

Application Bulletin 209/3 e

Water in insulating oils, hydrocarbons, and their products

Accurate and reliable determination by Karl Fischer titration

Branch

Energy, power plants; petrochemistry, biofuels; organic chemistry; solvents

Keywords

Karl Fischer titration; coulometric titration; KFC; gas extraction; vial oven technique; automation; water content; insulating oil; turbine oil; hydraulic oil, crude oil; lubricant, transformer oil; petrochemistry; aromatics; organic chemistry; solvents; branch 3; branch 5; branch 14; branch 16: ASTM D6304; ASTM E1064; ASTM D1533; ASTM D3401; ASTM D4928; EN IEC 60814; EN ISO 12937; ISO 10337; GB/T 11146; DIN 51777

Summary

Water in crude, insulating, lubricating, and turbine oil can cause corrosion, which in turn leads to an increase in debris load resulting in diminished lubrication and blocked filters. As a result, a high water content could lead to infrastructure damage, higher maintenance costs, or even unwanted downtimes.

Due to the above-mentioned factors, the water content is an important factor regulated in many trade specifications and also defines the price of these substances. An accurate and reliable determination is therefore necessary, since even small deviations can have a large impact on the price.

As these substances have a low water content, coulometric Karl Fischer titration is the method of choice. Many substances can be analyzed by direct injection into a coulometric Karl Fischer cell. Other substances, especially if they contain additives, should be analyzed using a water vaporizer accessory. In this case, the sample is first placed into an oven, the water evaporates, and the liberated moisture is then transferred into a coulometric Karl Fischer cell for subsequent titration.

This Application Bulletin describes the direct determination according to ASTM D6304, ASTM E1064, ASTM D1533, ASTM D3401, ASTM D4928, EN IEC 60814, EN ISO 12937, ISO 10337, DIN 51777, and GB/T 11146. The oven technique is described according to ASTM D6304, EN IEC 60814, and DIN 51777.

Direct determination

Summary

This procedure is recommended only for samples with a low viscosity and without any expected interferences from the sample matrix.

Instruments

- Coulometric KF Titrator
- Magnetic stirrer

Electrodes

Double Pt wire electrode for coulometry	6.0341.100
Generator electrode with diaphragm	6.0344.100

Reagents

- HYDRANAL®-Coulomat CG (catholyte)
- HYDRANAL®-Coulomat Oil (anolyte)

Standards

Standards (with different water contents) suitable for the coulometric Karl Fischer titration are commercially available.

Preparations

Sample

The sample should be well homogenized before sampling.

System

The coulometric titration cell is filled with approximately 100 mL of anolyte solution. The generator electrode is filled with 5 mL catholyte solution. The titration cell is then conditioned.

Analysis

Each analysis consists of the following steps:

- Conditioning of the titration cell
- Injection of the sample into the titration cell
- Karl Fischer titration

Conditioning

Conditioning, or titrating the titration cell to dryness, is carried out while stirring. This conditioning step must be performed before each determination. When the titration system is conditioned, the titration can begin.

Injection of the sample

First, the syringe which is used to inject the sample into the coulometric cell must be rinsed with sample to remove any water adhering to the syringe. For this, a small amount of sample is aspirated into the syringe and distributed around the entirety of the syringe before discarding the sample.

A sample for the analysis is then aspirated into the same syringe and weighed on the balance. An appropriate amount of sample containing at least 50 µg water is injected into the titration cell, and the syringe is weighed again to determine the exact sample size. Table 1 lists the recommended sample size, which is dependent on the expected amount of water.

Table 1: Recommended sample size in dependence of the expected amount of water

Expected water content (%)	Sample size (g)
0.001 – 0.01	5
0.01 – 0.03	3
0.03 – 0.07	1
0.07 – 0.1	0.5
0.1 – 0.5	0.25
0.5 – 2.5	0.1

Karl Fischer titration

The titration is stopped as soon as the defined EP is reached and the drift value (amount of water per time) falls below a predefined value. Usually the parameter “relative drift” is used to stop a determination. The stop drift is calculated by adding the drift at the start of the determination to the value entered for the “relative drift”. The endpoint is reached if the actual drift is smaller than the sum of the two mentioned values. The higher the chosen value for the “relative drift”, the sooner the determination is stopped, and the more water remains in the sample.

