

## Coulometric water determination according to Karl Fischer

Of interest for:

General analysis, Organic chemistry, Pharmaceutical industry, Petrochemistry, Plastics, Cosmetics, Paints and Lacquers

1, 3, 4, 5, 6, 14

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### Introduction

#### Coulometry

Coulometric water determination is primarily used for the determination of small amounts of water. Larger amounts of water require a lot of time and/or may exceed the water capacity of the KF reagent, which could lead to incorrect results. Metrohm KF Coulometers work in a determination range of 10 µg...200 mg H<sub>2</sub>O with a resolution of 0.1 µg H<sub>2</sub>O.

Instead of a buret the electric current is used for generating a reagent – an «electronic buret», so to speak. The current releases the stoichiometrically corresponding amount of iodine from the iodide-containing KF reagent by electrolysis.

Faraday's law applies:

$$m = \frac{M \times Q}{z \times F}$$

m = mass of converted substance in g

M = molar mass in g/mol

Q = measured amount of charge in ampere-seconds

z = number of exchanged electrons (equivalence number, charge number)

F = electrochemical equivalent, 1 F = 96'485 coulomb/mol (1 coulomb = 1 C = 1 ampere-second = 1 A s)

Example for iodine:  $2 \text{I}^- - 2 \text{e}^- \rightarrow \text{I}_2$

z = 2, M = 253.8 (I<sub>2</sub>)

126.9 g iodine is released by 96'485 A in 1 s – or 1.315 mg iodine is generated by 100 mA in 10 s.

Requirements for coulometric titration are:

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

Metrohm KF Coulometers meet these requirements with modern coulometric reagents. They work according to the *galvanostatic coulometry* principle, i.e. with a *constant current*.

The same chemical processes take place as in a volumetric KF titration, i.e. 1 mol H<sub>2</sub>O consumes 1 mol I<sub>2</sub>. As the iodine is generated electrolytically from the iodide in the KF solution this means that the **coulometric determination of water is an absolute method – a titer does not need to be determined!**

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 measurements are made at the following current strengths: 100, 200 and 400 mA. For cells without diaphragms measurements are made at a constant current strength of 400 mA. 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 titration endpoint.

The instrument measures the time and current flow that is required to reach the titration endpoint. The product of time x current, Q is directly proportional to the amount of iodine generated and therefore to the amount of water determined.

The end point is indicated voltametrically by applying an alternating current of constant strength to a double Pt electrode. This results in a voltage difference between the Pt wires of the indicator electrode which is drastically lowered in the presence of minimal quantities of free iodine. This fact is used to determine the end point of the titration.

### Instruments and accessories

- 2.831.0010 Coulometer with diaphragmless cell
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- 2.831.0110 Coulometer with cell with diaphragm
- 2.756.0010 Coulometer with diaphragmless cell
- 2.756.0110 Coulometer with cell with diaphragm
- 2.728.0010 Magnetic stirrer
- 6.5617.000 Equipment for automatic reagent exchange (optional)
- 2.700.0020 Dosino (to 6.5617.000, optional)

### Reagents

Special coulometric KF reagents are available from Riedel-de Haën (Sigma Aldrich), Merck and Baker. These have been optimized for cells with and without diaphragms and also for special applications.

A selection of reagents is given below:

#### Riedel-de Haën

- Hydranal Coulomat E (based on ethanol, for cells with or without diaphragm; can be used both as anolyte and catholyte)
- Hydranal Coulomat AG (for cells without a diaphragm or as anolyte for cells with diaphragm, in this case in combination with Coulomat CG)
- Hydranal Coulomat AD (for cells without diaphragm)
- Hydranal Coulomat AG Oven (specially for oven applications; for cells without diaphragm or as anolyte for cells with diaphragm, in this case in combination with Coulomat CG)
- Hydranal Coulomat AG-H (specially for hydrocarbons, as anolyte for cells with diaphragm in combination with Coulomat CG)
- Hydranal Coulomat Oil (specially for oils, as anolyte for cells with diaphragm in combination with Coulomat CG)
- Coulomat AG-K (anolyte for cells with diaphragm, for determining the water content in ketones, in combination with Coulomat CG-K)
- Coulomat CG (catholyte for cells with diaphragm)
- Coulomat CG-K (catholyte for cells with diaphragm, for determining the water content in ketones, in combination with Coulomat AK)

