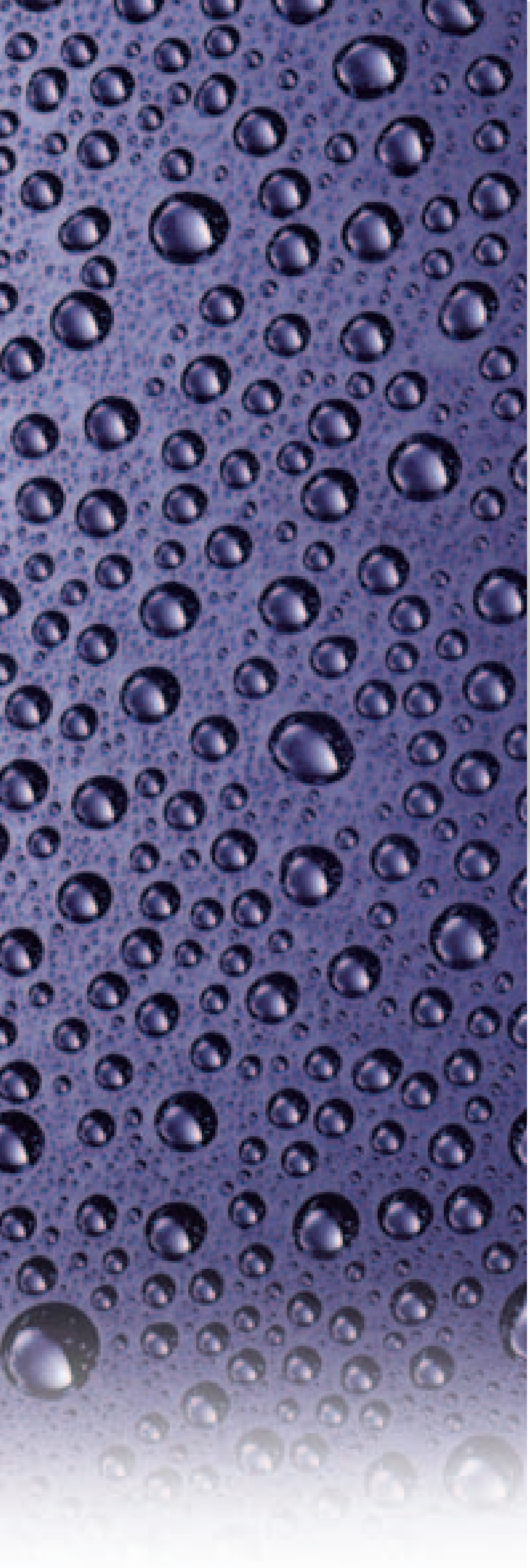
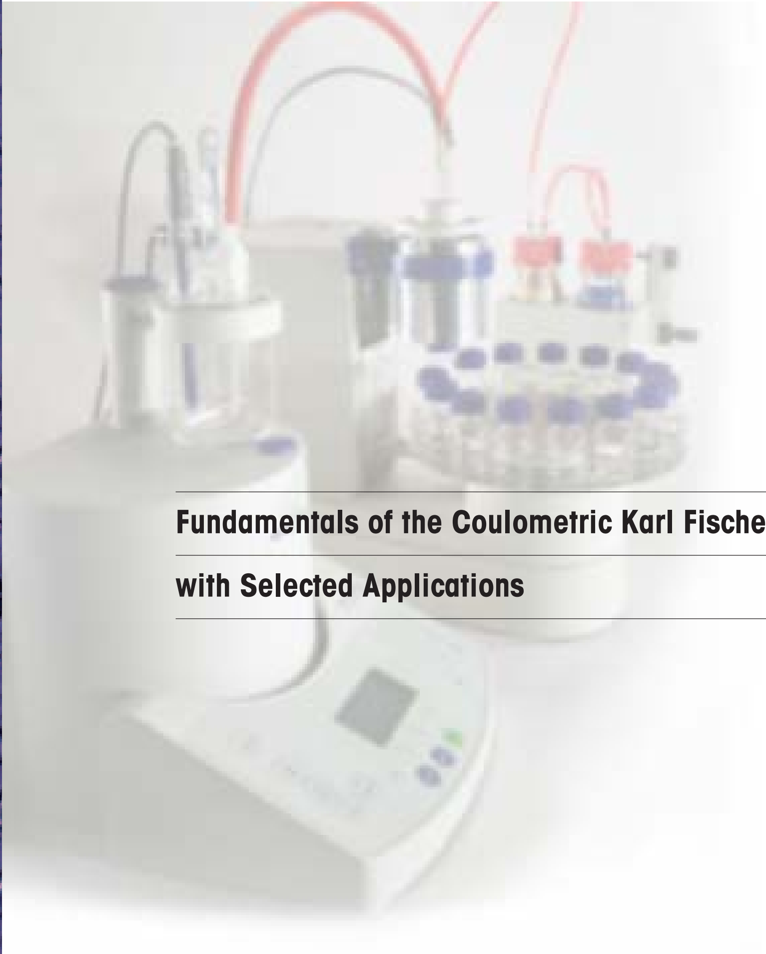




Fundamentals of the Coulometric Karl Fischer Titration

with Selected Applications

METTLER TOLEDO Titrators DL32/DL39

Applications brochure 32

METTLER TOLEDO

Editorial

Dear Reader,

to complete our family of new Karl Fischer titrators, we are happy to introduce you to our DL32 and DL39 KF coulometers. Based on the hardware and operating concept of the successful DL31 and DL38 volumetric KF titrators, the new coulometers include all the features and benefits now expected from METTLER TOLEDO titrators. These include a user-friendly interface to the operator, unsurpassed accuracy, precision and speed, and naturally, fully GLP compliant documentation.

In addition to the above and the possibilities with the previous DL36 and DL37 coulometers, the new instruments have the added options of a diaphragmless generating cell and a new ingenious automated oven sample changer. Nowadays automation is becoming the norm rather than the exception and we wanted this to be as easy as possible for you to implement. These new options offer many advantages to you, our customer. This applications brochure was designed to assist you with the theory and uses of coulometric Karl Fischer titration in order that you can exploit these new advantages to the fullest.

The information herein was again collected and compiled by Albert Aichert, long-time applications chemist with METTLER TOLEDO. The sample results included were generated by chemists in both our Market Support Group and our Research and Development department. We trust that you will benefit from the expertise and diligent work by all concerned.

Good luck in your analyses and happy reading.

Craig

Craig Gordon
Manager Marketsupport
Analytical Chemistry

R. Rohner

Rolf Rohner
Marketing Manager
Analytical Chemistry

Contents

1 Fundamentals of the Karl Fischer titration ... 4
1.1 Historic overview ... 4
1.2 The Karl Fischer reaction ... 5
1.3 Consequences for practical applications ... 6

2 Fundamentals of coulometry ... 7
2.1 KF coulometry ... 7
2.2 Anode and cathode reaction ... 8
2.3 Theory of coulometry ... 8
2.4 Iodine generation ... 9
2.5 Generator electrode without diaphragm ... 9
2.6 Applications of the cell without diaphragm ... 10

3 Control / End point determination ... 11
3.1 Indication ... 11
3.1.1 Principle of bivoltametric indication ... 11
3.1.2 End point and polarization current ... 12
3.2 Reaction rate and iodine production ... 13
3.3 Control of the titration ... 13
3.4 The termination parameters ... 14
3.4.1 Delay ... 14
3.4.2 Absolute drift stop ... 14
3.4.3 Relative drift stop ... 15
3.4.4 Maximum titration time ... 15
3.4.5 Application of the various termination criteria ... 15
3.5 Autostart ... 15

4 The Karl Fischer titration ... 17
4.1 The influence of atmospheric humidity (drift determination) ... 17
4.1.1 Titration stand ... 17
4.1.2 The drift ... 18
4.2 The electrolytes ... 18
4.2.1 Filling the titration cell ... 18
4.2.2 When do you have to replace the electrolyte? ... 19
4.2.3 Emptying the titration cell ... 19
4.3 Cleaning the titration cell ... 20
4.3.1 Cleaning the titration vessel ... 20
4.3.2 Simple cleaning and drying of the generator electrode ... 20
4.3.3 Thorough cleaning of the generator electrode ... 21
4.3.4 Cleaning the measuring electrode ... 21
4.4 Reagents and solvents ... 22
4.4.1 For samples soluble in methanol or ethanol ... 22
4.4.2 For samples poorly soluble in methanol or ethanol ... 22
4.4.3 For samples insoluble in methanol or ethanol ... 23
4.4.4 For ketones and aldehydes ... 23
4.4.5 For acids and bases (pH value) ... 24

4.5 Sampling 25
4.5.1 Taking the sample 25
4.5.2 Storing the sample 25
4.5.3 Amount of sample 25
4.5.4 Sample addition 26

5 Solid samples 28
5.1 External extraction 28
5.1.1 Performing an external extraction 28
5.1.2 Calculation of the external extraction 30
5.2 External dissolution 31
5.3 Lyophilized substance in septum bottles 32
5.4 Determination using the drying oven 33
5.4.1 Principle 33
5.4.2 Purge gas 33
5.4.3 Procedure (method) 34
5.4.4 Manual drying oven 35
5.4.5 STROMBOLI automatic drying oven 36

6 Measurement results 40
6.1 Resolution and detection limit 40
6.2 Measurement accuracy 40
6.2.1 Standards for Karl Fischer coulometry 40
6.2.2 Checking the Karl Fischer coulometer 40
6.2.3 Checking the drying oven 41
6.3 Repeatability 42

7 Troubleshooting 43

8 Applications 46
8.1 Foodstuffs 46
8.2 Cosmetics 47
8.3 Pharmaceuticals 48
8.4 Inorganic raw materials 50
8.5 Organic raw materials 52
8.6 Solvents 54
8.7 Petroleum products 56
8.8 Plastics 59
8.9 Agrochemicals 60
8.10 Surfactants 60
8.11 Paper and cement 61
8.12 Hazards and disposal 62
8.12.1 Reagents for coulometry 62
8.12.2 Safety data of the KF components and auxiliary solvents 62
8.13 Literature on the applications 63
8.13.1 Foodstuffs 63
8.13.2 Pharmaceuticals 64

8.13.3 Chemicals and solvents 64
8.13.4 Petroleum oils and plastics 64
8.13.5 Paints, surfactants, cellulose, minerals 65

9 Appendix 66
9.1 Literature references 66
9.2 Other literature used 66
9.3 Norms 67
9.4 ASTM standards 67

1 Fundamentals of the Karl Fischer titration

1.1 Historic overview

1935	Publication "Neues Verfahren zur massanalytischen Bestimmung des Wassergehaltes von Flüssigkeiten und festen Körpern" by Karl Fischer. [1]
1943	Publication: Dead-stop indication in Karl Fischer titration. (Wernimont, Hopkinson)
1950	Pyridine-containing two-component reagents and dead-stop titration instruments are commercially available.
1952	Use of Karl Fischer method spreads, promoted by numerous publications by E. Eberius [2]
1955	Publication: Stabilized single component reagent (Peters and Jungnickel)
1956	First DIN standard for the Karl Fischer titration (water determination of petroleum oil)
1958	Publication: Coulometric Karl Fischer titration (Oehme, Mayer, Boyd)
1960	Automatic KF titration instruments with burettes. Enormous spread of the use of KF titration
1970	Coulometric KF titration instruments commercially available
1980	Pyridine-free KF reagents commercially available
1984	First microprocessor controlled KF titrator (METTLER DL18) with automatic solvent dispensing and removal, and drift compensation
1985	First fully automatic KF titration with lab robots (DL18 and ZYMARK); DO185 drying oven for the DL18 Karl Fischer titrator
1989	First diaphragmless cell for coulometric KF titration
1990	DL37 KF coulometer from METTLER TOLEDO
1995	Water standard (10.0; 1.0 and 0.1 mg/g) with test certificate according to DIN 50 049-2.3
	First titrator (DL55) with an online curve E=f(t) and V=f(t) for Karl Fischer titration
1997	New DV705 KF titration stand with very low drift value (<2µg/min) for the DL53, DL55, DL58, DL67, DL70ES, DL77 titrators
1998	New KF titrators (DL31/DL38) with special fuzzy logic control for the rapid and accurate determination of water. Titrant specific standard parameters and LEARN titration
1999	New, less poisonous KF reagents using ethanol instead of methanol
2000	RONDO sample changer for automated volumetric Karl Fischer determination
2001	New improved DO307 manual drying oven
	New oven standards with water contents of 5.5% and 1%
2002	New DL32/39 KF coulometer (with and without diaphragm)
	STROMBOLI, new automatic oven for the analysis of a series of up to 13 samples

1.2 The Karl Fischer reaction

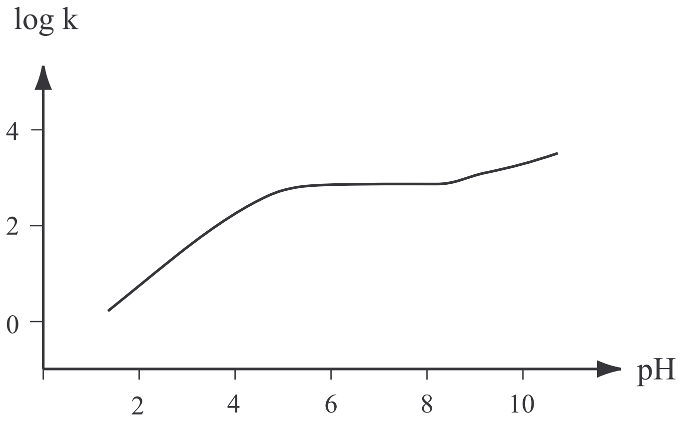
Studies by E. Scholz [4] resulted in the following reaction scheme being proposed for the Karl Fischer reaction:

$$
\begin{aligned}
\mathrm{ROH} + \mathrm{SO_2} + \mathrm{RN} &\rightarrow \mathrm{(RNH)\cdot SO_3\,R} \\
\mathrm{(RNH)\cdot SO_3\,R} + 2\,\mathrm{RN} + \mathbf{I_2} + \mathbf{H_2O} &\rightarrow \mathrm{(RNH)\cdot SO_4\,R} + 2\,\mathrm{(RNH)I}
\end{aligned}
$$

Experiments on the stoichiometry of the reaction showed that methanol can in fact be replaced by other alcohols (e.g. ethanol, 2-propanol, methoxyethanol, diethylene glycol monoethyl ether). This improves the titer stability.

