iodine. Volumetric Karl Fischer determination covers the range from 1 to 100 mg of water in the sample taken.

The titrant
The determination of water content is based on the oxidation of sulfur dioxide by iodine in the presence of water:

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4.$$

This chemical reaction is used in the Karl Fischer titration for quantitative water determination. The key component of the titrant is iodine. The key component of the solvent is sulfur dioxide. The key components of the titrant and solvent are dissolved in methanol.

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A base (noted RN, for example imidazole) and an alcohol (noted R-OH, for example methanol) are required for the reaction:

$$R\text{-}OH + SO_2 + RN \rightarrow (RNH)\bullet SO_3R$$

$$(RNH)\bullet SO_3R + I_2 + H_2O \rightarrow (RNH)\bullet SO_4R + 2(RNH)I$$

Recent studies have shown that oxidant molecules are not I_2 or $RN\bullet I_2$ but that I_2 partially splits up between I^- and RNI^+ into polar solvents and that it is the RNI^+ which reacts.

The solvent
The solvent or working medium must ensure the stoichiometry of the Karl Fischer reaction. It must be able to dissolve the sample and the products of the reaction. It must also enable the detection of the end point.

The indicator electrode
A double platinum electrode is used, polarized with an alternating square wave current. The detection of the end point of the titration is based on the detection of a small excess of iodine. This occurs when water is no longer present in the KF cell. That may be indicated visually by a slight yellow coloring of the working media.

3. Electrode and reagents

Electrode:	Combined Pt-Pt with temperature sensor: Intellical MTC695
Titrant:	Titrant 5E or Titrant 2E for volumetric two-component Karl Fischer titrations
Working medium:	Solvent E and chloroform
Standard:	Standard 5.00

Ethanol

Note: *For optimal results, the use of Hydranal® reagents is recommended.*

Safety considerations: *Reagents used for Karl Fischer titrations have to be handled carefully due to the chemical exposure hazard. Please read the MSDS document related to each chemical and adapt protective equipment accordingly (e.g. glasses, gloves, fume hood, white jacket, etc.)*

4. Karl Fischer titration: Key points

4.1. Guideline for titrations

Step 1: Titrant selection: The estimation of the amount of water present in the sample conditions the nature of the required titrant to optimize the titration in terms of time and accuracy.

For example:

- A Titrant 2E can trap 2.00 mg of water per mL of titrant (± 0.02 mg/mL) and is used for small amounts of water
- A Titrant 5E can trap 5.00 mg of water per mL of titrant (± 0.05 mg/mL) and is used for larger amounts of water

Step 2: Determination of the amount of sample: The amount of sample taken depends on the expected amount of water. The manufacturer recommends the use of less than 20 g of sample. Also, the injected sample must add at least 1 mg of water into the cell.

Step 3: Solvent determination (nature and mix ratio): Depending on the nature of the sample, select the most appropriate solvent. The role of the solvent is to contribute to the chemical reaction and to ensure the sample is releasing all its moisture content. Most liquid samples dissolve in ethanol. To determine the total amount of water, the sample must dissolve completely. Other solvents can be added to ethanol in specific proportions to liberate the water more efficiently. For example, chloroform is a good solvent for fats, and formamide improves the solubility of polar substances. Ethanol should always be present in the solvent in a proportion not lower than 25%. Otherwise unknown stoichiometric ratios will occur for the KF reaction.

Step 4: Frequency of solvent renewal: This parameter depends on the nature of the sample itself. The number of possible titrations using the same solvent has to be experimentally determined. Successive titrations with the same solvent are possible up to the drift of the measurements caused by the pollution of the cell.

4.2. Sampling, storage and sample introduction

Sampling depends on the nature of the sample but for moisture determination, handling has to exclude moisture absorption or desorption. Atmospheric moisture can affect the accuracy of the result.

Moisture determination of the sample has to be done as soon as possible after sampling. In the case of storage, keep the sample in a tightly sealed bottle.