Parameters

I(pol)	10 µA
Generator current	Auto
Stirring rate	8
EP at	50 mV
Titration rate	Optimal
Stop criterion	Relative drift
Relative stop drift	10 µg/min
Start drift	10 µg/min
Stabilizing time	0 s
Sample addition time	10 s

Calculation

$$\text{Water content in ppm} = \frac{m_{EP1}}{m_S}$$

m_{EP1} : Determined amount of water at the end of the titration in µg

m_S : Sample size in g

Example determination

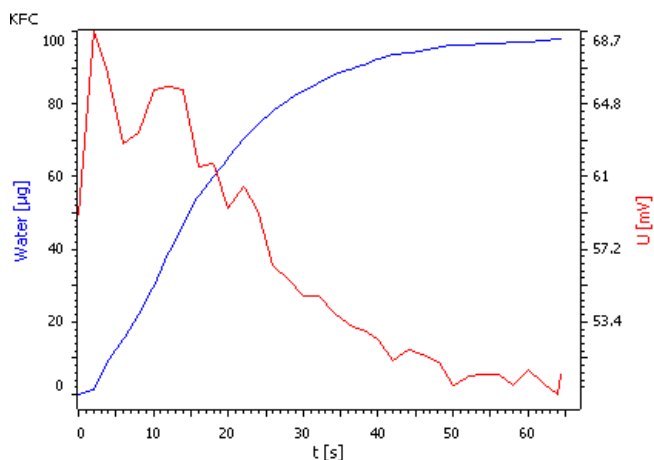


Fig. 1: Titration curve of the coulometric water determination in a turbine oil.

Comments

- In case larger sample sizes are used, the analyte solution will have to be exchanged more often (e.g., every 10 injections for samples sizes of 5–10 g) to keep the cell reagent ratios optimal.
- Coulometric reagents have a limited water capacity, which is equivalent to the amount of sulfur dioxide. Decreased sulfur dioxide concentrations (lower than half of the initial concentration) lead to longer determination times. The reagent should then be

completely replaced. Monitoring the reagent capacity and the exchange of the reagent can be done by the titration system and the software.

- ISO 10337, ASTM E1064 and ASTM D4928 differ from the herein described method in the recommended sample size in dependency of the expected water content.

Troubleshooting

Too high drift

- Check titration cell, septum and/or seals for leaks. If necessary, replace them.
- Check if the molecular sieve is exhausted. If necessary, replace it.
- Ensure thorough mixing.

Poor precision (reproducibility)

- Check the coulometric titration cell with a standard of similar water content and weight. This helps to determine sample matrix influences, to check the reagent condition, and sample handling procedure.
- Optimize the titration and control parameters.
- Clean electrodes according to the electrode leaflet.
- Check if the KF reagent is contaminated/exhausted. If so, change the solution; if possible use a different batch.
- Check electrical contacts; defective contacts can lead to an unstable measuring signal.
- Check the sample weight. Ideally, the sample should contain at least 50 µg water.

Checks at the balance

- Is the balance imprecise for the used sample size?
- Are there drafts, which prevent a stable reading of the sample size?

Oven technique

Summary

All kinds of samples can be analyzed with this technique. This procedure is especially recommended for samples with a high viscosity or with expected interferences from the sample matrix. In general, the matrix interference is lower with this method.

Instruments

- Vial oven suitable for the gas extraction
- Coulometric KF Titrator
- Magnetic stirrer

Electrodes

Double Pt wire electrode for coulometry	6.0341.100
Generator electrode without diaphragm	6.0345.100

Reagents

- HYDRANAL[®]-Coulomat AG Oven (anolyte)
- Nitrogen as carrier gas for the gas extraction

Standards

Standards (with different water contents) suitable for the oven technique are commercially available.

Preparation

Sample

The sample should be well homogenized before sampling.

System

The coulometric titration cell is filled with approximately 150 mL of anolyte solution. The flow rate of the nitrogen gas is set to 80 mL/min and the oven is heated up to the desired temperature. Table 2 lists a suggestion of oven temperatures for some possible samples. The titration cell and tubing are then conditioned to remove any water from the system.