Research on the Karl Fischer reaction by E. Barendrecht and J.C. Verhoff [3] showed that:

- pyridine is not directly involved in the reaction, i.e. it serves only as a buffer and can therefore be replaced by other bases.
- the rate of the Karl Fischer reaction depends on the pH of the medium (see diagram below).



$$-d[I_2] / dt = K\,[I_2] \cdot [\,SO_2\,] \cdot [H_2O]$$

One possible explanation for the influence of pH on the reaction rate is that it is not the sulfur dioxide itself that is oxidized by iodine under the influence of water, but rather the methyl sulfite ion. This is formed from sulfur dioxide and methanol according to the equation:

$$2\,\mathrm{CH_3OH} + \mathrm{SO_2} \rightarrow \mathrm{CH_3OH_2^+} + \mathrm{CH_3OSO_2^-}$$

The higher the pH of the solution, the more methyl sulfite is formed by the capture of protons, and the faster the rate of the Karl Fischer reaction. In the pH range 5.5 to 8, all the sulfur dioxide is present as methyl sulfite; the maximum reaction rate is reached here and cannot increase further. At pH values above 8.5, the reaction rate increases due to side reactions between iodine and hydroxide or methylate ions; in a titration, this results in a more sluggish endpoint and higher iodine consumption.

On the basis of this knowledge, in 1984, E. Scholz developed a pyridine-free Karl Fischer reagent with imidazole as base. This reagent not only replaced the toxic, pungent pyridine, but also facilitated faster and more accurate titrations because imidazole buffers in a more favorable pH range than pyridine.

E. Scholz [4] was also able to confirm the existence of basic methyl sulfite in methanol/SO_2/I_2 solutions during the titration. In 1988, A. Seubert [5] identified methyl sulfite in KF solutions with the aid of IR spectroscopy and isolated and identified methyl sulfate as the secondary product of the KF reaction.

The most recent studies have postulated that the oxidizing species are not I_2 or $RN \cdot I_2$, but that in the polar solvents the I_2 disproportionates partially to I^- and RNI^+ and the RNI^+ then reacts.

1.3 Consequences for practical applications

Influence of pH on the Karl Fischer reaction

Since the maximum rate of the Karl Fischer titration is in the pH range 5.5 to 8, pH values less than 4 and greater than 8 should be avoided in practice. With acidic or basic samples, you should adjust the pH value to the ideal range by adding buffering agents (for acids: imidazole, and for bases: salicylic acid).

Influence of the solvent on the Karl Fischer reaction

The stoichiometry (molar ratio of $H_2O:I_2$) depends on the type of solvent:

Alcoholic solvent	$H_2O:I_2 = 1:1$	(e.g. methanol)
Non-alcoholic solvent	$H_2O:I_2 = 2:1$	(e.g. dimethylformamide)

Studies by Eberius [2] showed that iodine and water react in the ratio of 1:1 if the percentage of methanol in the solvent is 20% or more. Methanol should therefore always be present in the minimum required amount . If you need to use a methanol-free titrant (for ketones or aldehydes), you can use other primary alcohols, e.g. ethylene glycol monomethyl ether.

Influence of the water content of the sample on the Karl Fischer reaction

The water content of the sample also influences the $H_2O:I_2$ molar ratio. J.C. Verhoff and E. Barendrecht [3] observed an increase in the titer with water contents greater than 1 mol/L. This, however, is not a serious limitation because the water concentration in the solvent is usually much less.

2 Fundamentals of coulometry

2.1 KF coulometry

Coulometric KF titration is based on the standard reaction equation for the KF reaction.

$$\mathrm{ROH} + \mathrm{SO_2} + \mathrm{RN} \rightarrow (\mathrm{RNH}) \cdot \mathrm{SO_3\,R}$$

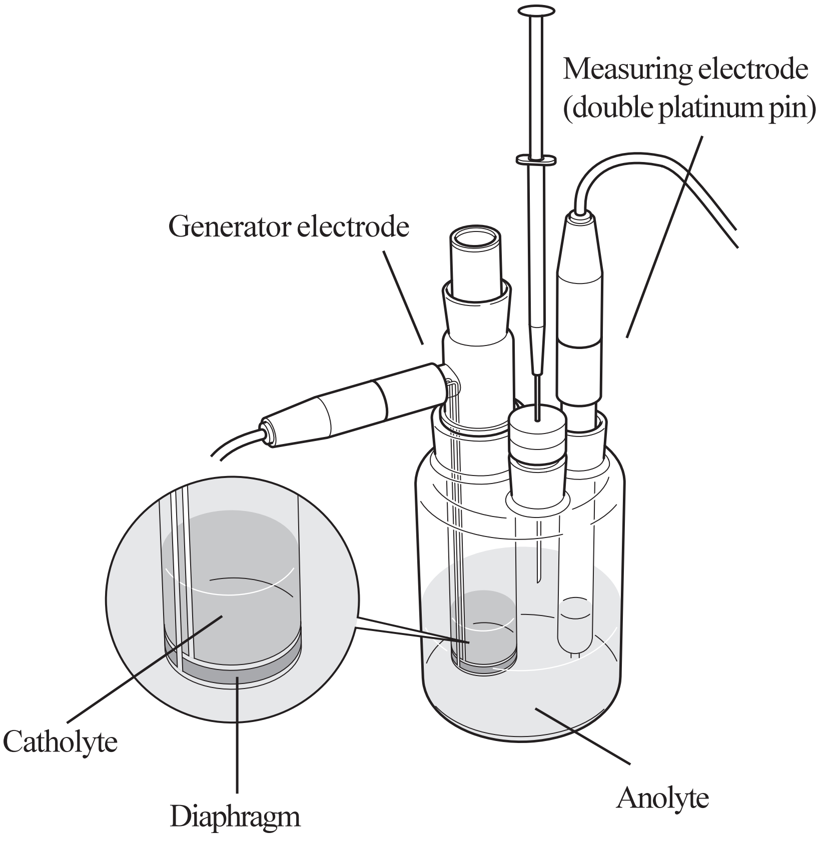
$$(\mathrm{RNH}) \cdot \mathrm{SO_3\,R} + 2\,\mathrm{RN} + \mathbf{I_2} + \mathbf{H_2O} \rightarrow (\mathrm{RNH}) \cdot \mathrm{SO_4\,R} + 2\,(\mathrm{RNH})\mathrm{I}$$

In coulometry, however, the iodine is generated electrochemically by anodic oxidation:

$$2\,\mathrm{I^-} \rightarrow \mathrm{I_2} + 2\,\mathrm{e^-}$$

Iodine generation occurs at a generator electrode* incorporated in the cell next to the measuring electrode* (a double platinum pin electrode to determine the end point) in the glass titration cell.

The titration cell consists of two parts, the anode compartment and the cathode compartment. Both parts are separated by a diaphragm.

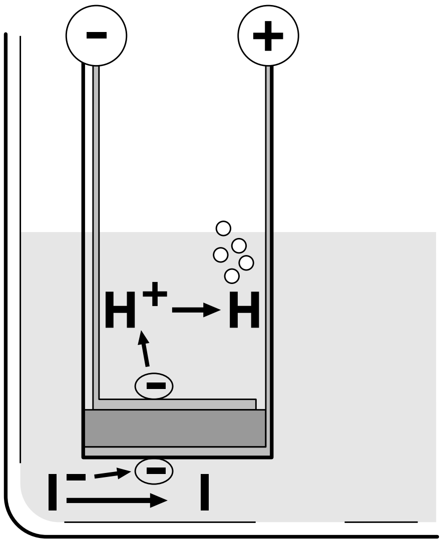


The anode compartment contains the anolyte. This consists of sulfur dioxide, imidazole and iodide. Methanol or ethanol is used as solvent. Depending on the application, other solvents such as chloroform, octanol, hexanol or ethylene glycol may be added (see Section 4.4 and Chapter 5).

The cathode compartment contains the catholyte. This is either a special reagent specific to the manufacturer, or the same reagent used in the anode compartment.

* The terms "generator electrode" and "measuring electrode" mean an arrangement of two electrodes (anode and cathode) to form an electrolytic cell.

2.2 Anode and cathode reaction



Anode reaction

At the anode, iodine is generated from iodide. The negative iodide ions release electrons at the anode and form iodine, which then reacts with water.

This is the reason why the anolyte contains iodide in addition to sulfur dioxide, imidazole and the solvents methanol or ethanol.

Cathode reaction

At the cathode, the positive hydrogen ions are reduced to hydrogen. This is the main product formed.

An ammonium salt is added to the catholyte in order to promote hydrogen production.

$$2\ [RN]H^+ \ + \ 2e^- \ \rightarrow \ H_2 \ + \ 2\ RN$$

The ammonium ions are then reduced with the formation of hydrogen and a free amine.

It is always possible that methyl sulfurous acid reaches the cathode compartment from the anode compartment. This is reduced to a sulfide (obnoxious smell!). This can cause the cathode to become black.

To avoid this, the catholyte should be replaced once a week.

2.3 Theory of coulometry

Definition Coulomb C:

One coulomb, C, is the quantity of charge that is transported by a current of 1 ampere in one second.

$$1\ C = 1\ A \cdot 1\ s$$

To produce one mole of a chemical substance that requires one electron, 96485 C are needed.

In the Karl Fischer reaction, two iodine ions with a total of two electrons are converted to iodine, that then reacts with water.

$$2\ I^- \rightarrow I_2 \rightarrow H_2O$$

Therefore 2 x 96485 C are needed for 1 mole of water, or expressed differently: 1 mg of water corresponds to 10.72 C.

In other words, the amount of iodine produced, and therefore the amount of water that has reacted with the iodine, can be calculated by measuring the current (amperes) and time (seconds). This of course assumes that the total amount of current has been used for iodine production. Since current and time are quantities that can be accurately measured, no standardization is necessary. Nevertheless we recommend that you check the coulometer regularly by measuring a standard.

Coulometry is therefore an absolute method. Due to this it is therefore often used as a reference method for the determination of water content.

2.4 Iodine generation

The iodine is generated with current pulses of 400, 200, 100 and 60 mA. The rate of iodine generation is adjusted by varying the pulse frequency and the pulse height (mA).

The maximum pulse height (400 mA) depends on the following factors:

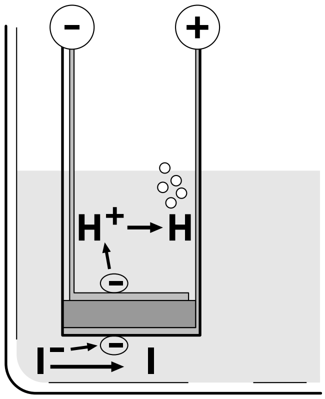
- conductivity of the anolyte
- voltage at the generator electrode
- surface of the electrode

The voltage at the generator electrode and the surface of the electrode depend on the type of coulometer. The conductivity of the anolyte is influenced by the samples and additional solvents (chloroform, hexanol, etc.).

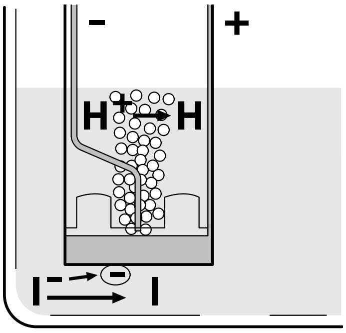
With normal conductivity, the DL32/DL39 operates with current pulses of 400 mA. This results in an iodine generation rate that corresponds to a maximum of 2100 µg water/min. Faster rates of iodine production are not possible because the current is no longer converted to iodine with 100% efficiency.

At very low conductivities (less than 10 µS/cm), the maximum possible current is 200 mA.

2.5 Generator electrode without diaphragm



with diaphragm



without diaphragm

The first commercially available diaphragmless cell for KF coulometry was introduced in 1989. The main advantages of this compared to cells with diaphragms are:

- no contamination or blockage of the diaphragm
- much easier cleaning
- lower drift

Originally, the diaphragm was made part of the generator electrode. The purpose of this was to prevent the iodine generated from being reduced back to iodide at the cathode (instead of reacting as desired with the water).

So that this cannot happen with the diaphragmless generator electrode, a different construction is used. The cathode is smaller and made in such a way that the iodine cannot reach the cathode so easily and therefore reacts beforehand with the water.