The optimal accuracy on the measurement is obtained using the back weighing technique. The sample and the vessel (e.g. plastic or glass syringe for liquid samples or weighing boat for solid samples) are weighed before the introduction of the sample into the cell and the empty vessel is weighed again after sample introduction. The weight obtained by the difference of the two will be used for further calculations.

For liquid samples: Adapted sampling steps to prevent atmospheric moisture absorption have to be considered, especially for low water content sample.

For solid samples: They can be directly introduced into the cell quickly after being weighed, to limit atmospheric exposure.

The table that follows gives sample weights based on the expected water content and the selected titrants:

Expected water content (%)	Sample weight (g)	
	With titrant concentration: 5 mg/mL	With titrant concentration: 2 mg/mL
100	< 0.02	-
10	0.05 – 0.20	0.02 – 0.08
1	0.5 – 2.0	0.2 – 0.8
0.1	5 – 20	2 – 8
0.01	-	20

4.3. Analysis steps

Refer to the user manual for additional information.

1. Fill the cell with the appropriate solvent in such a way that both the bottom of the electrode and the anti-diffusion tip are properly immersed in the solvent. An indication mark on the cell helps you to add the minimum volume required.

   The relative positions of the electrode and the anti-diffusion tip in the cell are crucial to achieve optimum results. The height between the bottom of the electrode and the bottom of the cell is defined by the supplied Karl Fischer white Teflon® conical adapter. The correct positioning of the anti-diffusion tip is defined by the conical adapter pre-assembled on the tube. It is highly recommended not to modify these settings. Refer to the user manual for additional information about the installation.

2. Launch the application. Cell conditioning begins and any moisture present in the cell is removed.
3. Prepare the sample and weigh both the sample and the sample container.
4. When required, introduce the sample into the cell and start the titration.

   Tips:
   - Avoid spills onto the cell walls.
   - When using a syringe equipped with a needle for introducing the sample, put the needle directly into the working medium to inject the sample. This makes sure that the entire sample is injected into the working medium and none is lost on the cell walls or electrode. Do not rinse the syringe by pumping back some solvent.

5. Weigh the empty sampling container and, by difference, determine the exact weight of the sample injected into the KF cell.
6. At the end of the titration and when prompted, enter the exact weight of the sample calculated in Step 5.

4.4. Recommendations for settings modifications

If needed, adapt the following parameters to optimize the titration to make it suit the analysis requirements.

- **Name of the sample:** With "?" the sample will be automatically incremented with a number for each analysis
- **Stirring:** An efficient stirring of the titration cell is crucial to have a homogeneous solution and avoid over-titration. Increase the speed until a vortex occurs without creating any bubbles. Make sure that both the titrant addition anti-diffusion tip and the PtPt electrode wires are kept immersed.
- **Delay before titration:** The time of stirring before the beginning of the titration helps to extract the water from the sample and has to be adjusted for each sample to increase the repeatability and accuracy of the measurement.
- **Drift threshold:** This value is set at 50 µg/min by default, but can be adjusted with regards to the level of humidity surrounding the titrator.
- **Minimum and Maximum titration times:** The minimum titration time setting avoids under estimation of the water content. The maximum titration time setting avoids taking into account any side reactions after the true determination of water content.

5. Hardware configuration

The KF1121 titrator is dedicated to the determination of moisture in different samples. It integrates automatic moisture drift compensation to avoid moisture drift errors that might cause a deviation from the true measurement. This instrument is equipped with a specific water tight cell, an MTC695 electrode installed onto the probe holder with a specific electrode adaptor, an addition tip equipped with an anti-diffusion tip, a tube to remove the cell content and a removable watertight cap.

To reinforce the repeatability and the accuracy of the measurements, the position of each element (electrode and addition tip) has been carefully defined and no modifications are required.

Depending on the environmental relative humidity conditions, it is recommended to replace the molecular sieve in the desiccant tubes with a fresh/dry one as frequently as required. This will prevent any moisture contamination of the measuring setup (titrant bottle, solvent bottle and KF cell). It is advised to use silica gel crystals which act as a visual indicator.

