

Application Bulletin 434/1 e

Water in lithium ion battery materials

Reliable and precise determination by Karl Fischer titration

Branch

Energy, power plants; research and education

Keywords

Karl Fischer titration; coulometric titration; KFC; gas extraction; vial oven technique; automation; lithium battery; raw materials; electrolytes; solvents; carbon black; graphite; anode slurry; coated anode foil; coated cathode foil; separator foil; water content; branch 16; branch 17

Summary

Lithium-ion batteries must be completely free of water (concentration of H₂O < 20 mg/kg), because water reacts with the conducting salt, e.g., LiPF₆, to form hydrofluoric acid.

All batteries consist of an anode and a cathode, a separator as well as an electrolyte. For lithium ion batteries, the anode and cathode materials (active materials) are coated onto metallic foils. To coat the metallic foils, the active materials are mixed with binders and applied onto the foils in the form of slurries. A typical anode material is carbon black / graphite, while lithium compounds are used for the cathode material. The anode, separator, and cathode foils are usually wound into roles or stacked. The separator thus prevent contact between the anode and cathode. Electrical conductivity between anode and cathode is established by the electrolyte. In general, mixtures of anhydrous, aprotic solvents and lithium salts are chosen as electrolytes.

The water content of several materials used in lithium ion batteries can be determined reliably and precisely by coulometric Karl-Fischer titration. In this Application Bulletin the determination for the following materials is described:

- raw materials for the manufacture of lithium-ion batteries (e.g., solvents for electrolytes, carbon black/graphite)
- electrode coating preparations (slurry) for anode and cathode coating
- the coated anode and cathode foils as well as in separator foil and in the combined material
- electrolytes for lithium-ion batteries

Electrolytes and solvents

Summary

Most electrolyte solvents are polar aprotic solvents. Water extraction by the oven method for such solvents is generally slow due to formation of hydrogen bonds. Therefore, as long as they do not undergo any side reaction with the titration reagents, direct titration is recommended for such solvents.

Instruments

- Coulometric KF Titrator
- Magnetic stirrer

Electrodes

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

Reagents

- Anolyte and catholyte solutions suitable for the generator electrode with diaphragm

Standards

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

Preparations

Sample

No sample preparation is required.

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 under stirring. This conditioning step must be carried out before each determination. When the titration system is conditioned, the titration can start.

Injection of the sample

In a first step the syringe used for injecting the sample into the coulometric cell is rinsed with sample to remove any water adhered to the syringe. For this a small amount of sample is aspirated into the syringe and distributed in the whole syringe before discarding it.

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 are injected into the titration cell and the syringe is weighed again to determine the exact amount sample size.

Karl Fischer titration

The titration is stopped as soon as 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 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. 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
Dynamics	70 mV
Max. rate	Maximum
Min. rate	15.0 µg/min
Stop criterion	Relative drift
Relative stop drift	3 µg/min
Start drift	10 µg/min
Stabilizing time	30 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

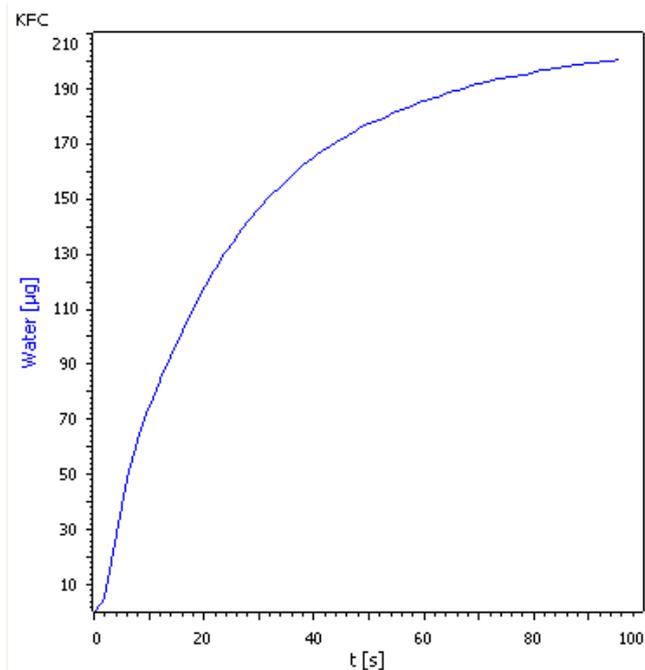


Fig. 1: Example titration curve of the coulometric water determination in an electrolyte solvent for lithium batteries.