#### Merck

- apura – CombiCoulomat frit (for cells with diaphragm; can be used both as anolyte and catholyte)
- apura – CombiCoulomat fritless (for cells without diaphragm)

#### Baker

- Hydra-Point Coulometric Gen (for cells without diaphragm)
- Hydra-Point Coulometric Oven (specially for oven applications; for cells without diaphragm)

- Hydra-Point Coulometric Ano (anolyte for cells with diaphragm)
- Hydra-Point Coulometric Kat (catholyte for cells with diaphragm)

### Procedure

#### 1. Selecting the generator electrode

The generator electrode without diaphragm is the best choice for most applications. It is particularly suitable for use with very polluting samples.

The 6.0344.100 Generator electrode with diaphragm should be used when your samples contain ketones and aldehydes because special reagents for aldehydes and ketones are only available for generator electrodes with diaphragms.

If your reagent has a low conductivity, e.g. if you had to add chloroform because of the solubility of the sample then you should use the generator electrode with diaphragm as first choice.

It can also be recommended when very good accuracy in the lowest trace analysis (absolute water content < 50 µg) ranges is required.

#### 2. Filling the electrolysis cell:

It is assumed that the cell 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 causes no problems; it is also easy to clean. It only needs **one** reagent and is quickly ready for use (no moisture deposits in the diaphragm!). Use only reagents that are specially intended for use with generator electrodes without a diaphragm.

Fill about 100 mL of the chosen reagent into the cell and close the ground joint opening 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 vessel and a cathode solution (catholyte) which is filled into the generator electrode.

Fill about 100 mL anolyte into the anode chamber and about 5 mL catholyte into the 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.

#### 3. Titration mode

The following modes can be selected:

- KFC: Coulometric KF Titration.

- KFC-B: KF titration with blank value correction
- BLANK: determination of the blank value
- GLP: Mode for system validation

The newly loaded modes are provided with standard parameters and immediately ready for use.

The modes differ in their standard calculation formulas, see the instructions for use.

#### Parameters

**Tab. 1:** Control and titration parameter.

	Parameter	Setting
Control parameter Coulometry:	EP at U	50 mV
	Dynamics	70 mV
	Max.Rate	max. µg/min
	Min.Rate	15 µg/min
	Stop crit	rel.drift
Titration parameter Coulometry:	rel.drift	5 µg/min
	Start drift	10 µg/min
Preselections Coulometry:	I(pol)	10 µA
	Generator I*	400 mA

\*For a generator electrode with a diaphragm the parameter Generator I 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.

**Tab. 2:** Control and titration parameter for Coulomat AK and CG-K.

	Parameter	Setting
Control parameter Coulometry:	EP at U	20 mV
	Dynamics	70 mV
	Max.Rate	max. µg/min
	Min.Rate	15 µg/min
	Stop crit	rel.drift
Titration parameter Coulometry:	rel.drift	20 µg/min
	Start drift	60 µg/min
Preselections Coulometry:	I(pol)	10 µA
	Generator I*	auto

#### 4. Conditioning and drift

The coulometer cell must first be dried before the determinations can be started. Initially conditioning is started by pressing the Start button; between the individual determinations the cell is then conditioned automatically. When the green LED lamp lights up the Start drift has been undercut and the titration can be started. However, you should still wait until a stable drift trend is indicated by the following arrow:



A constant drift of the order of about  $\leq 4$  µg/min is good. However, 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 the oven a drift  $\leq 10$  µg/min is good. The drift depends on the gas flow (the smaller the gas flow the lower the drift).

#### 5. Sample Addition

##### 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 or a short needle is used with the last drop being sucked 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 can also 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.

**Pastes, greases** can be placed in the measuring cell by using a syringe without a needle. The joint opening can be used for this purpose. If aspiration is additionally required the opening with the septum stopper can be used.

**The best way of determining the actual sample weight is by weighing the syringe before and after injection.**

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 <START> has been pressed as otherwise the drift and therefore the result of the analysis could be falsified.