Titrations and calibrations are performed using a 5 mL syringe.

6. Titrant calibration with Standard 5.00

To increase the accuracy of the measurement of moisture determination of the sample, it is recommended to perform a calibration of the titrant every day. When titrations are performed in very wet conditions, a calibration can be performed twice a day. Always perform a calibration for a new titrant installation.

6.1. Procedure

Standard 5.0 is used as a standard for volumetric Karl Fischer titration: nominal concentration of ≈5.00 mg/ml water corresponds to ≈5.8 mg/g at 20 °C (refer to analysis report from the supplier for an accurate value).

Standard 5.0 is added using a 2.5 mL glass syringe.

The amount of standard should be estimated so that the total volume of the syringe is added.

6.2. Settings

The detection of the end point of the titration is based on the detection of an excess of iodine based on the following settings: End Point at 200 mV and current at 20 µA.

At the end of the titrant calibration the concentration of the titrant is calculated and expressed in mg/mL. The saved value (real concentration) will be used for moisture determination.

6.3. Calibration of Titrant 2E

6.3.1. Standard and procedure

Standard: When a 2 mg H_2O/mL titrant is used in a 5 mL syringe, add exactly 1 mL Standard 5.00.

6.3.2. Settings

Name	Default parameters	Units
Application		
Application name	2-component ethanol T2E	
Advisable syringe	5 mL (Hamilton)	
Electrode		
Type	mV	
Recommended electrode	MTC695	
Current (titrant calibration)*	20	[µA]
Titrant: KF T2 2 mg/mL		
Name	KF T2E	
Real concentration	2.000	[mg/L]
KF T2 2 mg/mL method : Titrant calibration		
Active	Yes	
Calibration frequency	1	[Day(s)]
Stirring speed	25	[%]
Injection autodetect	No	
Proportionnal band*	450	mV
Drift threshold	50	[µg/min]
Min. titration duration	30	[s]
Max. titration duration	300	[s]
Min. titrant conc.	1.5	[mg/L]
Max. titrant conc.	2.1	[mg/L]
Standard name	Standard 5.00	
Standard amount	0.8400	[g]
Min. amount	0	[g]
Max. amount	5	[g]
Concentration**	0.58	[%]

* Do not change this parameter in Expert mode. The parameter was specially adapted for this application.
** Edit and modify the value of the standard concentration based on the value in the analysis report from the supplier.

6.4. Calibration of Titrant 5E

6.4.1. Standard and procedure

Standard: When a 5 mg H_2O/mL titrant is used in a 5 mL-syringe, add exactly 2.5 mL Standard 5.00.

6.4.2. Settings

Name	Default parameters	Units
Application		
Application name	2-component ethanol T5E	
Advisable syringe	5 mL (Hamilton)	
Electrode		
Type	mV	
Recommended electrode	MTC695	
Current (titrant calibration)*	20	[µA]
Titrant: KF T5 5 mg/mL		
Name	KF T5E	
Real concentration	5.000	[mg/L]
KF T5 5 mg/mL method: Titrant calibration		
Active	Yes	
Calibration frequency	1	[Day(s)]
Stirring speed	25	[%]
Injection autodetect	No	
Proportionnal band*	450	mV
Drift threshold	50	[µg/min]
Min. titration duration	30	[s]
Max. titration duration	300	[s]
Min. titrant conc.	3.8	[mg/L]
Max. titrant conc.	5.1	[mg/L]
Standard name	Standard 5.00	
Standard amount	2	[g]
Min. amount	0	[g]
Max. amount	5	[g]
Concentration**	0.58	[%]

* Do not change this parameter in Expert mode. The parameter is specially adapted for this application.
** Edit and modify the value of the standard concentration based on the value in the analysis report from the supplier.

7. Moisture determination with 2-component ethanol T2E

7.1. Principle

Motor oils contain compounds which are slightly soluble in ethanol. The addition of chloroform makes solubility better. Chloroform is a good solvent for motor oils and is used together with ethanol. The ethanol content must be at least 25%.