Comments

- For direct coulometric water determination in vinylene carbonate, Hydranal Coulomat AK reagent together with 10 g benzoic acid are required. Because the correct pH range and operating in a methanol-free system are critical for the success of this application, the cell should only be cleaned with methanol-free solvents.
- The “relative drift” value should not be higher than 5 µg/min. If high accuracy is required and for small water contents the “relative drift” should be reduced (e.g. to 2 µg/min).
- Electrolyte solutions are hydrophilic and will show an increasing concentration of water with exposure to air. The exposure time of the sample to the air should therefore be minimized.

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

Troubleshooting

Too high drift

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

Poor precision (reproducibility)

- Check the coulometric titration cell with a standard of similar water content and weight. This helps to find influences of the sample matrix, to check condition of the reagent and sample handling.
- Optimize the titration and control parameters
- Clean electrodes according to the electrode leaflet
- Check if the KF reagent is contaminated/exhausted. If yes, 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, preventing a stable reading of the sample size?

Carbon black / graphite

Summary

While determination of the water content of carbon black / graphite by direct titration is possible, the sample will contaminate the titration cell resulting in tedious cleaning. A titration by gas extraction offers a simpler alternative where less cleaning is required.

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

- Analyte solution suitable for the generator electrode without diaphragm and gas extraction technique
- Nitrogen as carrier gas for the gas extraction

Standards

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

Preparation

Sample

0.5 g carbon black/graphite is weighed into a sample vial and the vial is sealed. To settle down the sample, the vial can be slightly tapped on the laboratory bench.

System

The coulometric titration cell is filled with approximately 150 mL of analyte solution. The flow rate of the nitrogen gas is set to 50 mL/min and the oven is heated up to 170 °C. The titration cell and all tubing are then conditioned to remove any water from the system.

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 right 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 *Sample*. The mean value of the three blank determinations is saved as variable.

Sample

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 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 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.

Parameters

I(pol)	10 µA
Generator current	Auto
EP at	50 mV
Dynamics	70 mV
Max. rate	Maximum µg/min
Min. rate	15 µg/min
Stop criterion	rel. drift
Relative stop drift	5 µg/min
Start drift	10 µg/min
Stabilizing time	60 s
Extraction time	180 s
Oven temperature	170 °C
Flow rate	50 mL/min

Calculation

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

water: Water content of the sample in ppm
 water_{EP}: Water content found at the end point in µg
 blank: Water content of the blank determination in µg
 m_S: Sample size in g

Example determination

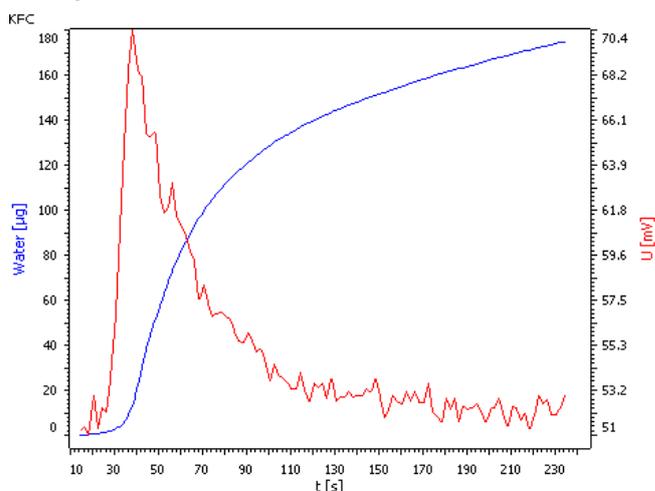


Fig. 2: Example titration curve of the coulometric water determination of carbon black/graphite using a vial oven at 170 °C

Comments

- For these kind of samples, the inlet needle must not be immersed into the sample as it will otherwise clog the needle. Therefore the needle holder 6.2049.050 is used.
- 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.
- The higher the chosen value for the “relative drift”, the sooner the determination is stopped and the more water remains in the sample. The “relative drift” value should not be higher than 5 µg/min. If high accuracy is required and for small water contents the “relative drift” should be reduced (e.g. to 2 µg/min).
- 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 be completely replaced. The 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, it is not important what kind of gas is used. 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.

