

Coulometric water determination according to Karl Fischer

Reagents and examples of applications

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The coulometric Karl Fischer technique is a micro-method that is particularly suitable for samples with low water content, from ~10 µg up to ~10 mg. It uses electrochemically generated iodine, produced from iodide-containing reagents by anodic oxidation at a generator electrode directly in the titration vessel. The amount of consumed iodine and therefore the amount of water from the sample is proportional to the total current consumption (current x time).

Its high precision and the convenient introduction of liquid samples with a syringe make coulometry a viable and easy technique for water determination.

Advantages of coulometric titration include:

- Easy to use
- Detects low concentrations of water
- High accuracy

Coulometric titration vessels

The coulometric technique can be carried out with two different types of generator electrodes: with or without diaphragm. The diaphragm separates the smaller cathode compartment, where protons are reduced to hydrogen, from the larger anode compartment, where iodide is oxidised to iodine. Generator electrodes without diaphragm also have anode and cathode, but the compartments are not separated. Reagents that are specially designed for diaphragm-less cells must be used.

The function of the diaphragm is to enable the exchange of certain anions and cations, and to prevent the diffusion of the generated iodine and its immediate reduction at the cathode, which causes erroneous results. In cells without diaphragm, the cathode construction is modified to prevent any disturbances.

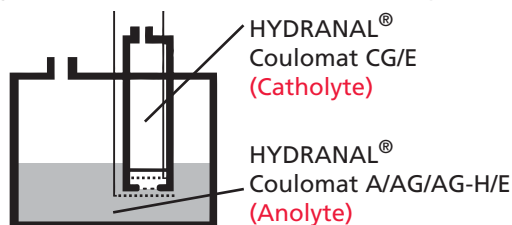
Coulometric Karl Fischer titrations in cells with diaphragm require two reagent solutions, an anolyte and a catholyte. Catholyte solution (5 mL) is added to the cathode chamber, and anolyte solution is added to the same level in the anode chamber (see **Figure 1**). The levels of liquids in the two chambers must be equal to prevent exchange of anolyte and catholyte by pressure compensation. In diaphragmless cells, the anolyte (~100 mL) is used as single solution.

When using reagents containing chloroform and/or xylene, or analysing samples with water content below 50 µg/g, using a generator electrode with diaphragm is recommended to ensure high precision.

Care and maintenance of the coulometric cell

Proper care and maintenance of coulometric cells can help maximise the sensitivity and reliability of Karl Fischer titrations.

Figure 1 Coulometric titration vessel with diaphragm



- Renew catholyte at least weekly, otherwise unpleasant odour, darkened electrodes and yellowish precipitates in the cathode chamber can occur.
- Remove remaining iodine from the anolyte by addition of wet methanol or 2-methoxyethanol.
- Solid samples cannot be analysed with a coulometric system directly, pre-dissolve them and run against blank samples.
- Clean glass anode chamber with water or a suitable solvent, then dry in an oven at 50°C or under a stream of warm air.
- Clean generator electrode with a diaphragm by placing it in a beaker of methanol or, if necessary, in nitric or chromosulphuric acid, then repeat with methanol.
- Clean generator electrode without diaphragm by rinsing it with water or a suitable solvent, if necessary it can be dipped in nitric or chromosulphuric acid, then repeat with water or solvent.

Reagents and Applications

- HYDRANAL Coulomat A type reagents are used as anolytes. They contain iodide and a sulphur dioxide/imidazole buffer in a suitable solvent.
- HYDRANAL Coulomat CG reagents are used as catholytes.
- The non-toxic HYDRANAL Coulomat E can be used as both anolyte and catholyte solution; it is based on ethanol and has a water capacity of over 1000 mg per 100 mL (100 mg per 5 mL when used as catholyte).

Water determination in petrol, unleaded (Application Report L428)

The solubility of petrol in the methanolic medium of the Karl Fischer titration is limited, therefore the use of reagents containing solubilisers is recommended. In 100 mL HYDRANAL Coulomat A, up to 50 mL of petrol can be dissolved. Also, HYDRANAL Coulomat E is suitable, since 100 mL dissolves up to 35 mL of this sample. HYDRANAL Coulomat E (5 mL) is added to the cathode compartment; the anode chamber is also filled with HYDRANAL Coulomat E to the same liquid level as in the cathode chamber. If HYDRANAL Coulomat A is used in the anode chamber, the cathode chamber is filled with 5 mL HYDRANAL Coulomat CG. After titrating to dryness with low and stable drift, the samples can be injected.

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HYDRANAL Coulomat AG, AD and AG-H are analytes free of halogenated hydrocarbons, whereas HYDRANAL Coulomat A contains chloroform for better solubility of fat-containing substances. The chloroform content may still be increased, but it should not exceed 30%, otherwise the conductivity will decrease. The minimum conductivity differs from instrument to instrument, so an exact maximum chloroform volume cannot be given.

