Application Bulletin 137/6 e

Coulometric water content determination according to Karl Fischer

Branch

All branches

Keywords

Titration; Karl Fischer titration; coulometric; KFC; water content determination; ASTM E 1064

Summary

This Application Bulletin gives an overview of the coulometric water content determination according to Karl Fischer. Amongst others, it describes the handling of electrodes, samples, and water standards. The described procedures and parameters comply with the ASTM E 1064.

Introduction

Coulometric water content determination is primarily used for the determination of small amounts of water. Metrohm KF Coulometers work in a determination range of 10 µg – 200 mg water. However, larger amounts of water (> 10 mg) require a lot of time and/or may exceed the water capacity of the KF reagent, which could lead to incorrect results.

Instead of a buret, the electric current is used to generate the iodine needed for the Karl Fischer reaction. The current releases a stoichiometrically corresponding amount of iodine from the iodide-containing reagent.

Faraday's law applies and can be used to calculate the water content of the sample.

$$m = \frac{M \times Q}{z \times F} \qquad (1)$$

m	Mass of converted substance in g
M	Molar mass in g/mol
Q	Measured amount of charge in As
z	Number of exchanged electrons (equivalence number, charge number)
F	Faraday constant, 1 F = 96485 coulomb/mol (1 coulomb = 1 C = 1 ampere second = 1 As)

Example for iodine: $2\ I^- - 2\ e^- \rightarrow I_2$

126.9 g iodine is released by 96485 A in 1 s – or 1.315 mg iodine is generated by 100 mA in 10 s.

Requirements for coulometric titrations are the following:

- The process must take place with 100% current efficiency.
- No side reactions must occur.
- Oxidation or reduction must lead to a defined oxidation state.

Metrohm KF Coulometers meet these requirements with commercially available reagents. The instruments work according to the galvanostatic principle, i.e. with a constant current.

The same chemical processes as in a volumetric KF titration take place, i.e., 1 mol H_2O consumes 1 mol of I_2. As the iodine is generated electrolytically from the iodide in the KF reagent, the coulometric water content determination is an absolute method and a titer determination is not necessary.

In order to generate iodine at the anode of the generator electrode, Metrohm KF Coulometers work with variable current strengths and pulse lengths. For generator electrodes with diaphragms following current strengths are used: 100, 200 and 400 mA. For cells without diaphragms a constant current of 400 mA is applied. Higher current strengths have not been able to establish themselves – side reactions occur and heat is produced. Working with variable pulse lengths allows precise «iodine addition» even in the region of the endpoint.

The instrument measures the time and current flow that is required to reach the titration endpoint. The product of time and current Q is directly proportional to the amount of iodine generated and therefore to the amount of water determined (see formula 1).

The endpoint is indicated voltammetrically by applying an alternating current of constant strength to a double Pt wire-electrode. This results in a voltage difference between the Pt wires. The voltage drastically decreases in the presence of minimal quantities of free iodine. This fact is used to determine the endpoint of the titration.

Instruments

- Titrator with a mode for coulometric Karl Fischer titration

Electrodes

Double Pt wire-electrode (indicator electrode for coulometric Karl Fischer titration)
Generator electrode with or without diaphragm

Reagents

Special coulometric KF reagents are available from various manufacturers (e.g. Sigma-Aldrich, Merck, …). The reagents have been optimized for the use with generator electrodes with and without diaphragms and also for special applications (e.g. water content determination in ketones).

Additionally, liquid water standards are available. These standards can be used to check the system (recovery of added water, see formula 2).

Filling the generator electrode

It is assumed that the generator electrode is dry and has been assembled according to the Instructions for Use.

Generator electrode without diaphragm:

Handling the 6.0345.100 Generator electrode without diaphragm is simple. It only needs one reagent and is quickly ready for use (no moisture deposits in the diaphragm!). Only reagents that are specially intended for use with generator electrodes without a diaphragm must be used. About 100 mL of the chosen reagent is filled into the titration cell and the ground joint opening is closed with the stopper.

Generator electrode with diaphragm:

Reagents for coulometric water determination with generator electrodes with diaphragms consist of an anode solution (anolyte), which is filled into the titration cell and a cathode solution (catholyte) which is filled into the generator electrode.

About 100 mL anolyte is filled into the titration cell (anode chamber) and about 5 mL catholyte into the generator electrode with diaphragm (cathode chamber). We recommend that you use an injection syringe for filling in the catholyte. The filling level should be about the same or 2-3 mm lower than that in the anode chamber.

Parameters

Table 1: Method parameter for a coulometric KF titration

	Parameter	Setting
General	I(pol)	10 µA
	Generator current*	400 mA
Control parameter	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
Conditioning	Start drift	10 µg/min

*For a generator electrode with a diaphragm the parameter Generator current is set to «auto»

If ketone reagents are used, then the endpoint, start and stop drift must be adjusted, as the ketone reagents suppress the side reactions, but do not prevent them completely.