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 clogged and possibly clean it with water and methanol. Dry the components 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 yes,
 - 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 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

Anode slurries

Summary

The determination of the water content of anodes slurries made from graphite and n-methyl-2-pyrrolidon (NMP) by direct titration is not possible, as the sample will interfere with the indication; a titration by gas extraction is therefore required.

Additionally, xylene is added to the sample before the gas extraction to reduce the hydrophilic properties and viscosity of the sample resulting in a better release of the water.

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

- Mixed xylene, p.a.
- Anolyte solution suitable for the generator electrode without diaphragm and gas extraction technique
- 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 is thoroughly mixed. Make sure the sample does not change its water content during the mixing. In the case of the anode slurry, mixing for 30 min on a mechanical shaker is recommended.

1.5 – 2 g anode slurry is weighed into a sample vial. A small stirring bar and 2.0 mL mixed xylene are added and the vial is sealed. The mixture is then homogenized on a magnetic stirrer for 30 s.

System

The coulometric titration cell is filled with approximately 150 mL of anolyte solution. The flow rate of the nitrogen gas is set to 50 mL/min and the oven is heated up to 180 °C. The titration cell and all tubing are then conditioned to remove any water from the system.

Analysis

Conditioning

Conditioning or titrating the titration cell to dryness is carried out under stirring in the conditioning position. This conditioning step must be carried out before every determination.

During “conditioning” the needle is located in the conditioning vial; 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 temperature is reached and the titration system is conditioned, the first measurement can start.

Blank

For the blank determination three sample vials are prepared as described under *Preparation/Sample* omitting the sample. The titration is then carried out as described under *Sample*. The mean value of the three blank determinations is saved as variable.

Sample

The dried 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 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 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.

Parameters

I(pol)	10 µA
Generator current	Auto
EP at	50 mV
Dynamics	70 mV
Max. rate	Maximum µg/min
Min. rate	15 µg/min
Stop criterion	rel. drift
Relative stop drift	5 µg/min
Start drift	10 µg/min
Stabilizing time	60 s
Extraction time	180 s
Oven temperature	180 °C
Gas flow	50 mL/min

Calculation

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

water: Water content of the sample in ppm
 water_{EP}: Water content found at the end point in µg
 blank: Water content of the blank determination in µg
 m_S: Sample size in g

Example determination

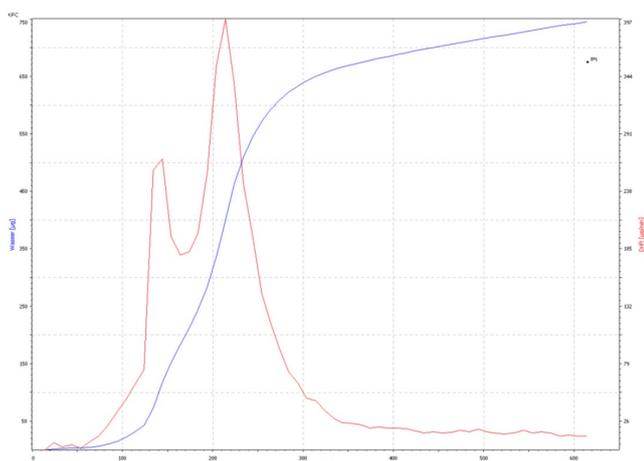


Fig. 3: Example titration curve of anode slurry at 180 °C with 2.0 mL mixed xylene added

Comments

- The release of the water by gas extraction without the addition of xylene is very slow and oscillating, resulting in low reproducibility. This is due to the hydrophilic nature of the NMP as well as the high viscosity of the sample.
- To obtain reproducible results, it is important that the sample is well homogenized. It is recommended to agitate the sample thoroughly before the sampling.
- For these samples, the inlet needle must not be immersed into the sample, as it will otherwise clog the needle. Therefore the needle holder 6.2049.050 is used.
- For drift correction, the drift value measured at the start of the determination is multiplied by the determination time and subtracted from the water content found in the sample at the end of the determination.
- The higher the chosen value for the “relative drift”, the sooner the determination is stopped and the more water remains in the sample. The “relative drift” value should not be higher than 5 µg/min. If high accuracy is required and for small water contents the “relative drift” should be reduced (e.g., to 2 µg/min).
- 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 be completely replaced. Monitoring of the reagent capacity and the exchange of the reagent can be performed by the titration system and the software.
- The coulometric cell will slowly filled with xylene evaporated from the sample vials
- 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, it is not relevant, which kind of gas is used. 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.
- For samples, whose temperature behavior is unknown, a temperature gradient is run (available temperature range: 50 to 250 °C). For more information please refer to AB-280.