Table 2: Suggested oven temperature for some samples

Sample type	Oven temperature in °C
Transformer oil	150
Mineral oil	120
Additive	120
Lubricating oil	120

The minimal recommended oven temperature is 90 °C. For further information regarding how to determine the ideal oven temperature for a sample, please refer to Metrohm Application Bulletin AB-280.

Analysis

Conditioning

Conditioning or titrating the titration cell to dryness is carried out under stirring in the so-called *conditioning position*. This conditioning step must be carried out before each determination.

During “conditioning”, the needle remains in the conditioning vial; any water contained in the system is removed until a constant low drift in the range of 1 to 10 µg/min is achieved. If the automatic drift correction is activated, the drift value must be stable. A stabilizing time can be defined to ensure a stable drift value.

When the defined temperature is reached and the titration system is conditioned, the first measurement can be started.

Blank

For the blank determination, three empty sample vials are sealed. The titration is carried out as described under the procedure below (*Sample*). The mean value of the three blank determinations is saved as a variable.

Sample

The sample is directly weighed into the sample vial. Table 3 lists the recommended sample size in dependence of the expected amount of water.

The carrier gas is passed through the sample vial and transfers the released water into the titration cell where the water content is determined.

The titration and the gas extraction of the sample is stopped as soon as the defined endpoint is reached and the drift value (amount of water per time period) falls below a predefined value. Usually the parameter “relative drift” is used to stop a determination. The stop drift is calculated by adding the drift at the start of the determination and the value entered for the “relative drift”. The endpoint is reached if the actual drift is smaller than the sum of the two mentioned values.

Table 3: Recommended sample size in dependence of the expected amount of water

Expected water content in %	Sample size
0.005	> 6 g
0.01	> 3 g
0.05	0.6 – 10 g
0.1	0.3 – 5 g
0.5	0.06 – 1 g

Parameters

I(pol)	10 µA
Stirring rate	15
Generator current	400 mA
EP at	50 mV
Titration rate	Optimal
Stop criterion	Relative drift
Relative stop drift	8 µg/min
Start drift	10 µg/min
Stabilizing time	60 s
Extraction time	120 s
Flow rate	80 mL/min

Calculations

$$\text{blank}_{\text{rel}} = \frac{(V_{\text{vial}} - V_{\text{sample}})}{V_{\text{vial}}} \times \text{blank}_{\text{empty vial}}$$

- blank_{rel}: Relative blank value in µg
 V_{sample}: Volume of sample in sample vial in mL
 V_{vial}: Total volume of sample vial in mL
 blank_{empty vial}: Blank value of empty sample vial in µg

$$\text{water} = \frac{\text{water}_{\text{EP}} - \text{blank}_{\text{rel}}}{m_{\text{S}}}$$

- water: Water content of the sample in mg/L
 water_{EP}: Water content found at the end point in µg
 blank_{rel}: Relative blank value in µg
 m_S: Sample size in g

Example determination

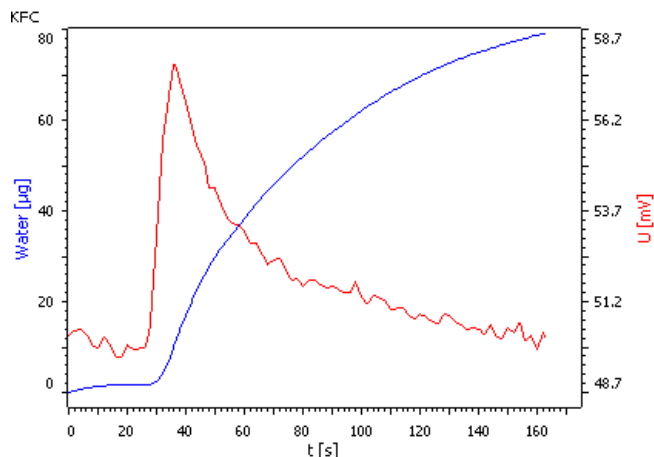


Fig. 2: Titration curve of the coulometric water determination in a turbine oil using a KF oven for the water evaporation.