The iodine generated is distributed more rapidly by using a relatively high stirrer speed. It can then react more efficiently with the water.

The hydrogen generated at the cathode forms a film of gas on its surface. This makes it almost impossible for the iodine to reach the cathode and be reduced to iodide. This effect is further enhanced by the special geometry of the cathode.

Despite these measures, it is still possible for a very small proportion of the iodine to reach the cathode. The relative error due to this effect can be minimized by using a larger amount of sample.

In practice, the cell with diaphragm really only needs to be used for the measurement of samples of very low water content (< 50 µg water/sample) and for very accurate determinations.

Limitations for the use of the cell without diaphragm:

The cell without diaphragm is not suitable for samples that are easily reduced.

Nascent hydrogen is formed at the cathode. This is a very good reducing agent, especially for nitrocompounds, e.g. nitrobenzene.

$$\text{R-NO}_2 + 6\,\text{H} \rightarrow \text{R-NH}_2 + 2\,\text{H}_2\text{O}$$

Besides this, other easily reducible substances such as unsaturated fatty acids, etc. may also be reduced at the cathode with the formation of water.

2.6 Applications of the cell without diaphragm

The diaphragmless cell is ideal for the determination of the water content of the following compounds:

- hydrocarbons
- alcohols
- esters
- ketones (with special reagent)
- etheric oils and essences
- petroleum oils
- chlorinated hydrocarbons
- phenols (most)
- ethers
- acetamide
- edible oils

A cell with diaphragm is necessary for:

- samples of very low water content (< 50 µg water/sample)
- very accurate determinations
- nitrocompounds
- unsaturated hydrocarbons (especially when easily reducible)

3 Control / End point determination

In the same way as the addition of titrant is controlled in volumetric titration, iodine production must be precisely controlled in coulometric Karl Fischer titration. Iodine generation should be as fast as possible and must be stopped precisely at the end point. Only then can the iodine consumption and hence the water content be determined with the desired accuracy.

Control of the titration is only possible if the end point is indicated. The titration rate depends on the following factors:

- the generation of iodine
- the reaction rate between iodine and water
- the stirrer speed and distribution of the iodine generated
- the control algorithm
- the termination of the titration as soon as all the water has reacted with the iodine.

3.1 Indication

3.1.1 Principle of bivoltametric indication

Coulometric Karl Fischer titration uses a bivoltametric indication (in electrochemical terminology this is also called "2-electrode potentiometry").

A small current - the polarization current (Ipol) - is applied to a double platinum pin electrode, for example 2 µA.

The DL32/DL39 uses direct current polarization.

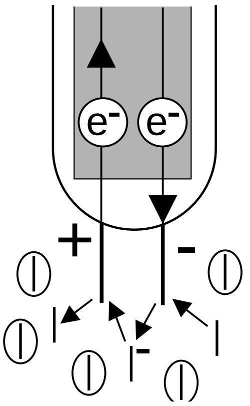
At the beginning and during the titration:

As long as the iodine generated reacts with the water, there is no free iodine in the anolyte. A voltage of 400 mV to 500 mV is necessary to maintain the preset polarization current at the electrode.

At the end of the titration:

As soon as all the water in the sample has reacted with the iodine, free iodine is present in the anolyte solution. This free iodine gives rise to "ionic conduction". Now, only a significantly lower voltage of 50 mV to 100 mV is needed to keep the polarization current constant. This drop in voltage is used to indicate the end of the titration.

"Ionic conduction"



With "ionic conduction", the iodine takes up an electron at the negatively charged platinum pin and is thereby reduced to iodide (I^-). The iodide, which is present in excess in the anolyte solution, then releases the electron again at the positively charged platinum pin and is again oxidized to iodine.

Stirrer speed

Very good mixing of the titration solution is necessary in order to achieve constant "ionic conduction". The iodine is present only at low concentration in the anolyte. If mixing is poor, no iodine reaches the negatively charged platinum pin. This leads to a termination of "ionic conduction" and the measurement signal becomes very unstable.

3.1.2 End point and polarization current

The Karl Fischer titration is terminated when free iodine is detected in the anolyte, i.e. the titration end point is reached when the potential at the polarized double platinum pin electrode drops below a certain value. This value of the end point depends mainly on the polarization current but also in certain cases on the type of electrode and anolyte used.

(Double platinum pin electrode; pin length: 3 - 4 mm, pin diameter: 1 mm).

Polarization current	End point
0.5 - 2 µA	100 mV
5 µA	150 mV

The same end points can be used for ethanol-based reagents.

With anolytes for ketones, in which methanol is replaced by 2-methoxyethanol, use end points about 20% higher.

What polarization current should be used?

The higher the polarization current, the greater the excess of iodine (yellow coloration of the anolyte) there has to be for "ionic conduction" to begin and so enable the end point to be determined. The aim of the Karl Fischer titration is to work with an iodine excess that is as low as possible. The value of the polarization current should therefore be set as low as possible.

On the other hand, the smaller the polarization current, the smaller and steeper the potential jump at the end of the titration. This makes it more difficult to stop the titration at the right moment and increases the risk of overtitration.

The DL32/DL39 were optimized for a polarization current of 2 µA.

Influence of the electrode

The potential jump at the end of the titration also depends on the surface of the electrode.

Electrodes with a larger platinum surface area, e.g. longer pins, double ring or plates instead of pins, exhibit a smaller potential jump and the end point is somewhat lower.

The larger the platinum surface, the smaller the current density

The current density can be compared to a water pipe through which a certain amount of water has to flow. The larger the diameter of the pipe, the lower the pressure needed to transport the desired amount of water through the pipe (= smaller pressure difference).

Electrodes with very short platinum pins (< 3 mm = lower platinum surface area) exhibit a large potential jump and also a higher end point.

The condition of the electrode has an influence on the potential jump

After long use, a layer is formed on the surface of the platinum pin electrode (an iodine-platinum complex). This increases the electrode resistance. With used electrodes, this causes a larger potential jump compared with an electrode that has been cleaned or a new electrode (without layer). The layer is formed during the first ten titrations and then remains constant.

Example:

Potential in the anolyte without excess iodine (polarization current: 2 µA; anolyte: Coulomat AG)

New or cleaned platinum pin:	330 mV
After about eight titrations:	450 mV

The potential then remains constant.

3.2 Reaction rate and iodine production

The reaction rate of the Karl Fischer titration depends on:

- the water concentration
- the sulfur dioxide concentration
- the iodine concentration
- the pH value of the solution (see Chapter 1)

$$-d[I_2] / dt = k \cdot [I_2] \cdot [SO_2] \cdot [H_2O]$$

For the titration this means:

At the beginning, when the water content is high, the reaction rate is also high. Iodine generation can proceed rapidly because the iodine produced immediately reacts with the water.

Toward the end of the titration, when the water concentration is lower, the reaction rate also decreases; the iodine must be generated more slowly because only a small amount of water is still present that can react with the iodine. Iodine generation is usually the rate determining factor.

In the anolyte there is a large excess of sulfur dioxide. Sulfur dioxide is however consumed with each additional sample measured. The sulfur dioxide concentration in the anolyte therefore slowly decreases. This leads to lower reaction rates with anolytes that have been used a lot.

3.3 Control of the titration

With the DL32/DL39 Karl Fischer coulometers, iodine generation is controlled in the conventional way. The rate of iodine generation is proportional to the distance from the end point, i.e. the closer the end point, the slower the generation of iodine.

The iodine is generated with pulses of 400, 200, 100 and 60 mA. Variation of the pulse length (time), pulse frequency and pulse height (mA) are used as control parameters.

The control system provides three different control modes for iodine generation

Slow:

Suitable for samples of very low water contents (less than 50 µg water per sample).

Iodine generation is very cautious, i.e. the maximum iodine generation rate is 144 µg/min.

Normal:

Suitable for medium water contents (50 - 1000 µg water per sample)

Initially, iodine generation is also cautious so that low water contents can also be accurately determined in this mode. The first 30 µg water are measured in the slow mode; iodine generation is then increased to the maximum rate in about 10 seconds (corresponding to 2100 µg water/min).

Fast:

Suitable for very high water contents (over 1000 µg water per sample)

Iodine generation is immediately increased (within about 5 seconds) to the maximum rate (corresponding to 2100 µg water/min).

3.4 The termination parameters

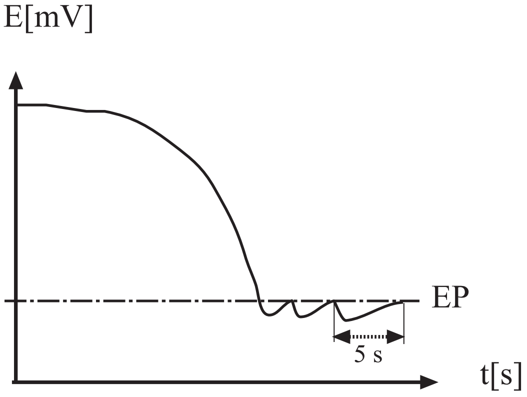
The DL32/39 Karl Fischer coulometers have four different termination criteria:

- Delay
- Absolute drift stop
- Relative drift stop
- Maximum titration time

3.4.1 Delay

With this termination criterion, the titration is terminated as soon as the potential remains below the end point for a defined period of time (e.g. 5 s) following the addition of an increment of iodine. The increment (= smallest increment) must be set sufficiently large to compensate the drift, otherwise the termination criterion is never satisfied and an infinite titration results.

Since with the DL32/DL39, the smallest increment is set to 0.1072 mC (corresponds to 0.01 µg water), the delay time has to be adapted to the drift.



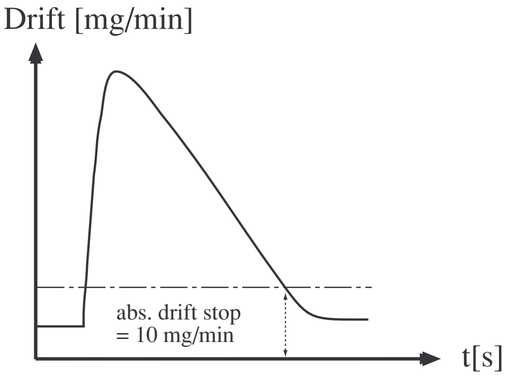
Typical delay time: 5 seconds

Advantage: well-known method

Disadvantage: the delay time has to be adapted to the initial drift.

3.4.2 Absolute drift stop

The titration is terminated as soon as the actual drift drops below the absolute drift value defined. The value of the absolute drift stop must therefore be greater than the initial drift, otherwise the termination criterion will never be satisfied and an infinite titration results.



Typical value for the absolute drift stop: 20 µg/min

Advantage: method is easily understood

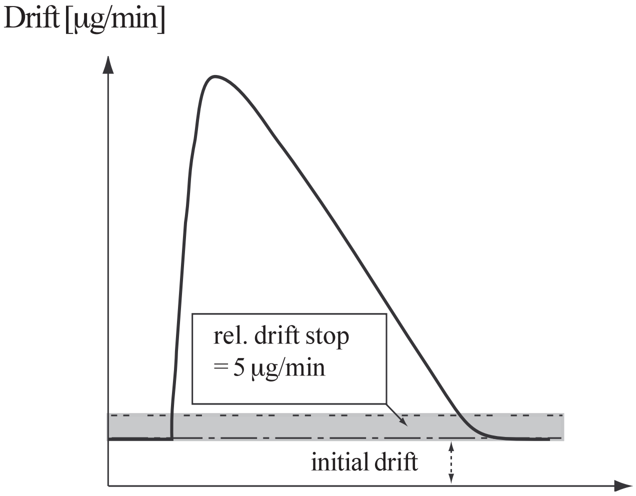
Disadvantage: the value for the absolute drift stop has to be adapted to the initial drift.

3.4.3 Relative drift stop

The titration is terminated as soon as the actual drift drops below the sum of the initial drift (the drift before titration) and the relative drift.

Typical value for the relative drift stop: 5µg/min

Advantage: independent of the initial drift



3.4.4 Maximum titration time

After the defined time has elapsed, the titration is terminated and the result is printed.

DL32/DL39 Karl Fischer coulometer: a maximum titration time of 0 seconds means that this termination criterion is not active.

3.4.5 Application of the various termination criteria

Relative drift stop for trouble-free, soluble samples

The relative drift stop is independent of the initial drift. This is why this termination criterion is the simplest and most universal to use. The value of the relative drift stop influences the reproducibility and the titration time.

- Drift stop (low value) → better reproducibility → long titration time
- Drift stop (high value) → poorer reproducibility → short titration time

Maximum titration time for samples whose water contents are determined with the drying oven

When using the drying oven, the drift at the end is often greater than the initial drift. The reason for this is either a very slow release of the last traces of water or a slow thermal decomposition of the sample. The vaporization of water is also irregular in the final stages, so that the reproducibility of the titration termination using drift stop is poor.

In practice, therefore, the maximum titration time has proven to be best termination criterion. It gives you the best accuracy and repeatability of results.

3.5 Autostart

With the DL32/DL39 KF coulometers there are two ways to start a titration.

Manual start ("Autostart: No")

The titration of a sample is started with the RUN key. The sample is added and the addition then confirmed by pressing the RUN key.

The first time you press the RUN key, the standby titration is stopped and measurement of titration time begins. The titration time is used for drift compensation in the calculation of the result.