Many long-chained mineral oils cannot be dissolved completely; they must be analysed in reagents containing solubilisers or dispersion agents. For example, the water content of finely dispersed oil can be determined very easily with reproducible results. Based on Methanol and with addition of aromatic and halogenated hydrocarbons, HYDRANAL Coulomat Oil is very well suited for the analysis of oil samples. It should be used in coulometric cells with diaphragm using HYDRANAL Coulomat CG as catholyte.

Water determination in rapeseed oil (Application Report L319)

Rapeseed oil does not dissolve in a methanolic KF working medium. The addition of chloroform helps to finely disperse the sample in the medium. In addition, it is important to choose a delay time of 30 seconds in the titration software to ensure that all contained water is titrated. HYDRANAL Coulomat Oil, which contains chloroform and xylene as solubilisers, is very well suited for coulometric determination in fats and oils.

HYDRANAL Coulomat CG (5 mL) is added to the cathode compartment of a titration vessel with diaphragm. HYDRANAL Coulomat Oil (~100 mL) or a mixture of HYDRANAL Coulomat A and 30% chloroform are added to the anode compartment up to the same liquid level.

HYDRANAL Coulomat AK is an analyte for the coulometric determination of water in ketones. Its water capacity is approximately 100 mg per 100 mL. HYDRANAL Coulomat CG-K is the corresponding catholyte, free of halogenated hydrocarbons.

Water determination in octamethylcyclotetrasiloxane (Application Report L519)

When determining the water content of octamethylcyclotetrasiloxane coulometrically in a methanol-containing reagent, the drift increases with each injected sample. An esterification takes place as a side-reaction. However, the substance can be determined with stable end points and without increasing drift in a methanol-free reagent.

HYDRANAL Coulomat CG-K (5 mL) is placed in the cathode compartment of the coulometric cell. The anode compartment is filled up to the same level with HYDRANAL Coulomat AK.

Coulometric cells without diaphragm require only one reagent. HYDRANAL Coulomat E, AD, AG, AG-H, AG Oven and AK can be used with diaphragmless cells; no catholyte solution is needed.

Toxicity

Except for HYDRANAL Coulomat AK, which contains 2-methoxyethanol, all HYDRANAL Coulomat reagents are free of pyridine,

carbon tetrachloride and 2-methoxyethanol. In most reagents, methanol is the most hazardous component. Using HYDRANAL Coulomat E, which is based on ethanol, can eliminate even this.

Use of the Karl Fischer Oven

Many substances release their water only at high temperatures, making them inappropriate for direct KF titration.

Water determination in poly-L-lactide, PLLA, with KF oven (Application Report L577)

This sample is an uncoloured granulate, which cannot be dissolved for direct titration in the alcohol-containing media of KF reagents, not even by addition of chloroform.

To evaluate its temperature behaviour, a sample was gradually heated from 50°C to 250°C (see **Figure 2**). At 50°C, the adherent water is released. Above 60°C, the included water is released. Water release is completed at 210°C. According to literature, thermal decomposition occurs at 230°C.

This heating ramp shows that sample heating at 210°C for 10-15 minutes is recommended.

HYDRANAL Coulomat CG (5 mL) is added to the cathode chamber of a coulometric cell with diaphragm; the anode compartment is filled to the same level with ~100 mL HYDRANAL Coulomat AG Oven.

After starting the instrument, it automatically titrates to dryness. Once the drift is low (<10 µg H₂O/min.) and stable, the carrier gas is switched on. As soon as the original stable drift value is reached with the carrier gas, about 0.5 g of the sample, weighed precisely, can be heated.

The water in these substances can be evaporated in a Karl Fischer oven at 100°C to 300°C, depending on the sample. It is then transferred to the KF titration cell by purging with a dry, inert gas. The coulometric titration cell is filled with HYDRANAL Coulomat AG-Oven, which is especially suitable for use with Karl Fischer ovens as it shows high drift stability, or HYDRANAL Coulomat E for non-toxic applications.

This method of water determination can be applied to:

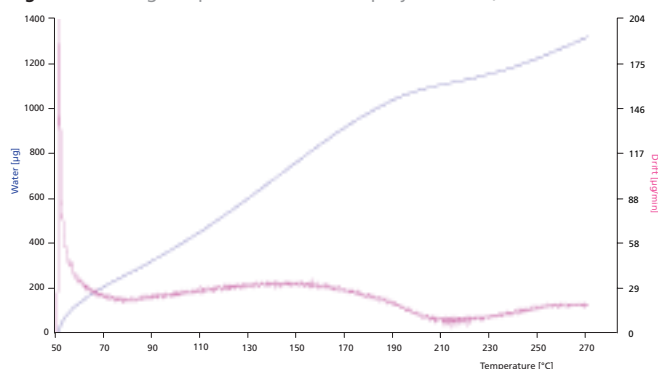
- Insoluble solids that only release their inherent water at temperatures above 60°C (e.g. plastics, salts)
- Solids and liquids that undergo side reactions with conventional Karl Fischer titration reagents (ascorbic acid, mineral oils), assuming that the matrix is not vaporised at these temperatures and that none of the substances decompose to products that can interfere with the Karl Fischer reaction.