Waste motor oils can cause special problems because they contain metallic particles in suspension and different residues, and because the water is frequently non-homogeneously distributed. A solvent mixture with ethanol and chloroform is recommened for this product.

7.2. Reagents

Titrant: Titrant 2E
Working medium: 20 mL Solvent E + 20 mL chloroform

7.3. Procedure

The sample is injected using a plastic syringe with a needle. The actual weight is determined from the difference between the full and empty vessel.

7.4. Settings

Name	Default parameters	Units
Application		
Application name	2-component ethanol T2E	
Advisable syringe	5 mL (Hamilton)	
Sample		
Name	Sample ? *	
Amount	4.5000	[g]
QC		
Name	QC Sample	
Electrode		
Type	mV	
Recommended electrode	MTC695	
Current (sample analysis)**	20	[µA]
Titrant: KF T2 2 mg/mL		
Name	KF T2E	
Real concentration	2.000	[mg/L]
Method : KF titration		
Stirring speed	25	[%]
Delay	0	[s]
Injection autodetect	No	
Proportionnal band**	450	mV
Drift threshold	50	[µg/min]
Min. titration duration	30	[s]
Max. titration duration	300	[s]
Result 1 (R1) name	Water content	
R1 hide	No	
R1 min.	0	[%]
R1 max.	100	[%]
R1 QC min.	0	[%]
R1 QC max.	100	[%]

* "?" in the name, indicates that the instrument automatically increments the sample name with a number for each analysis
** Do not change this parameter in Expert mode. The parameter is specially adapted for this application.

7.5. Example of water content determination in used motor oil

This is an example of moisture determination in used motor oil using the default parameters.

Sampling: 0.2800 g of used motor oil. Three tests were done using the same working medium.

		Units
Number of replicates	6	
Average	0.1397	[%]
Standard deviation	0.0065	[%]
RSD	4.6	[%]

8. Moisture determination with 2-component ethanol T5E

8.1. Principle

Most liquid samples dissolve in ethanol. If needed, other solvents can be added to ethanol in specific proportions to release the water more efficiently. For example, chloroform is a good solvent for fats, and formamide makes the solubility of polar substances better. Ethanol should always be in the solvent in a proportion not lower than 25%. Otherwise, unknown stoichiometric ratios will occur for the KF reaction.

8.2. Reagent

Titrant: Titrant 5E
Working medium: 40 ml Solvent E

8.3. Procedure

The sample is injected using a plastic syringe with a needle. The actual weight is determined from the difference between the full and empty vessel.

8.4. Settings

Name	Default parameters	Units
Application		
Application name	2-component ethanol T5E	
Advisable syringe	5 mL (Hamilton)	
Sample		
Name	Sample ? *	
Amount	0.2600	[g]
QC		
Name	QC Sample	
Electrode		
Type	mV	
Recommended electrode	MTC695	
Current (sample analysis)**	20	[µA]
Titrant: KF T5 5 mg/mL		
Name	KF T5E	
Real concentration	5.000	[mg/L]
Method : KF titration		
Stirring speed	25	[%]
Delay	0	[s]
Injection autodetect	No	
Proportionnal band**	450	mV
Drift threshold	50	[µg/min]
Min. titration duration	30	[s]
Max. titration duration	300	[s]
Result 1 (R1) name	Water content	
R1 hide	No	
R1 min.	0	[%]
R1 max.	100	[%]
R1 QC min.	0	[%]
R1 QC max.	100	[%]

* "?" in the name, indicates that the instrument automatically increments the sample name with a number for each analysis
** Do not change this parameter in Expert mode. The parameter is specially adapted for this application.

8.5. Example of water determination in shampoo

This is an example of moisture determination in shampoo using the default parameters.

Sampling: 0.0250 g of shampoo. Three tests were done using the same working medium.

		Units
Number of replicates	6	
Average	82.0	[%]
Standard deviation	1.0	[%]
RSD	1.2	[%]