Autostart ("Autostart: Yes")

The titration of a sample is started with the RUN key. The sample is then added. This causes the potential to jump suddenly. The coulometer detects this increase in potential and starts the titration. If a sample is not added within 30 seconds of pressing the RUN key, the coulometer returns to the standby titration state.

The Autostart has been optimized so that the coulometer can also detect the increase in potential caused by the addition of samples with very low amounts of water (down to 10 µg water).

Note

With very high drifts (>10 µg/min), the increase in potential is relatively steep so that the coulometer could interpret this as the addition of a sample and then start the titration without in fact a sample having been added.

To prevent this, the DL32/DL39 KF coulometers blocks an Autostart when the drift is >10 µg/min. The error message appears: "Drift too high for Autostart".

General

To obtain accurate and reliable results, you should only work with the coulometer when the drift is less than 10 µg/min. If the drift is greater than 10 µg/min, you should take measures to reduce the drift. See Chapter 7.

4 The Karl Fischer titration

Various factors must be taken into account with Karl Fischer titration to obtain correct results. The factors include:

- the atmospheric humidity
- the working medium (the anolyte)
- the pH value of the sample
- the side reactions between the sample and the Karl Fischer reagent

4.1 The influence of atmospheric humidity (drift determination)

Atmospheric humidity is the biggest single cause of error in Karl Fischer titration. Moisture can enter the sample, the titrant and the titration stand. This problem is particularly common in tropical climates or in coastal regions, where the relative humidity can be more than 80%.

The assumption that air-conditioned rooms have a lower atmospheric humidity is often not true: the majority of air-conditioning systems simply cool the air. However, since cold air cannot absorb as much moisture, the relative humidity increases. The higher the atmospheric humidity in the laboratory, the greater its influence on the results of the Karl Fischer titration. The air-conditioning system should therefore be equipped with a moisture condenser.

The Karl Fischer titrator should never be installed near a ventilator of the air conditioning system!

4.1.1 Titration stand

The titration stand must be sealed as tightly as possible against atmospheric moisture. The following rules should be observed:

1. Close all openings in the titration stand.
2. Condition the titration cell before use.

   When you assemble the titration stand for the first time, there will be moisture on the glass surface of the titration cell and the inserts. The air inside the titration vessel also contains moisture. After the anolyte has been added, it is titrated to dryness during pretitration, i.e. until it is absolutely free of water. The drift, however, remains high because the moisture present on the glass walls and the air in the titration cell diffuse only slowly into the anolyte. This can take 1 - 3 hours. You can titrate the total moisture more quickly by moving the vessel from side to side gently so that solvent swirls up the side of the vessel to pick up moisture adsorbed on the glass walls. Try to avoid shaking so vigorously that solvent gets on the injection part. The residual moisture then dissolves more rapidly in the anolyte.

   KF Coulometer DL32/DL39: After shaking three to four times (with intervals of 3 - 5 minutes) a stable drift 2 µg/min is obtained after only 15 minutes.
3. Protect the titration cell with a desiccant (molecular sieves 3Å and silica gel).

   The desiccant absorbs the moisture and protects the titration cell against the ingress of moisture. The drying capacity of the desiccant is limited; it depends on the humidity and can be exhausted after 2 - 4 weeks (silica gel turns red).

   Silica gel can be regenerated at 150 °C and molecular sieves at up to 300 °C.

4.1.2 The drift

No titration stand is completely water tight; minute traces of water will always find a way into the titration stand.

The quantity of water that enters the titration stand over a defined period, t, is referred to as the drift and is given in µg water/minute.

The titration cell of the DL32/DL39 KF coulometers is extremely well sealed. The normal value for the drift is 1 - 2 µg water/minute.

In the standby-titration, the DL32/DL39 KF coulometers continuously titrate the water that diffuses into the cell and continuously display the drift value. Different arrows show whether the drift value is increasing or decreasing or whether it is stable. At the start of a sample titration, the last measured drift value is automatically taken over. This value is used in the calculation of the result.

Result = amount of water determined - (drift • titration time).

For accurate results, the drift value should therefore be as low as possible and stable before the start of a titration!

4.2 The electrolytes

4.2.1 Filling the titration cell

Titration cell with generator electrode with diaphragm

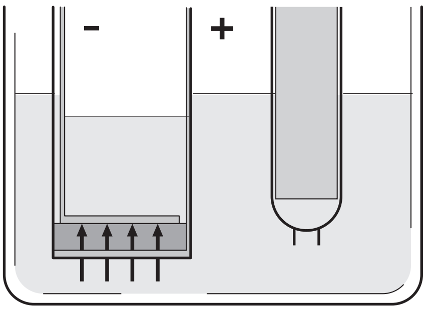
First transfer 5 mL catholyte to the cathode compartment. Take approx. 5 mL from the bottle with a syringe and inject it into the generator electrode or empty an ampoule of catholyte into the generator electrode.

Then fill the anode compartment with approx. 100 mL anolyte. Make sure that the level of the anolyte is approx. 3 - 5 mm higher than that of the catholyte. The catholyte always contains traces of water. If the level of the catholyte is the same or higher, a flow occurs from the cathode compartment to the anode compartment; the moisture enters the diaphragm and is slowly released in the anode compartment, which leads to a higher drift. This can be avoided as follows:

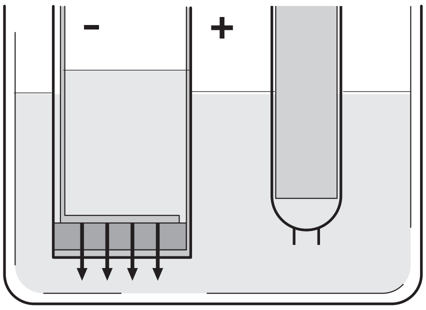
a) The catholyte can be dehydrated with a few drops of a single component volumetric KF titrant.

b) By ensuring that the level of the anolyte is higher.

Level of the anolyte higher:
→ drift is low



Level of the anolyte lower:
→ drift is high



The difference in level between the anolyte and catholyte is maintained as long as the stirrer is in operation. As soon as the stirrer is switched off, the levels slowly become the same.

When a sample is injected into the anode compartment, the level of the anolyte becomes higher again. However, when the drying oven is used, the level of the anolyte drops due to evaporation. In this case, the anolyte should be topped up from time to time with anhydrous methanol or fresh anolyte.

Titration cell with diaphragmless generator electrode

Pour approx. 100 mL electrolyte solution (anolyte) into the titration cell.

The generator electrode should dip approx. 2.5 cm into the electrolyte solution.

Note:

In production, some anolytes are given an excess of iodide and the solution is colored brown. Normally this brown coloration disappears on filling the titration cell because the iodine excess is consumed. If this is not the case, you must add some moist methanol or sample so that the color changes to yellow.

4.2.2 When do you have to replace the electrolyte?

The electrolyte must be replaced in the following situations:

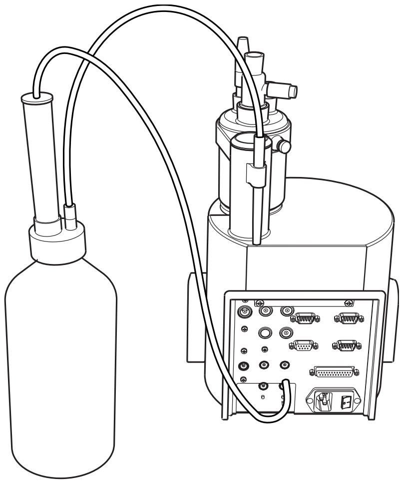
- If the capacity of the electrolyte is exceeded.
  With anolytes (100 mL) after 1000 mg water, with catholytes (5mL) after 200 mg water. This is monitored by the DL32/DL39 KF coulometers.
- If after adding samples, the level of the anolyte exceeds the 150 mL mark.
  The higher the level in the anode compartment, the worse the stirring efficiency and the risk of over titration increases.
- If the conductivity of the anolyte drops below 10 µS.
  This can happen if large amounts of samples of low conductivity are titrated.
- If an emulsion forms in the anode compartment.
  With poorly soluble samples, the dissolving power of the anolyte is exhausted and an emulsion is formed. This can lead to wrong results (see Section 4.4).
- If the drift is too high.
  If an electrolyte is used for a long period without replacement, the drift slowly increases.
- After being used for a week.
  In the cathode compartment sulfides and mercaptans are formed that lead to an obnoxious smell and a higher drift (see Section 2.2).

In practice, when using a generator electrode with diaphragm, it is usual to replace both the anolyte and catholyte at the same time.

4.2.3 Emptying the titration cell

The easiest way to empty the titration cell is to use the suction bottle supplied as standard with every DL32/DL39 KF coulometer.

Connect the suction bottle to the pump and press the pump button. Lead the suction tube into the anode and cathode compartments and suck out the electrolyte. Starting the pump automatically resets the electrolyte capacity to zero.



Note:

The electrolyte should be sucked out as rapidly as possible so that as little moisture as possible enters the titration cell.

4.3 Cleaning the titration cell

From time to time, the titration cell and both electrodes should be cleaned, especially if dirty samples are analyzed.

The generator electrode with diaphragm must be cleaned periodically because contamination accumulates in the diaphragm over a longer period of time. This ultimately leads to a higher drift. The contaminants can originate from samples or are side products that have been formed in the cathode compartment through reduction (see Section 2.2).

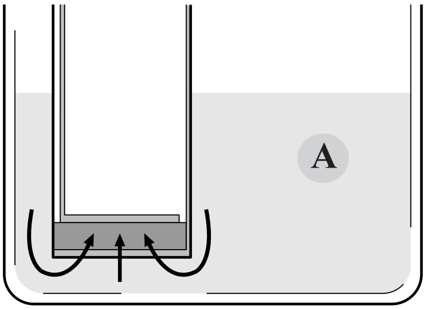
4.3.1 Cleaning the titration vessel

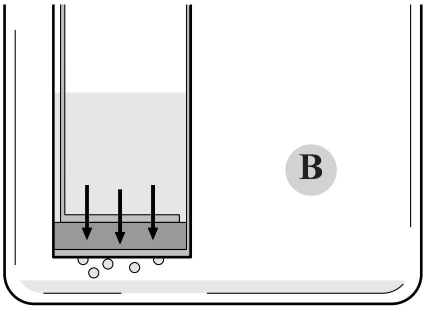
You can clean the titration vessel itself with water or a suitable solvent. Afterward, dry the vessel in a drying oven at 100 °C or with a hot air drier. If you want to use the titration vessel immediately, you can rinse it with anhydrous methanol.

4.3.2 Simple cleaning and drying of the generator electrode

Method A:

Place the empty generator electrode in anhydrous methanol. The methanol flows through the diaphragm into the cathode compartment. Moisture and contaminants are rinsed out of the diaphragm.





Method B:

Fill the generator electrode with anhydrous methanol. The methanol flows through the diaphragm and rinses out moisture and contaminants.

This cleaning procedure should be repeated at least once.

Afterward you can dry the generator electrode in a drying oven at max. 50 °C or with a hot air drier. If you use the generator electrode immediately, drying is not necessary.

4.3.3 Thorough cleaning of the generator electrode

If the generator electrode and the diaphragm are badly contaminated, the most effective cleaning agent is chromic acid. The procedure is the same as described above. Place the empty generator electrode in the chromic acid or fill the generator electrode with chromic acid and let it flow through.

Afterward, thoroughly rinse the generator electrode with water, then with anhydrous methanol and dry it as described above.

4.3.4 Cleaning the measuring electrode

Normally the measuring electrode does not need cleaning.

As has already been described in Section 3.2.1, in the first few titrations, a layer is formed (platinum-iodine complex) on the platinum surface, which causes the potential jump to increase. The layer should therefore not be removed by cleaning.

In some cases, samples may be deposited on the polar surface of the electrode. The resistance of the electrode is then greatly increased, which prevents good indication of the end point. This also becomes noticeable through a dark coloration of the anolyte at the end point. In this case, the measuring electrode must be cleaned.

A) Clean the platinum pin with a paper tissue. This is sufficient in most cases.

B) With very heavily contaminated electrodes, place the measuring electrode in 0.5 mol/L sulfuric acid and pass a current of about 400 mA for 60 seconds across the platinum pins (start the KF titration). For this disconnect the S7 connection of the indication electrode and connect the S7 connection of the generator electrode with the indication electrode. Reset the titrator when the titration series is finished so that the polarization current at the indication electrode is stopped. Like this cleaning has to be done less frequently.

4.4 Reagents and solvents

To determine its total water content, the sample must completely dissolve in the anolyte. If the sample does not completely dissolve, an emulsion is formed. In this case, part of the water content is not measured, i.e. the water content determined is lower than the actual water content of the sample.

This means that if an emulsion is formed in the anolyte, the anolyte must be immediately replaced.

A number of different anolytes are available to dissolve the various types of samples encountered in practice. Alternatively, more solvent can be added to the anolyte

4.4.1 For samples soluble in methanol or ethanol

These include: hydrocarbons (to C_{10}), chlorinated hydrocarbons (to C_{10}), alcohols, ethers, esters, nitrocompounds, acetamide, etc.