Troubleshooting

Too high drift

Switch off the gas flow.

- If drift value decreases:
 - Check if the molecular sieve of the drying bottle 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 clogged and possibly clean it with water and methanol. Dry the components afterwards.
- Check the transfer tube and clean it with water and methanol to remove condensates and dirt.
- Check if the KF reagent is contaminated/exhausted: If yes,
 - 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 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

Coated anode and cathode foils and separator foil

Summary

The water content in the anode and cathode foils as well as the separator foils and the final combined material can be easily determined using the gas extraction technique.

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

- Anolyte solution suitable for the generator electrode without diaphragm and gas extraction technique
- 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 materials are cut into small pieces of approx. 3 cm length rolled up using tweezers. Then they are weighed (accurately to 0.1 mg) into the sample vials.

System

The coulometric titration cell is filled with approximately 150 mL of anolyte solution. The flow rate of the nitrogen gas is set to 100 mL/min and the oven is heated up to the recommended temperature (see table below). The titration cell and all tubing are then conditioned to remove any water from the system.

Sample	Min. Temperature / °C
Anode foil	120
Cathode foil	120
Separator foil	180
Combined materials	180

Analysis

Conditioning

Conditioning or titrating the titration cell to dryness is carried out under stirring in the conditioning position. This conditioning step must be carried out before every determination.

During “conditioning” the needle is located 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 temperature is reached and the titration system is conditioned, the first measurement can start.

Blank

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

Sample

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 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 and the value entered for the “relative drift”. The endpoint is reached, when the actual drift is smaller than the sum of the two mentioned values.

Parameters

I(pol)	10 μ A
Generator current	Auto
EP at	50 mV
Dynamics	70 mV
Max. rate	Maximum μ g/min
Min. rate	15 μ g/min
Stop criterion	rel. drift
Relative stop drift	5 μ g/min
Start drift	10 μ g/min
Stabilizing time	60 s
Extraction time	Min. 600 s
Oven temperature	See table <i>Preparation/System</i>
Gas flow	100 mL/min

Calculation

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

water:	Water content of the sample in ppm
water _{EP} :	Water content found at the end point in μ g
blank:	Water content of the blank determination in μ g
m _S :	Sample size in g

Example determination

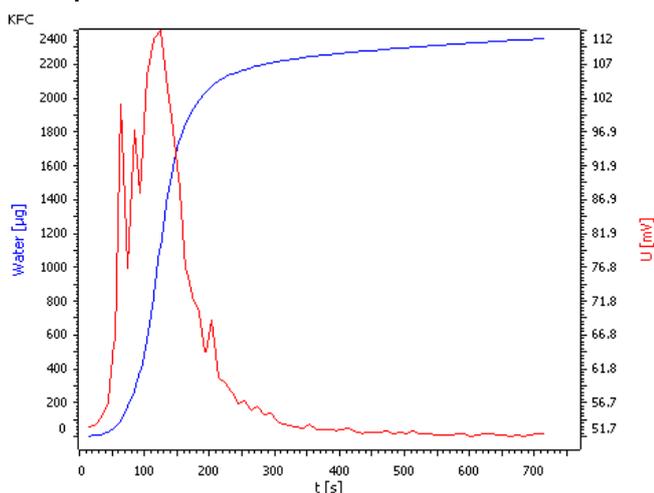


Fig. 4: Example titration curve of a separator material at 180 °C

Comments

- For drift correction, the drift value measured at the start of the determination is multiplied by the determination time and subtracted from the water content found in the sample at the end of the determination.

- The higher the chosen value for the “relative drift”, the sooner the determination is stopped and the more water remains in the sample. The “relative drift” value should not be higher than 5 μ g/min. If high accuracy is required and for small water contents the “relative drift” should be reduced (e.g., to 2 μ g/min).
- 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 be completely replaced. Monitoring of the reagent capacity and the exchange of the reagent can be performed 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 it is not relevant, which kind of gas is used. 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.
- For samples whose temperature behavior is unknown, a temperature gradient is run (available temperature range: 50 to 250 °C). For more information please refer to AB-280.

Troubleshooting

Too high signal 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 clogged and possibly clean it with water and methanol. Dry the components afterwards.
- Check the transfer tube and clean it with water and methanol to remove condensates and dirt.
- Check if the KF reagent is contaminated/exhausted: If yes,
 - 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 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

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