Suitable carrier gases are air or nitrogen, with nitrogen preferred when the sample is sensitive to oxidation at temperatures of 100-300°C. The carrier gas must be dried, for example with 34241 HYDRANAL Molecular Sieve 0.3 nm.

The working conditions must be optimised for each product analysed. The temperature chosen depends on the properties of the substance being investigated. Of particular importance is the determination of the optimum oven temperature to remove the water.

The temperature must be high enough to drive off the water in the sample within 10-15 minutes. At the same time, the temperature must be low enough to prevent vaporisation of the sample matrix, which could interfere in the Karl Fischer titration, but again high enough to prevent condensation in the transfer tubing.

Figure 2 Heating ramp from KF oven for poly-L-lactide, 50°C to 270°C



Control of accuracy

In order to control the accuracy of reagents and instrument according to ISO 9000, the use of liquid 34828 HYDRANAL Water Standard 1.00, 1 g (1 mL) contains 1 mg = 0.10% water (at 20°C), and 34847 HYDRANAL Water Standard 0.10, 1 g contains 0.10 mg = 0.01% water, is recommended. As solid standards for the control of KF oven systems, 34748 HYDRANAL Water Standard KF Oven 220°C-230°C and 34693 HYDRANAL Water Standard KF Oven 140°C-160°C are recommended.

Table 1 HYDRANAL reagents for coulometric KF titration

Cat. no.	Brand	Description	Package size
34807	Fluka	HYDRANAL Coulomat A	500 mL
34836	Fluka	HYDRANAL Coulomat AG	500 mL, 1 L
34810	Fluka	HYDRANAL Coulomat AD	500 mL
34843	Fluka	HYDRANAL Coulomat AG-H	500 mL
34739	Fluka	HYDRANAL Coulomat AG Oven	500 mL
34726	Fluka	HYDRANAL Coulomat E	500 mL
34820	Fluka	HYDRANAL Coulomat AK	500 mL
34868	Fluka	HYDRANAL Coulomat Oil	100 mL, 500 mL
34840	Fluka	HYDRANAL Coulomat CG	50 mL
34821	Fluka	HYDRANAL Coulomat CG-K	50 mL

Expert technical support

Take advantage of our more than twenty-five years of experience with KF titration. We are happy to answer any questions you might have. Complete application reports can be obtained from our HYDRANAL specialists:

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New Fluka-Brand Drug Standards for Ecstasy and Cannabis

Nicole Amann, Product Manager Analytical Standards nicole.amann@sial.com



To analysts in the forensic and clinical markets, we are pleased to introduce high-purity standards of phenylethylamine derivatives and THC compounds for the European market. With Switzerland as the country of origin, export is allowed into all EU countries.

MDMA (3,4-methylenedioxyamphetamine, ecstasy) along with MDA, MDEA and others are members of the

phenethylamine class of psychoactive drugs. A popular party drug, especially in the rave culture, MDMA is one of the most commonly used illicit drugs world wide.

THC (Δ^9 -tetrahydrocannabinol), derived from the Cannabis sativa plant, is considered to be the most wide spread illegal drug and, according to the United Nations Office on Drugs and Crime (UNODC) in Vienna, as the most important agricultural raw material worldwide.

Table 1 New Fluka-brand MDMA standards

Cat. no.	Brand	Description	Package size
56296	Fluka	(-)- Δ^9 -Tetrahydrocannabinol (Δ^9 -THC) solution, 1 mg/mL in ethanol	1 mL
91613	Fluka	(-)- Δ^9 -Tetrahydrocannabinol (Δ^9 -THC) solution, 10 mg/mL in ethanol	1 mL
90899	Fluka	Cannabidiol solution, 10 mg/mL in ethanol	1 mL
51853	Fluka	Cannabidiol solution, 1 mg/mL in ethanol	1 mL
39961	Fluka	Cannabidiolic acid	1 mg
39382	Fluka	Δ^9 -Tetrahydrocannabinolic acid A	10 mg
65963	Fluka	(\pm)-3,4-Methylenedioxyamphetamine hydrochloride (MDMA)	10 mg, 50 mg
18087	Fluka	(\pm)-3,4-Methylenedioxyamphetamine hydrochloride (MDMA) solution, 1 mg/mL in methanol	1 mL
56458	Fluka	(\pm)-3,4-Methylenedioxyamphetamine hydrochloride (MDA) solution, 1 mg/mL in methanol	1 mL
50499	Fluka	(\pm)-3,4-Methylenedioxy-N-ethylamphetamine hydrochloride (MDEA) solution, 1 mg/mL in methanol	1 mL
14232	Fluka	(\pm)-4-Bromo-2,5-dimethoxyamphetamine hydrochloride	10 mg