For cells with diaphragm:

Methanol-based reagents:	anolyte:	HYDRANAL® Coulomat AG (Riedel-de Haën)
		APURA combiCoulomat frit (MERCK)
	catholyte:	HYDRANAL® Coulomat CG (Riedel-de Haën)
		APURA combiCoulomat frit (MERCK)
Ethanol-based reagents:	anolyte:	HYDRANAL® Coulomat E (Riedel-de Haën)
	catholyte:	HYDRANAL® Coulomat E (Riedel-de Haën)

For cells without diaphragm:

Methanol-based reagents:	electrolyte:	HYDRANAL® Coulomat AD (Riedel-de Haën)
		APURA combiCoulomat fritless (MERCK)

4.4.2 For samples poorly soluble in methanol or ethanol

These include: etherial oils, edible oils, ointments, hydrocarbons (C_{10} to C_{20}), etc.

Octanol or hexanol can be added to the anolyte to improve the solubility of these samples. This is limited to a maximum of 30% to prevent the conductivity from falling too low.

For cells with diaphragm:

Methanol-based reagents:	anolyte:	HYDRANAL® Coulomat AG-H (Riedel-de Haën)
		contains approx. 30% hexanol
		APURA combiCoulomat frit (MERCK)
		+ 30% hexanol
	catholyte:	HYDRANAL® Coulomat CG (Riedel-de Haën)
		APURA combiCoulomat frit

For cells without diaphragm:

Methanol-based reagents:	electrolyte:	HYDRANAL® Coulomat AD (Riedel-de Haën)
		+ 20% hexanol
		APURA combiCoulomat fritless (MERCK)
		+ 20% hexanol

4.4.3 For samples insoluble in methanol or ethanol

These include: petroleum oils, transformer oils, silicone oils, hydrocarbons (above C_{20}), etc.

Chloroform must be added to the anolyte to ensure the solubility of these samples. This is limited to a maximum of 30% in order to prevent the conductivity from becoming too low.

For cells with diaphragm:

Methanol-based reagents:	anolyte:	HYDRANAL® Coulomat A (Riedel-de Haën) + 20% chloroform HYDRANAL® Coulomat AG (Riedel-de Haën) + 30% chloroform APURA combiCoulomat frit (MERCK) + 30% chloroform
	catholyte:	HYDRANAL® Coulomat CG (Riedel-de Haën) APURA combiCoulomat frit (MERCK)

For cells without diaphragm:

Methanol-based reagents:	electrolyte:	HYDRANAL® Coulomat AD (Riedel-de Haën) + 30% chloroform APURA combiCoulomat fritless (MERCK) + 30% chloroform

4.4.4 For ketones and aldehydes

Ketones and aldehydes react with methanol to form a ketal, or an acetal, with the formation of water.

Acetal formation: $CH_3COH + 2\ CH_3OH \rightarrow CH_3CH(OCH_3)_2 + H_2O$

Ketal formation: $(CH_3)_2CO + 2\ CH_3OH \rightarrow (CH_3)2C(OCH_3)_2 + H_2O$

Special methanol-free reagents must be used for these substances.

For cells with diaphragm:

Methanol-free reagents:	anolyte:	HYDRANAL® Coulomat AK (Riedel-de Haën)
	catholyte:	HYDRANAL® Coulomat CG-K (Riedel-de Haën)

For cells without diaphragm:

Methanol-free reagents:	electrolyte:	HYDRANAL® Coulomat AK (Riedel-de Haën)

Notes on ketones:

- When changing from normal KF anolytes to ketone reagents, the entire titration cell must be thoroughly cleaned because even traces of methanol can cause serious interference.

  If you measure ketones regularly, we recommend the use of a second titration cell.
- If you have titrated a number of ketone samples, the drift is higher because of the very slow side reaction. After a longer standby period, it is possible that the anolyte is exhausted after a few days even though no further titrations have been performed.

- Choose relatively small samples (approx. 1 mL); with reactive ketones such as cyclohexanone use only 0.2 mL to 0.5 mL. The larger the sample, the more important the effect of side reactions becomes, i.e. the drift increases from sample to sample so strongly that the determination of the endpoint becomes difficult.
- The special reagent for ketones can also be used for other samples. It is important to note that alcohols that react with ketones should not be titrated in this reagent.

Notes on aldehydes:

- Short chain aldehydes (e.g. acetaldehyde) are oxidized at the anode with the formation of water. Coulometric KF titration cannot be used to determine these compounds; the substances can, however, easily be measured with volumetric KF determination.
- Aromatic aldehydes (e.g. benzaldehyde) can also be determined by coulometric KF titration. It should be noted that the bisulfide-addition reaction is very strong with aromatic aldehydes. This is why one should wait for the reverse cleavage reaction of the bisulfide compound before aborting the titration (ensure that the drift drops down again to the initial value).

4.4.5 For acids and bases (pH value)

A noisy titration or a sluggish end point can indicate a pH shift. In these cases the pH value of the anolyte should be measured.

Measure the pH with a glass electrode adjusted with aqueous buffers. To do this, take an aliquot of anolyte from the titration cell. The measurement should not be performed in the titration cell because the electrode introduces too much water.

Measurement with moistened indicator paper also gives an approximate indication of the pH value of the anolyte.

With Karl Fischer titrations of acidic and basic samples, the pH value of the anolyte must be adjusted to the range 5.5 to 7 (see Section 1.2).

For acidic samples, e.g. acetic acid, formic acid, etc.:

Use the HYDRANAL® buffer (Riedel-de Haën). The use of imidazole leads to a high pH value in the anolyte.

Fill the anode compartment with approx. 80 mL of anolyte and 20 mL HYDRANAL® buffer.

For basic samples, e.g. amines:

Basic samples must be neutralized with salicylic acid or benzoic acid.

Fill the anode compartment with approx. 90 mL of anolyte and 5 g salicylic acid or benzoic acid.

4.5 Sampling

4.5.1 Taking the sample

When taking samples for water determination, you must be extremely careful to exclude atmospheric moisture - the most common source of error. If the water content of a sample changes during sampling due to moisture being absorbed or desorbed, you will no longer be able to determine its true water content.

"An analysis cannot be better than the actual sample!"

When taking samples, you should pay attention to the following points:

1. The sample must contain the same average amount of water as the material as a whole.
2. The sample should be taken quickly to exclude, or at least minimize, the absorption or release of moisture.
3. Heterogeneous water distribution in samples:
   In non-polar liquids, e.g. oils, the water is not uniformly dispersed. It floats on the surface or sinks to the bottom. Liquids of this type must be thoroughly mixed (by shaking) before a sample is taken.
4. Hygroscopic solids may exhibit a higher water content on the surface than inside if they have absorbed atmospheric moisture during storage.
5. Substances of very low water content are always very hygroscopic. Sampling must be done very quickly and with a perfectly dry syringe.

4.5.2 Storing the sample

After you have taken the sample, you should determine its water content as soon as possible. If you have to store the sample, keep it in a tightly sealed bottle.

- Glass bottles are preferable to plastic bottles because plastic is not completely water vapor-tight.
- Use sample bottles with openings that are as small as possible in order to minimize the ingress of moisture. Use bottles with a septum stopper for liquids of very low water content.
- Use a bottle whose volume is optimum for the amount of sample: the smaller the gas space above the sample, the lower the amount of moisture.
- With liquid samples, rinse the bottles two or three times with the sample itself beforehand.

With samples in which the water is not dissolved, e.g. oils, the water can separate out if the sample is left to stand for a long time. This is also possible when a sample cools and the solubility limit for water is exceeded. In such cases you can stabilize the solution with a solubility promoter, e.g. 2-propanol.

4.5.3 Amount of sample

The amount of sample used depends on the water content expected and the desired accuracy.

The optimum amount of water is 0.5 to 2 mg water per sample.

In trace analysis, reproducible results can be obtained even with 0.1 mg water per sample. Under optimum measurement conditions, 10 μg water can be detected if no great demands are placed on reproducibility.

In general, accuracy is greater with larger sample amounts because the absorption of atmospheric moisture during sampling or sample addition becomes less important relatively (see also Chapter 6).

For optimum accuracy with determinations in the range 1 ppm to 1% water, you should use the minimum sample weights given in the table below:

Water content [ppm]	1	10	50	100	500	1000	5000	1%
Minimum sample weight [g]	10	8	5	4	2	1	0.2	0.1
Amount of water [mg]	0.01	0.08	0.25	0.4	1.0	1.0	1.0	1.0

4.5.4 Sample addition

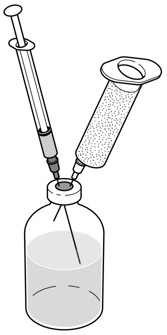
When adding liquid samples, you must take suitable precautions to prevent atmospheric moisture from being absorbed, especially if the samples have a low water content. The following procedures are suitable for the different types of liquid sample:

hygroscopic	e.g. methanol, hexane, toluene, benzene, edible oils. Inject the sample using a 1-mL or 10-mL syringe through a septum cap.
thick, viscous	e.g. glycerol, hydraulic oils, silicone oil, massage oil Inject the sample using a 5-mL or 10-mL syringe with a thick needle into the titration cell. Possibly warm the sample slightly to lower the viscosity.
very viscous	e.g. ointments, creams Fill the sample into a 5-mL or 10-mL syringe from behind and inject it into the titration cell using a wide-bore needle.
waxy	e.g. candles, paraffin, ski wax, suppositories Liquefy the sample in a drying oven at approx. 50 °C and fill it into a syringe. The syringe is heated together with the wax. This prevents the sample from solidifying in the syringe during the weighing.

Taking samples from a bottle with septum stopper

After several samples have been taken, a vacuum develops in the bottle with septum stopper and it will no longer be possible to take a sample. To avoid this, you must aerate the bottle with dry air (equalize the pressure).

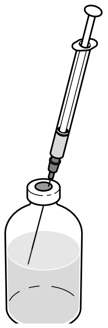
Fill a syringe without a plunger with molecular sieves, seal it with cotton wool and insert it into the septum bottle using a short needle. Air flows over the molecular sieves into the bottle when you take a sample.



Sample addition of liquids with the back weighing technique

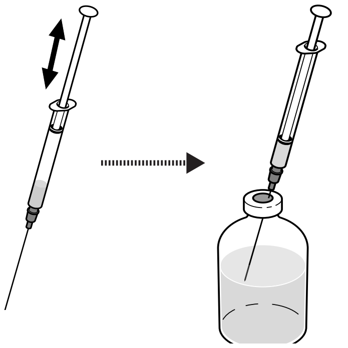
Fill the syringe to a quarter with sample. If the sample is hygroscopic or has a low water content (< 1000 ppm), use bottles with a septum stopper and pressure equalization

Withdraw the plunger and rinse the syringe with the sample by shaking it.

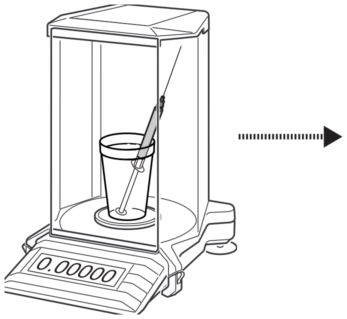


Empty the syringe (into the waste bottle) and repeat the rinsing two or three times.

Fill the syringe with sample and wipe the needle with a paper tissue.



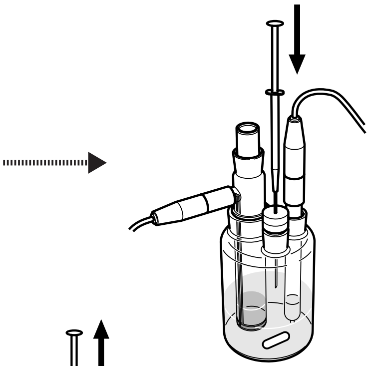
Place the syringe (upside down) in a beaker on the balance pan and tare the balance to "0".



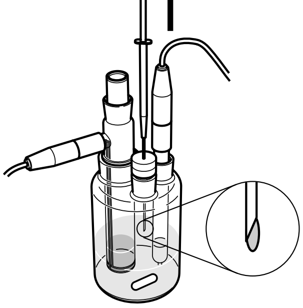
Start the titration method

Press the <RUN> button

Inject the sample into the titration cell through the septum stopper.



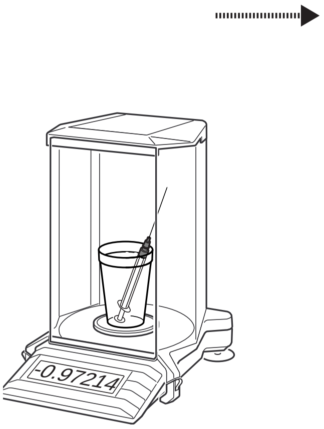
Withdraw the plunger so that the drop at the tip of the needle is sucked back into the needle. Otherwise when the syringe is removed, the drop will adhere to the septum.



Replace the syringe with the remainder of the sample on the balance and back weigh it.

Enter the weight in the titrator or transfer it automatically.

Start the titration.



5 Solid samples

It is not possible to titrate solid samples directly using KF coulometry - when the titration cell is opened to add the solid sample, about 50 - 100 µg water enter the anode compartment, depending on the ambient humidity. With an optimum sample weight of 1 mg water/sample, this would lead to an error of 5% to 10%. For this reason, other methods have to be used for solid samples.

Other possible methods are:

- External extraction
- External dissolution
- Drying oven

5.1 External extraction

External extraction is used for insoluble solids.

Definition of external extraction:

Extraction of a sample with a defined quantity of solvent of known water content.