Table 2: Control and titration parameter for ketone reagents

	Parameter	Setting
General	I(pol)	10 µA
	Generator current*	auto mA
Control parameter	EP at	20 mV
	Dynamics	70 mV
	Max. rate	maximum µg/min
	Min. rate	15 µg/min
	Stop criterion	rel. drift
	Relative stop drift	20 µg/min
Conditioning	Start drift	60 µg/min

*For a generator electrode with a diaphragm, the parameter Generator current is set to «auto»

Conditioning and drift

The titration cell must first be dried before the determinations can be started. The conditioning is started to remove water contained in the reagent and water on the surfaces of the equipment (titration cell, electrodes, …). The water content determination of the sample should only be started once a low and stable drift is reached.

A constant drift equal or lower than 4 µg/min is acceptable. Lower values are certainly possible. If higher, stable values occur then the results are normally still good as the drift can be compensated.

When working with an oven, a drift equal or lower than 10 µg/min is acceptable. The drift depends on the gas flow (the smaller the gas flow the lower the drift).

Sample addition

Generally the coulometric titration cell should never be opened to add samples. The influence of the humid air entering the titration cell would falsify the results.

Liquid samples

Liquid samples are added with the aid of a syringe. Either a syringe with a long needle is used with the needle being immersed beneath the surface of the reagent during injection. Alternatively a short needle can be used, with the last drop being drawn back into the needle. The best way of determining the actual sample weight is by weighing the syringe before and after injection.

Volatile or low-viscosity samples should be refrigerated before the sample is taken, in order to prevent handling losses. In contrast, the syringe itself should not be directly refrigerated as this could cause the formation of condensate. For the same reason aspirating air into a syringe which has been cooled by taking up a refrigerated sample should be avoided.

Highly viscous samples can be warmed to lower their viscosity; the syringe must also be warmed. The same goal (lower viscosity) can be reached by dilution with a suitable solvent. In this case the water content of the solvent must be determined and deducted as a blank value correction.

With samples containing a lot of water, care must be taken that the needle is not introduced into the measuring cell through the septum before the determination has been started, otherwise the drift and therefore the result of the analysis could be falsified.

With samples containing only traces of water the syringe must be thoroughly dried beforehand. If possible the syringe should be rinsed with the sample solution by taking up the sample solution several times and then discarding it.

Solid samples

Whenever possible solid samples should be extracted or dissolved in a suitable solvent and the resulting solution injected. A blank value correction should be made for the solvent.

If no suitable solvent can be found for a solid sample, or if the sample reacts with the Karl Fischer solution, a drying oven should be used.

Sample size

The sample size should be small so that as many samples as possible can be titrated in the same electrolyte solution and the titration time is kept short. However, take care that the sample contains approximately 50 µg H_2O. The following table provides guidelines for the sample weight.

Table 3: Water to be determined and water content with corresponding sample size

Water content of sample	Sample size	H_2O to be determined
100000 ppm = 10%	50 mg	5000 µg
10000 ppm = 1%	10 – 100 mg	100- 1000 µg
1000 ppm = 0.1%	0.1 – 1 g	100- 1000 µg
100 ppm = 0.01%	1 g	100 µg
10 ppm = 0.001%	5 g	50 µg

Tips and tricks

Reagent exchange

In the following cases, the electrolyte solutions should be exchanged:

- When the titration vessel is too full.
- When the capacity of the reagent is exhausted.
- If the drift is too high and shaking the cell does not result in any improvement.
- If a two-phase mixture is formed in the titration vessel. In this case only the sample phase can be aspirated off.
- If during the determination the error message "check generator electr." appears.

For the generator electrode, with diaphragm the catholyte should be exchanged approximately once a week. Extended use may cause darkening of the catholyte and yellow precipitation in the cathode compartment. An unpleasant smell also indicates the need for catholyte exchange.

Indicator electrode

A new indicator electrode may require a certain running-in period for the formation of the surface. This may cause unusually long titration times and measurement results which are too high. These phenomena vanish after a short period of use. In order to speed up the running-in of a new indicator electrode the Coulometer can be conditioned overnight, for example.

A polluted indicator electrode can be carefully cleaned with an abrasive cleansing agent (aluminum oxide (6.2802.000 Polishing Set) or toothpaste). After cleaning it should be rinsed with ethanol.

The two Pt wires of the indicator electrode should be as parallel to one another as possible. Check on insertion.

Cleaning

The electrolyte solution can normally be exchanged without any special cleaning of the parts. If cleaning is necessary then care should be taken that the Pt grid of the generator electrode is not damaged.

Generator electrode with diaphragm

- Resinous deposits on the diaphragm → Hang the generator electrode vertically from a support rod, fill with conc. HNO_3 and allow standing overnight. Then rinse with water followed by methanol/ethanol*.
- Pollutants containing oil → Clean with a solvent (e.g. hexane) and then rinse with methanol/ethanol*.
- Salt-like deposits → Clean with water and then rinse with methanol/ethanol*.