Comments

- It is essential that the needle is completely immersed in the sample so that the gas flow mixes the sample. Therefore, a minimum of one-third of the vial should be filled with sample.
- The high filling level of the sample vials requires the use of a relative blank value. For more information on the relative blank value, please refer to AN K-048.
- For drift correction, the drift value measured at the start of the determination is multiplied with the determination time and subtracted from the water content found in the sample at the end of the determination.
- Coulometric reagents have a limited water capacity. The capacity is equivalent to the amount of sulfur dioxide. Decreasing sulfur dioxide concentrations (lower than half of the initial concentration) lead to longer determination times. The reagent should then be completely replaced. Automatic monitoring of the reagent capacity and the exchange of the reagent can be done by the titration system and the software.
- Due to the constant gas flow during measurements, methanol contained in the reagents evaporates. The methanol loss should be compensated regularly to avoid too high results.
- The carrier gas transports the released water into the titration vessel. In principle, the type of gas used is not important. However, due to oxidation reactions with oxygen, the thermal stability of organic substances at higher temperatures is often poor when using dry air as carrier gas. Inert gases, usually nitrogen, offer more flexibility and reliability.

- In case high accuracy is needed, the use of a generator electrode with diaphragm is recommended.
- For samples whose temperature behavior is unknown, either several samples are titrated at different temperatures or, if available, a so-called temperature gradient is run (available temperature range: 50 to 250 °C). For more information please refer to AB-280.
- For the oven technique, the absolute amount of water transferred to the titration vessel is recommended to be in the range of 300 to 5000 µg. If the absolute amount of water for a sample cannot be reduced (e.g., smaller sample size) also larger amounts of water (> 5000 µg) can be determined using the oven technique. Please be aware that in such cases the determination times will increase.

Troubleshooting

Too high drift

Switch off the gas flow.

- If drift value decreases:
 - Check if the molecular sieve of the drying bottles is exhausted and replace it.
 - Check the needle system and transfer tube and clean it e.g., with methanol.
- If drift value does not change:
 - Check titration cell, septum and/or seals for leaks.
 - Check if the molecular sieve of the drying tube on the generator electrode is exhausted.
 - Check if the reagent is contaminated.
 - Check that the reagents are properly conditioned.
 - Ensure thorough mixing.

Poor precision (reproducibility)

- Optimize the titration and control parameters.
- Check whether the sample vials are tightly sealed.
- Clean electrodes according to the electrode leaflet.
- Check if the needle system is blocked, and possibly clean it with water and methanol. Dry the components thoroughly afterwards.
- Check the transfer tube and clean it with water and methanol to remove any condensates or dirt.
- Check if the KF reagent is contaminated/exhausted. If so:
 - Refill methanol to 150 mL
 - Change the solution; if possible use a different batch.

- Check electrical contacts; defective contacts can lead to an unstable measuring signal.
- Check if the chosen oven temperature is suitable for sample analysis.
- Check if the sample is well homogenized before the analysis.
- Check the sample weight. Ideally, the sample should contain at least 100 µg water.

Checks at the balance

- Is the balance imprecise for the used sample size?
- Are there drafts or is the temperature equilibrium between sample and environment not reached when the sample is weighed out?

References

- **Metrohm Application Bulletin 280**
Automatic Karl Fischer water content determination with the 874 Oven Sample Processor
- **Metrohm Application Note AN-K-048**
Sample preparation with the oven technique – relative blank
- **ASTM D6304**
Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
- **ASTM E1064**
Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration
- **ASTM D1533**
Standard Test Method for Water in Insulating Liquids by Coulometric Karl Fischer Titration
- **ASTM D3401**
Standard Test Methods for Water in Halogenated Organic Solvents and Their Admixtures
- **ASTM D4928, API MPMS 10.9**
Standard Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration
- **EN IEC 60814**
Insulating liquids - Oil-impregnated paper and pressboard - Determination of water by automatic coulometric Karl Fischer titration
- **EN ISO 12937**
Petroleum products - Determination of water - Coulometric Karl Fischer titration method
- **ISO 10337**
Crude petroleum - Determination of water - Coulometric Karl Fischer titration method

- **GB/T 11146**
Crude petroleum - Determination of water - Coulometric Karl Fischer titration method
- **DIN 51777**
Petroleum products - Determination of water content using titration according to Karl Fischer

Author

CC Titration

Metrohm International Headquarters

Date

November 2019