The solvents used are:

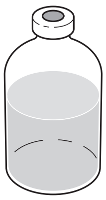
- methanol	for insoluble organic solids
- formamide	for natural substances (almonds, pepper, curry) and dehydrated products
- chloroform	for sugar (surface water)

Pure solvents can be used for the extraction. They do not have to contain methanol.

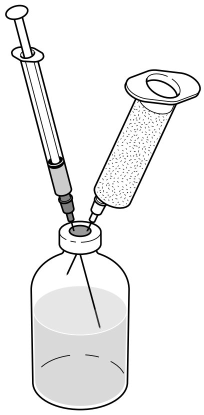
5.1.1 Performing an external extraction

The external extraction is carried out in four steps.

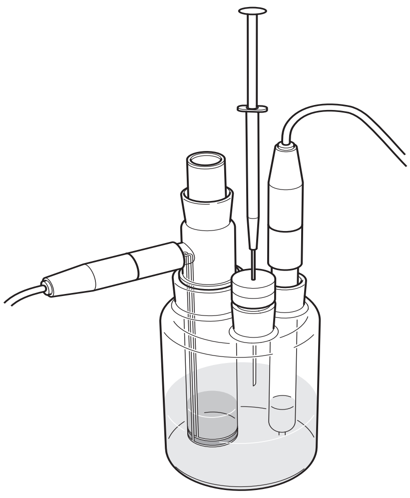
Step 1: Blank value determination



Solvent in
septum bottle



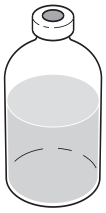
Take a sample of
solvent



Determine the water content
of the solvent
= blank value (f1)

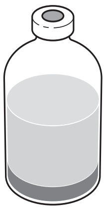
- The water content of the solvent must be much less than that of the sample.
- Pay attention to the water capacity of chloroform (max. 350 ppm) and toluene (max. 600 ppm).
- Provide sufficient solvent for the blank value determination so that enough solvent is available for the extraction.

Step 2: Weigh-in solvent and sample



Weigh solvent
= (**f2**)

Add sample

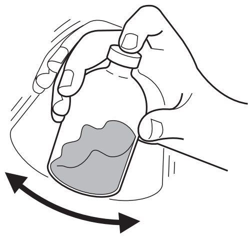


Weigh sample
= (**f3**)

- Cut the sample into small pieces so that it releases its water more quickly and efficiently.

- Add sufficient sample. The larger the sample, the smaller the relative error because the total error is calculated with the sample weight.
  A dilution factor of 10 - 20 is normally used.

Step 3: Extraction

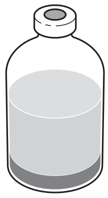


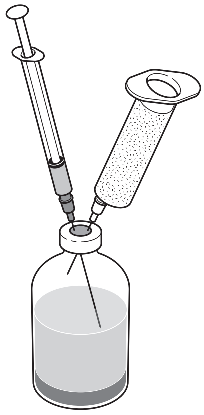
Shake, ultrasonic bath with heating or homogenizer

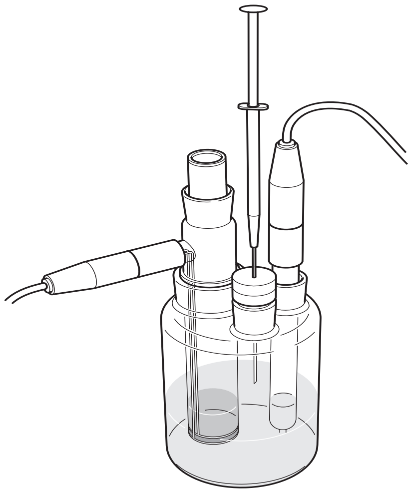
Shaking is the method usually used for extraction. A mechanical shaker is normally used because the extraction time is often long (two hours or overnight).

For the extraction of tablets, the addition of dry quartz sand has proven useful for improving and speeding up the extraction.

Step 4: Allow to settle, take aliquot and titrate


Allow to settle


Take aliquot of the extraction solution


Titrate sample

5.1.2 Calculation of the external extraction

The following equation is used to calculate the water content of the extracted sample:

$$\text{Water content [ppm]} = \frac{100}{100-x}\left[x \cdot \frac{f2}{f3} - \frac{f1 \cdot f2}{f3}\right]$$

x: water content of the aliquot of the supernatant extraction solution [ppm]

f1: blank value (water content) of the solvent [ppm]

f2: amount of solvent [g] after determining the blank value

f3: amount of sample [g] extracted with the solvent

DL39:

The equation for the calculation of the water content of the extracted sample is stored in the titrator. In the method you have to add the following information:

- select "x [ppm]ext.extr." or "x [%]ext.extr." as the result for "Calculation 1", and enter the blank value of the solvent for the factor (**f1**) .

  (Note: Enter the blank value in the units selected for the result.)
- select "No calculation" as the result for "Calculation 2", and enter the amount of solvent for the factor (**f2**)
- select "No calculation" as the result for "Calculation 3", and enter the amount of sample extracted for the factor (**f3**)

Example:

Sample	Result	srel	Solvent
sucrose (surface water)	72 ppm	4.2%	chloroform

5.2 External dissolution

External dissolution is used for soluble solids or for samples of high water content.

KF coulometry is however not suitable for samples with water contents of 10% to 100% because a very small amount of sample would have to be used. The sample is effectively diluted through external dissolution so that a larger amount of sample can be used.

Definition of external dissolution:

Dissolve a sample in a defined amount of solvent of known water content.

The following solvents are used:

- methanol for organic solids
- formamide for sugar products
- chloroform for petroleum oils and adhesives
- toluene for tar, waxes and suppositories

Pure solvents can be used to dissolve the samples; the addition of methanol is not necessary.

The method corresponds to external extraction except that the sample dissolves completely in the external solvent which means that a different equation for the calculations must be used:

$$\text{Water content [ppm]} = x \cdot \left(\frac{f2 + f3}{f3}\right) - \left(\frac{f1 \cdot f2}{f3}\right)$$

x: water content of the aliquot of the external solution [ppm]

f1: blank value (water content) of the solvent [ppm]

f2: amount of solvent [g] after the blank value determination

f3: amount of sample [g] extracted in the solvent

DL39:

The equation for the calculation of the water content of the extracted sample is stored in the titrator. In the method you have to add the following information:

- Select either "x [ppm]ext.extr." or "x [%]ext.extr." as the result for "Calculation 1", and enter the blank value of the solvent (**f1**) for the factor.

  (Note: Enter the blank value in the units selected.)
- Select "No calculation" as the result for "Calculation 2" and enter the amount of solvent (**f2**) for the factor.
- Select "No calculation" as the result for "Calculation 3" and enter the amount of extracted sample (**f3**) for the factor.

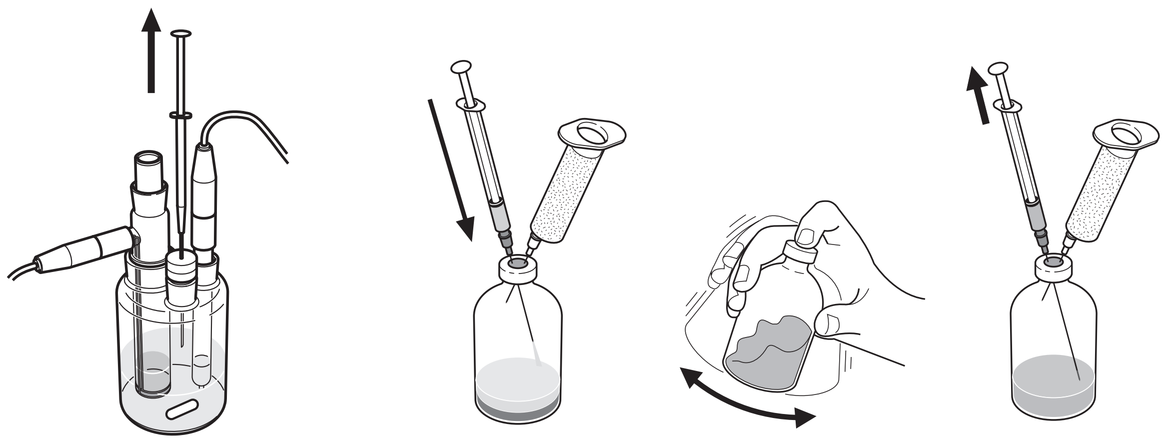
See also the notes on extraction (Chapter 5.1).

Examples:

Sample	Result	srel	Solvent
sucrose (total water)	533 ppm	4.2%.	formamide
naphthalene	35 ppm	10.2%	methanol
phenol	174 ppm	1.8%	methanol
salicylic acid	116 ppm	2.9%	methanol
contact adhesive (rubber cement)	278 ppm	5.3%	chloroform

5.3 Lyophilized substance in septum bottles

The extremely low water content of freeze-dried substances (e.g. biological tissue, serum, foodstuffs) in septum bottles means that external extraction or external dissolution as described in Section 5.1 and 5.2 is not recommended. The blank value correction is too large in comparison with the amount of water in the sample. You should therefore proceed as follows:



Take an aliquot of solution from the titration cell and inject it in the septum bottle

Shake

Take aliquot and titrate

Procedure:

- Remove approx. 10 mL of anolyte titrated to dryness from the titration cell using a 20-mL syringe with a long needle and then return it to the titration cell. Rinse the syringe two or three times in this way.
- Draw 10 - 20 mL of anolyte titrated to dryness into the syringe, weigh it and inject it into the septum bottle. Determine the weight of anolyte injected by back weighing.
- Shake the bottle or place it in an ultrasonic bath for 5 minutes so that the lyophilized substance dissolves or forms a suspension.
- Draw an aliquot into the same syringe again, weigh it and inject it into the titration cell. Determine the weight by back weighing.

Calculation:

If the sample dissolved completely:

use the calculation equation for the "External dissolution" (Chapter 5.2).

If a suspension formed:

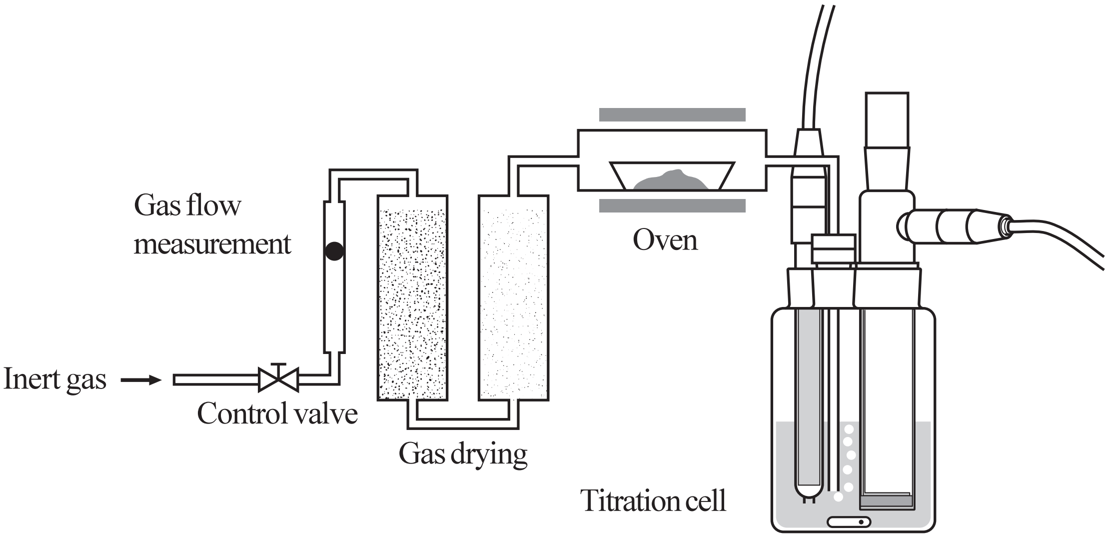
use the calculation equation for the "External extraction" (Chapter 5.1).

Note: With both methods, zero must be entered for the blank value (f1) of "Calculation 1", because anolyte titrated to dryness has a blank value of "0".

5.4 Determination using the drying oven

This method is suitable for solids and liquids that undergo side reactions with the Karl Fischer reagent or that release water only very slowly.

5.4.1 Principle



The sample is heated in an oven, causing the water in the sample to vaporize. The water is transferred to the titration cell in a current of dry inert gas (purge gas) and the amount of water is determined.

5.4.2 Purge gas

Air contains oxygen, which could react with the sample at higher temperatures. Air should therefore only be used for non-oxidizable, inorganic samples; if you use air for organic samples, the oven temperature should not exceed 160 °C.

If you use nitrogen from a gas cylinder, you should use a two-stage pressure regulator so that the final pressure is in the range 0.5 - 1 bar.

Purge gas drying

The purge gases normally used contain moisture, e.g.:

- air with 50% humidity:	about 11 mg/L
- nitrogen from a cylinder:	8.0 - 1.4 mg/L

For Karl Fischer titration, the residual moisture in the purge gas should be less than 20 µg/L.