With **samples containing only a trace 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 the 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 kept short. However, take care that the sample contains at least 50 µg H<sub>2</sub>O. The following table provides guidelines for the sample weight.

**Tab 3:** sample size against water to be determined

Content of sample	Sample size	H <sub>2</sub> O to be determined
100000 ppm = 10 %	50 mg	5000 µg
10000 ppm = 1 %	10 mg...100 mg	100 µg...1000 µg
1000 ppm = 0.1 %	100 mg...1 g	100 µg...1000 µg
100 ppm = 0.01 %	1 g	100 µg
10 ppm = 0.001 %	5 g	50 µg

## 6. Tips und 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 approx. 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 being necessary. 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<sub>3</sub> and allow to stand overnight. Rinse with water followed by ethanol.

##### **Pollutants containing oil:**

Clean with a solvent (e.g. hexane) and then rinse with ethanol.

##### **Salt-like deposits:**

Clean with water and then rinse with ethanol.

##### **Cleaning (rinsing) the diaphragm:**

Fill the cathode compartment of the generator electrode with methanol 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 ethanol.

##### **Salt-like deposits:**

Clean with water and then rinse with ethanol.

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 and validating 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 validation of the instrument as a fully integrated measuring system (the 1.00 mg/g

standard is easier to handle and is therefore to be preferred).

Recommended initial weight range:

**Tab 4:** Recommended sample sizes:

Liquid standard 1.0 mg/g	0.2-2.0 g
Liquid standard 0.1 mg/g	0.5-1.5 g

The exact procedure of a validation is described in Application Bulletin 273/3e.

## 7. 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.
- Min. 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 max. rate higher.

## 9. Literature

Metrohm Monograph water determination by Karl Fischer Titration. 8.026.5003 – 2003-09

HYDRANAL Multi Media Guide. Version 2.0 Sigma-Aldrich / Riedel-de Haën 2004

HYDRANAL Manual. Eugen Scholz Reagents for Karl Fischer Titration Sigma-Aldrich / Riedel-de Haën 2001

Apura Application data base for water determinations acc. to Karl Fischer, Version 1/2004, Merck

### Metrohm Application Bulletins

- No. 109 Karl Fischer water determination with the KF drying oven
- No. 141 Analysis of edible fats and oils
- No. 142 Karl Fischer water determination in gases
- No. 145 Determination of low water contents in plastics using the KF oven method
- No. 209 Coulometric water determination according to Karl Fischer in insulating oils as well as in hydrocarbons and their derivatives
- No. 217 Karl Fischer water determination in pharmaceuticals using the oven method
- No. 273 Validation of Metrohm KF Coulometers according to GLP/ISO 9001
- No. 280 Automatic Karl Fischer water determination using the 774 Oven Sample Processor

### Standards

American Society for Testing and Materials

IEC 814

Determination of water in insulating liquids by automatic coulometric Karl Fischer titration

ASTM D 3401-97	Standard Test Method for Water in Halogenated Organic Solvents and Their Admixtures
ASTM D 4928-89	Standard Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration
ASTM D 5460-98	Standard Test Method for Rubber Compounding Materials – Water in Rubber Additives
ASTM D 6304 - 04a	Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
ASTM D6869-03	Standard Test Method for Coulometric and Volumetric Determination of Moisture in Plastics Using the Karl Fischer Reaction (the Reaction of Iodine with Water)
ASTM E 1064a-04	Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

British Standard

BS 6829:1.5:1990	Analysis of surface active agents (raw materials). Part 1. General Methods. Section 1.5 Methods for determination of water content
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International Organization for Standardization

ISO TC 158/SC 2	Methods of analysis of natural gas and natural gas substitutes. Direct determination of water by Karl Fischer method, coulometric Method
ISO 10101-1: 1993	Natural gas – Determination of water by Karl Fischer method. Part 1: Introduction
ISO 10101-3: 1993	Natural gas – Determination of water by Karl Fischer method. Part 3: Coulometric procedure
ISO 10337: 1997	Crude petroleum – Determination of water – Coulometric Karl Fischer titration method

European Pharmacopoeia (Pharm.Europe), 4th Edition plus Supplements 2002

Karl Fischer Titration Methods. Methodology and water determination in 442 different substances

International Electrotechnical Commission, Geneva