Cleaning (rinsing) the diaphragm → Fill the cathode compartment of the generator electrode with methanol/ethanol* and allow the filling to drain out. Repeat the process 2-3 times. This process should also be carried out when the electrode has been cleaned as described above.

Generator electrode without diaphragm:

- Pollutants containing oil → Clean with a solvent (e.g. hexane) and then rinse with methanol/ethanol*.
- Salt-like deposits → Clean with water and then rinse with methanol/ethanol*.

*Please make sure the ethanol does not contain any ketone additives.

Dry all parts thoroughly after cleaning. A hot-air blower can be used for this. If the parts are dried in a drying oven take care that the temperature does not exceed 70 °C (plastic components!).

Checking the instrument

Commercial, certified water standard solutions with a water content of 1.00 ± 0.003 mg/g and/or 0.10 ± 0.005 mg/g should be used for checking the instrument as a fully integrated measuring system.

Table 4: Recommended sample sizes:

Liquid standard 1.0 mg/g	0.2 – 2.0 g
Liquid standard 0.1 mg/g	0.5 – 5.0 g

Handling of the liquid water standard

1. Open the ampoule containing the standard as recommended by the manufacturer.
2. Aspirate approximately 1 mL of the standard into the syringe and then eject the standard into the waste.
3. Aspirate the remaining content of the ampoule into the needle (in case air is aspirated, eject the air out of the syringe).
4. Remove excess liquid from the outside of the needle with a paper tissue.
5. Place the needle on a balance and tare the balance.
6. Then start the determination and inject a suitable amount of standard (see table 1 to 3) through the septum into the titration vessel. Do not inject the whole content of the syringe! Please take care that the standard is injected into the reagent and not at the electrode or the wall of the titration vessel. This leads to unreproducible results.
7. After injecting the standard, place the syringe again on the balance.
8. Enter the injected sample weight in the software.

Repeat step 4 to 8 at least three times. If the complete content of an ampoule has been injected, the needle can be filled with fresh standard (same batch). In this case the needle does not need to be rinsed again. Start directly with step 4.

There are two possibilities to add liquid standard. It can be injected with the tip of the needle above the reagent level. In this case the last drop must be aspirated back into the syringe. Otherwise it is wiped off at the septum and might not be determined although the weight of it is taken into account.

If the needle is long enough, it can be immersed in the reagent directly. In this case there is no last drop and the needle can be pulled out of the titration vessel without aspirating back any liquid.

Troubleshooting

Drift too high

- Depots containing water in the titration vessel → shake titration vessel.
- Reagent exhausted or contaminated → exchange.
- Moisture penetrating into titration vessel:
  - Molecular sieve exhausted?
  - Septum pierced?
  - Seals not OK?
  - Ground joint sleeves not smooth?
- Generator electrode diaphragm polluted or moist.
- Sample matrix consumes iodine. Change reagent more often.
- When working with Oven/Oven Sample Processor:
  - Molecular sieve of Oven/Oven Sample Processor exhausted?
  - Gas flow too high?
  - Allow to run overnight.
  - Screw seals tight?

Drift unstable

- Poor stirring → Stir so, that mixing is efficient, but without the formation of air bubbles.
- Reset the control parameters to standard values.

Result too high

- Titration vessel not properly conditioned → shake and wait until drift has stabilized.
- With the generator electrode without diaphragm → set generator current to 400 mA.
- Sample contains substances which can be oxidized.
- Set stop drift higher.
- Drift correction too small, e.g. with unstable drift or with manual drift correction.

Result too low

- Drift correction too large, i.e. the drift was too high at the start or unstable drift.
- Stop drift too high.
- Minimal titration rate too low.
- Sample releases iodine.

Results are widely scattered

- Inhomogeneous sample? Poor reproducibility of sample addition?
- Drift unstable.

Titration times too long

- Wait until drift during conditioning becomes stable.
- Amount of water too large
- Set stop drift higher.
- Set control range smaller.
- Set maximal titration rate higher.

Literature

- Metrohm Monograph water determination by Karl Fischer Titration. 8.026.5003 – 2003-09
- HYDRANAL Multi Media Guide, Sigma-Aldrich
- HYDRANAL Manual, Eugen Scholz, Reagents for Karl Fischer Titration, Sigma-Aldrich
- Merck Apura Analytical Application Notes Finder: Karl Fischer (Merck Webpage)

Metrohm Application Bulletins

- AB 141 Analysis of edible fats and oils
- AB 209 Coulometric water determination according to Karl Fischer in insulating oils as well as in hydrocarbons and their derivates
- AB 280 Automatic water content determination using gas extraction
- AB 357 Determination of water in gases and liquefied gases with the 875 KF Gas Analyzer
- AB 421 Automated coulometric Karl Fischer titration

Author

Competence Center Titration

Metrohm International Headquarters