Method	Residual moisture	Residual moisture flow for 200 mL/min
sulfuric acid, 100%	50 - 80 µg H_2O/L	10 - 15 µg H_2O/min
phosphorus pentoxide	40 - 50 µg H_2O/L	8 - 10 µg H_2O/min
KF single component reagent	15 - 20 µg H_2O/L	3 - 4 µg H_2O/min
silica gel	50 - 60 µg H_2O/L	10 - 12 µg H_2O/minn
molecular sieves 3Å	5 - 10 µg H_2O/L	1 - 2 µg H_2O/min

You can use the following desiccants to dry the purge gas:

Molecular sieves are the best drying agent as far as residual moisture is concerned, but their water absorption capacity is low. Silica gel is appreciably better in this respect. We therefore recommend drying the gas with a combination of silica gel and molecular sieves. Start off with the silica gel to absorb the bulk of the water and then use molecular sieves to reduce the residual moisture to a minimum. Silica gel and molecular sieves have the advantage that they can be regenerated, in contrast to other desiccants:

Silica gel at 150 °C, molecular sieves at up to 300 °C.

5.4.3 Procedure (method)

There are two different methods for performing a KF titration with the drying oven:

Method 1: The water evolved is continuously titrated

After a brief mix time (20 - 60 s), the titration starts and the water evolved is continuously titrated. The short mix time is necessary so that a delayed vaporization of water does not lead to premature termination of the titration.

At the end of the titration, the vaporization is often very irregular. To ensure that the determination is nevertheless reproducible, you should set the maximum titration time as the termination parameter (deactivate the drift stop).

Method 2: The water is first vaporized and then titrated afterward

During a defined mix time, all the water is vaporized and transferred to the titration cell. The KF titration is then started. The relative drift stop or the maximum titration time can be used as the termination criterion.

With some samples the drift at the end of the titration is significantly higher than the initial drift. This is caused by slow release of the final traces of water or slow thermal decomposition of the sample. In such cases you should use the maximum titration time as termination parameter (deactivate the drift stop).

Anolyte loss

Passing the gas stream into the titration cell causes anolyte to vaporize, especially methanol. The amount depends on the gas flow and the type of anolyte:

a) Normal anolyte containing methanol (e.g. Coulomat AG or combiCoulomat frit)

at 150 - 200 mL/min, oven temperature 200 °C → 3,5 - 4,5 mL/hour

b) Anolyte with added ethylene glycol (e.g. Coulomat AG Oven)

at 150 - 200 mL/min, oven temperature 200 °C → ca. 1 mL/hour

From time to time, you should replace the anolyte lost through vaporization with anolyte or anhydrous methanol. Make sure that the level of the anolyte does not sink below that of the catholyte (higher drift! - see Section 4.2.1).

Recovery

Due to the vaporization of the methanol, there is a small loss of water, i.e. the recovery is not 100%. The recovery therefore depends on the amount of methanol vaporized and the method used.

In other words - the less methanol vaporized and
- the faster the water is titrated,

the better the recovery

Example:

Method	Anolyte	Gas flow	Recovery
1	Coulomat AG	166 mL/min	99.7%
1	Coulomat AG oven	183 mL/min	99.95%
2	Coulomat AG	166 mL/min	98.2%
2	Coulomat AG oven	106 mL/min	99.1%

5.4.4 Manual drying oven

The METTLER TOLEDO DO307 drying oven has a temperature range of 50 - 300 °C. It has a large sample boat capable of holding up to 10 cm^3 of sample. This is particularly important with low-weight samples (e.g. fibers) or with samples of low water content.

The DO307 is equipped with a gas drying unit with two bottles for silica gel and molecular sieves, as well as a gas flowmeter. An air pump is available as an accessory.

The procedure for the determination of water content is described in the operating instructions.

Notes regarding the operation of the DL32/DL39 coulometers with the DO307 drying oven

1. Set a gas flow of 150 - 200 mL/min.
2. When working with the drying oven, the drift should be 5 - 15 µg H_2O/min. If the drift is higher than 20 µg H_2O/min, replace the silica gel and molecular sieves in the bottles of the gas drying unit or replace the anolyte
3. With the DL32/DL39 generator electrode, you must replace the internal drying tube with an external drying tube so that solvent condensing in the drying tube does not drop into the cathode compartment.
4. Some samples have surface water that is lost as soon as the oven is purged with dry gas. This leads to a result that is too low. In such cases, you should proceed as follows:
   - Open the stopcock, purge the "cold zone", close the stopcock and purge the "hot zone".
   - If the drift is constant, start the titration so that the drift value is automatically entered; then add the sample through the tapered joint and slide the glass boat with the sample into the oven.
5. To check the titrator/drying oven system, you can use Riedel-de Haën HYDRANAL® water standard KF oven 5.55% or MERCK water standard KF oven 1% (for results see Chapter 6).

Examples with DO307:

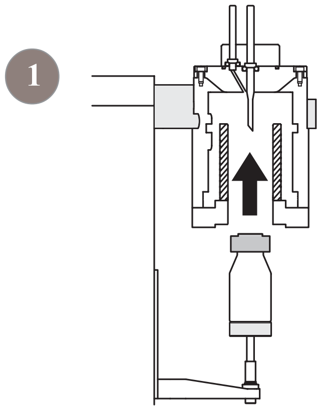
Sample	Result ppm	n	srel %	Temperature °C	Time min
polyamide	5547	6	0.8	190	15
polyethylene	68	6	6.9	280	10
motor oil	842	6	9.9	140	15
cement	8200	6	2.2	300	20
cooking salt	360	5	4.2	300	10
carbon black	3583	5	1.5	200	15

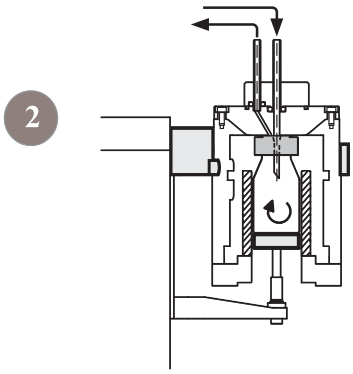
5.4.5 STROMBOLI automatic drying oven

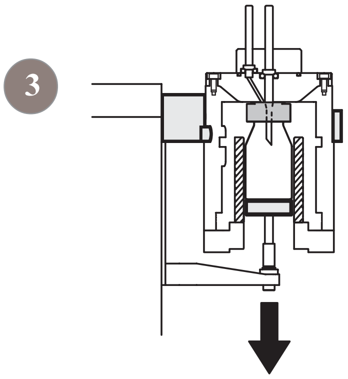
The METTLER TOLEDO STROMBOLI oven sample changer is a drying oven for automatic coulometric Karl Fischer titration for use with the DL39 KF coulometer.

The drying oven has a temperature range of 50 - 300 °C. STROMBOLI is completely controlled from the DL39; all the parameters for the determination (incl. oven temperature) are included in a DL39 method.

Besides the 13 places for glass sample vials, STROMBOLI also has two fixed places on the sample rack for empty sample vials for the determination of the drift and the blank value.





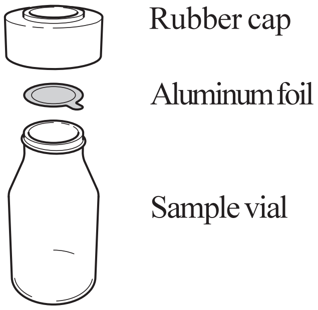


Principle:

During a sample series:

1) The sample vials are moved upward into the oven by a lift. The blue rubber cap seals the sample vial tightly against the oven, while a glass tube pierces the aluminum foil cover. The oven heats the sample to the desired set temperature.
2) The purge gas flows through the sample vial and the water vaporized is transported via the transfer tube into the titration cell of the coulometer.
3) After the analysis, the lift is moves downward and gravity facilitates the removal of the sample vial from the oven.

Sample vials:



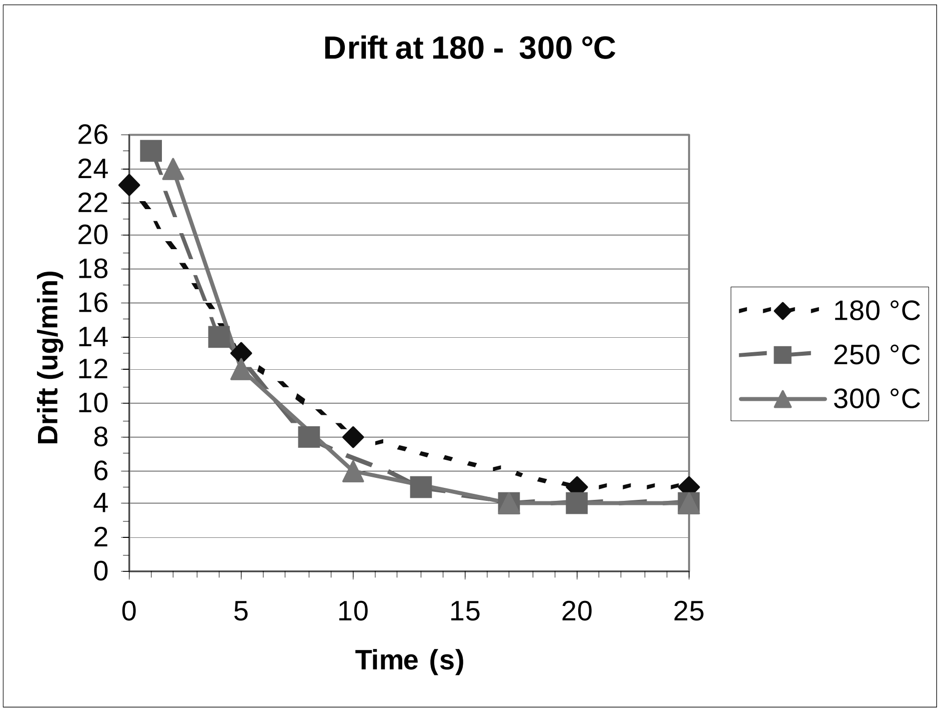
The glass sample vials have a large volume (up to 25 mL). This is particularly important with light samples (e.g. fibers) or with samples of low water content. The sample vials are sealed with self-sealing aluminum foil and a rubber cap.

Drift determination:

The drift determination is performed with the empty sample vial at the "Drift" position of the sample rack.

The drift is the moisture that is introduced into the titration cell by the purge gas. To determine the drift value accurately, the moisture in the empty sample vial has to be removed. This takes 10 - 20 minutes, as can be seen in the following diagram.

Important: After the empty sample vial is moved from the "Drift" position of the sample rack into the oven, you must wait 10 - 20 minutes before you perform the drift determination in order to obtain a correct value.



The drift value measured at a gas flow of 150 mL/min should be in the range 4 - 10 µg H_2O/min. If the drift is higher than 15 µg H_2O/min, replace the silica gel and molecular sieves in the bottles and of the gas drying unit or replace the anolyte.

Blank value determination:

The blank value determination is performed with the empty sample vial at the "Blank" position of the sample rack.

The blank value is the amount of water contained in an empty sample vial (moisture in the air that is in the sample vial and the moisture adsorbed on the glass walls of the vial) minus the drift value.

The blank value should be determined before each series because the humidity can change and the moisture adsorbed on the glass walls of the sample vials is not always the same.

The blank value is in the range 70 - 300 µg water.

Important: After a blank value determination, the sample vial used no longer has the same properties as the "fresh" sample vials (the moisture content is somewhat lower). It is therefore important to use a new sample vial for each blank value determination (i.e. one with the same properties as the sample vials into which the samples are filled.)

Performing the drift and blank value determination

In general, you should perform a blank value determination before each series of samples because the conditions (humidity, moisture in the sample vial, gas flow, etc.) are always slightly different.

If you use the maximum titration time as termination criterion in the method - which is what we recommend - the times taken for the determination of the blank value and for each sample are the same. In this case, the blank value determination also takes the actual drift into account. It is therefore not necessary to perform a drift determination before each series. In the method you should select "No" for drift (the stored drift value of the previous determination is used).

In spite of this, you should still perform a drift determination at least once a day so that if the drift is too high (> 15 µg H_2O/min), you can replace the silica gel and molecular sieves in the bottles of the gas drying unit or replace the anolyte.

Notes regarding the operation of the DL39 coulometer with the STROMBOLI oven sample changer

1. Set a gas flow of 100 - 150 mL/min.

   The delivery tube has a T-piece that causes a small leak flow. This is necessary so that anolyte solution is not sucked into the hot sample vial if Stromboli is not properly shut down while it is still hot. The leak rate is 40 - 50 mL/min.
2. With the DL39 generator electrode you must replace the internal drying tube by an external drying tube so that solvent condensing at the drying tube does not drop into the cathode compartment.
3. With STROMBOLI, you can not only determine solids but also liquid samples. These are partially vaporized (e.g. motor oil) or completely vaporized (e.g. toluene, see also list of results).
4. The amount of moisture adhering to the glass surface of the sample vials strongly depends on how the vials were treated beforehand (cleaning, drying and storage). This has a large effect on the blank value and therefore on the result. Sample vials that have undergone different treatment can show differences in the blank value of 50 - 150 µg water.

   Use sample vials that have the same properties for a sample series and for the blank value determination. Allow sample vials that have been used or cleaned to stand overnight in the atmosphere for conditioning before you make measurements.
5. To check the titrator/drying oven system, you can use Riedel-de Haën HYDRANAL® water standard KF oven 5.55% or MERCK water standard KF oven 1% (for results see Chapter 6).
6. STROMBOLI measures the temperature in the oven. The temperature in the sample is 10% to 20% lower, depending on the actual temperature and gas flow. The higher the temperature and the faster the gas flow, the greater the temperature difference.

Examples with STROMBOLI:

Sample	Sample weight g	Result	n	srel %	Temperature °C	Time min
polypropylene film	0.5	2743 ppm	4	1.2	170	10
polyethylene granule	0.8	1858 ppm	3	3.1	200	20
motor oil	1.2	316 ppm	5	4.5	170	12
toluene	3 - 4	257 ppm	3	0.8	250	10
aluminum oxide	0.45	6072 ppm	6	0.8	250	10
barium chloride dihydrate	0.03	14.77%	7	1.9	220	11
washing powder	0.05	13.8%	5	1.1	150	10

6 Measurement results

6.1 Resolution and detection limit

With the DL32/DL39 instruments, the smallest increment is 0.1072 mC. This corresponds to 0.01 µg water. The detection limit is approx. 10 µg water per sample. With a 10 g sample, 1 ppm water can be determined.

6.2 Measurement accuracy

Measurement accuracy depends on all the factors that have been described and explained in the previous chapters. Sampling, sample treatment, sample size, condition of the reagents, electrodes and titration cell, etc.

The coulometric Karl Fischer titration is an absolute method in which the amount of water is determined by measuring current and time. The measurement accuracy of the Karl Fischer coulometer can be checked with the aid of standards.

6.2.1 Standards for Karl Fischer coulometry

a) For direct measurements:
   MERCK APURA water standard 0.01%
   MERCK APURA water standard 0.1%
   Riedel-de Haën HYDRANAL®-Water Standard 0.1 mg/g (100 ppm)
   Riedel-de Haën HYDRANAL®-Water Standard 1.00 mg/g (1000 ppm)

b) For measurements with an oven:
   MERCK APURA water standard oven 1%
   Riedel-de Haën HYDRANAL®-Water Standard KF-Oven 5.55%

6.2.2 Checking the Karl Fischer coulometer

To check the Karl Fischer coulometer, use the 0.01% and 0.1% respectively 0.1 and 1.0 mg/g standards. These standards are supplied in glass ampules and the water content is declared on a test certificate supplied with every pack.

Procedure:

- Open the ampule shortly before the measurement according to the enclosed instructions.
- Rinse a 5-mL syringe with approx. 0.5 mL water standard.
- Draw the remaining contents of the ampule into the syringe.
- Inject portions of 0.8 - 1 mL and determine the weight by back weighing. The contents of the ampule is sufficient for 3 - 4 determinations.

Notes:

1. We recommend that you use the 0.01%, i.e. the 0.1 mg/g standard to check the Karl Fischer coulometer. The deviation should not be greater than 3%.
2. The standards are hygroscopic! Use a new ampule for each test because moisture can enter a ampoule that has been opened. The result would then be wrong.

3. By drawing the entire contents of the ampule into the syringe, you reduce the ingress of atmospheric moisture.
4. Plastic syringes can release moisture. Previous rinsing and conditioning of the syringe reduces this error.

Results:

Sample	Expected ppm	Sample weight g	Result ppm	n	srel %	Dev. %
Standard 1.00 mg/g (1000 ppm)	997	0.2 - 0.5	1001.2	5	0.22	0.4
Standard 0.10 mg/g (100 ppm)	105	0.5 - 0.8	106.7	6	2.7	1.6

6.2.3 Checking the drying oven

To check the drying ovens DO307 or STROMBOLI use the following oven standards:

MERCK APURA Water standard oven 1% (tungstate)

Riedel-de Haën HYDRANAL®-Water Standard KF-Oven 5.55% (potassium citrate monohydrate)

These standards are not hygroscopic. The water content is declared on a test certificate supplied with every vial.

Procedure:

The procedure is the same as for a normal sample (see operating instructions).

Measurement parameters for Riedel-de Haën HYDRANAL®-Water Standard KF-Oven 5.55%:

Sample weight:	40 - 50 mg	
Oven temperature:	STROMBOLI:	280 °C,
	DO307:	240 °C
Measurement time:	STROMBOLI:	18 - 20 minutes
	DO307:	15 - 17 minutes

Measurement parameters for MERCK APURA water standard oven 1%:

Sample weight:	40 - 50 mg	
Oven temperature:	STROMBOLI:	220 °C,
	DO307:	200 °C
Measurement time:	STROMBOLI:	18 - 20 minutes
	DO307:	10 - 15 minutes

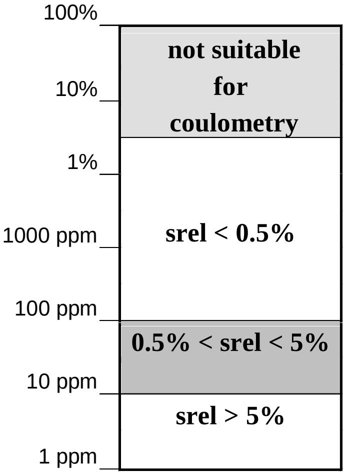
Results:

Sample	Expected %	Result %	srel. %	Dev. %	Temp. °C	Time min	Oven
Water Standard KF-Oven 5.55%	5.53	5.52	1.6	-0.2	260	20	STROMBOLI
Water Standard KF-Oven 5.55%	5.53	5.46	0.4	-1.3	230	15	DO307
Water standard oven 1%	1.00	0.99	0.8	-1.0	220	20	STROMBOLI
Water standard oven 1%	1.00	1.03	2.1	+3.0	180	10	DO307

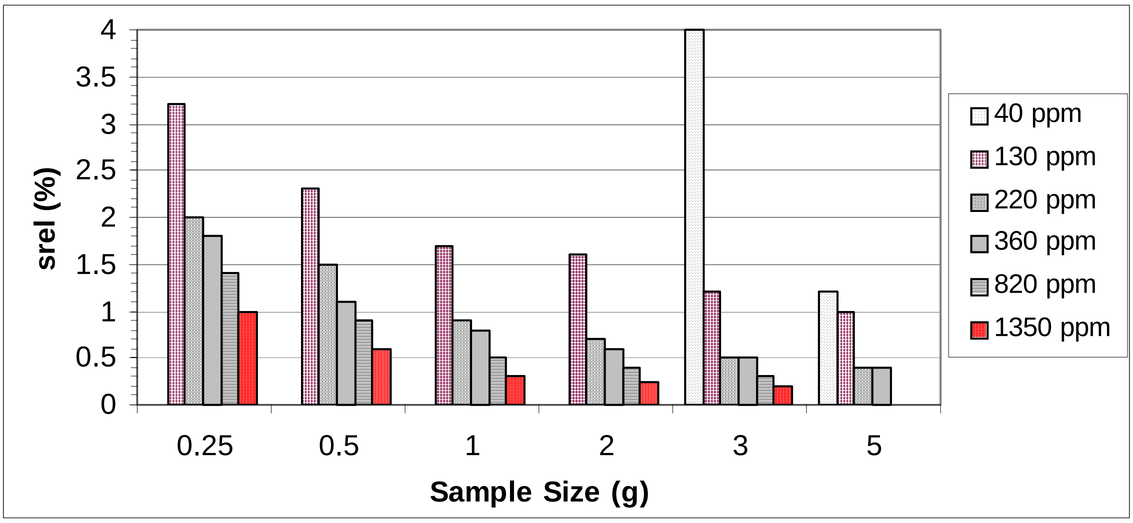
6.3 Repeatability

The closeness of the agreement between the results of successive measurements of the same sample can be expressed quantitatively as the relative standard deviation, srel. With optimum sample amount and control, the following values can be obtained for this value under test conditions for repeatability.

The graph shows the relative standard deviation for different water contents.



Sample amount versus srel for different water contents:



7 Troubleshooting

Problem	**Possible causes and action to take**
Anolyte is not bright yellow, but dark yellow to brown	- Clean the platinum pins of the measurement electrode with paper tissue - Measurement electrode is not plugged in - Measurement electrode is faulty
Drift is too high after the pretitration of a fresh anolyte	*Titration stand not protected against moisture* - Replace molecular sieves and silica gel in drying tube - Check whether titration stand is completely tight. Grease the tapered joints
The drift remains too high during standby titration	*Moisture from cathode compartment and diaphragm* - Replace anolyte - Add a little single component KF titrant to the catholyte (see Section 4.2.1). - Level of anolyte should be higher than that of the catholyte - Clean titration cell (see Section 4.3). - Check whether titration stand is completely tight.
Drift is too high after the titration of a sample	*Side reaction with the anolyte* - Use a different method see also Section 4.4.4 *Oven: water not completely vaporized* - Higher oven temperature - Lengthen vaporization time (increase t max)
Long titration time, titration never ends	*Wrong control parameters* - Use rel. drift stop as termination parameter. - Increase value for rel. drift stop - Increase end point anolyte conductivity too low - Replace anolyte *Oven: water vaporizes very slowly and irregularly* - Use t max as termination parameter - Use higher oven temperature - Lengthen vaporization time (increase t max)

Problem	Possible causes and action to be taken
Very long pretitration	*Potential too low (< 350 mV)* With a new or freshly cleaned measurement electrode, the potential is initially below 350 mV. For this reason the iodine generation is too slow - Increase the polarization current to 5 μA
Poor reproducibility of the results	*Amount of sample too small* Increase amount of sample to ensure that 1 mg water per sample is present (see Section 4.5.3). *Water distribution in the sample is not homogeneous* Homogenize sample, if possible increase amount of sample (see Section 4.5.3). *Wrong sample preparation and sample addition* The reproducibility is very dependent on proper sample preparation and sample addition, especially with samples of low water content (< 1000 ppm) (see Section 4.5).
Values too low	*The titration was terminated too soon* - Reduce the value for rel. drift stop *Incomplete sample addition* - Use back weighing (see Section 4.5.4). *Sample not dissolved (emulsion)* - Replace anolyte - Use an anolyte containing chloroform (see Section 4.4).
Values too high	*The titration was too fast ⇨ overtitration* - Replace or change the anolyte - Clean titration cell and measurement electrode *Poor sample preparation and addition* Samples of low water content (< 1000 ppm) are always hygroscopic. If the sample preparation and addition is done carefully, contamination with atmospheric moisture occurs (see Section 4.5).

Problem	Possible causes and action to take
The results within a series change continuously (decreasing water content)	*The dissolving capacity of the anolyte is exhausted* Replace anolyte - Use an anolyte containing chloroform (see Section 4.4).
Platinum parts of the generator electrode are colored black	*Generator electrode is contaminated* Clean with chromic acid (see Section 4.3.3).

8 Applications

8.1 Foodstuffs

Sample	**Sample weight** g	n	**Result** ppm	**srel** %	**Reagents**	**Method**
sucrose surface water	0.2	6	71.5	4.2	Coulomat AG Coulomat CG	External extraction: 10 g sample in 55 g chloroform; 15 min at 25 °C Addition: 3mL syringe without needle
sucrose total water	0.1	7	533.7	4.7	Coulomat AG Coulomat CG	External dissolution: 6 g sample in 60 g formamide; 15 min at 50 °C Addition: 1mL syringe with needle
olive oil	1.0	5	8.36	0.7	60 mL Coulomat AG and 40 mL decanol Coulomat CG	Addition: syringe with needle Fill syringe from behind. Stirring time: 10 s
rape oil	1.0	4	424	0.88	60 mL Coulomat AG and 40 mL decanol Coulomat CG	Addition: syringe with needle Fill syringe from behind. Stirring time: 10 s
cooking salt	1.0	5	359.6	4.2	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven 300 °C, 200 mL air/min Stirring/titration time: 60/600 s
cinnamon powder	0.05	5	4.8	0.4	Coulomat AG oven Coulomat CG	Drying with STROMBOLI oven sample changer 180 °C, 100 mL air/nin Stirring/titration time: 300/480 s
garlic powder	0.05	5	10.1	2.2	Coulomat AG oven Coulomat CG	Drying with STROMBOLI oven sample changer 180 °C, 100 mL air/min Stirring/titration time: 300/600 s
Titration parameters for the direct titrations: Ipol: 2 µA End point: 100 mV Generation rate: normal Termination criterion: rel. drift stop: 3 µg/min Online drift determination, Autostart						
Titration parameters for the titrations with the DO307 drying oven Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay time 60 s Online drift determination, manual start						
Titration parameters for the titrations with the STROMBOLI drying oven: Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay time 60 s manual start of the titration						

Reagents

Coulomat A:	anode reagent	HYDRANAL® Coulomat A	Riedel No. 34807
Coulomat AG:	anode reagent	HYDRANAL® Coulomat AG	Riedel No. 34836
Coulomat AG oven	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840

All these applications can also be performed with a titration cell without diaphragm.

Reagents

Coulomat AD:	anode reagent	HYDRANAL® Coulomat AD	Riedel No. 34810
Coulomat AG oven;	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739

Comments on the applications

Sucrose

A short external extraction in pure chloroform dissolves practically only the surface water. The diffusion of water can be neglected.

At 50 °C, sucrose dissolves completely in formamide. The total water can be measured in this way.

Oils

Oils cannot be drawn into a syringe because of the high viscosity. Dispensing with a syringe is nevertheless possible. The oil must be filled into the syringe from behind, or use a thick needle.

8.2 Cosmetics

Sample	**Sample weight**		**Result** ppm	**srel** %	**Reagent**	**Method**
	g	n				
nail varnish remover (non acetone cont.)	1.5	7	745.1	0.21	Coulomat AG Coulomat CG	Addition: syringe with needle Stirring time: 10 s
nail varnish (non acetone containing)	0.5	4	3278.2	0.86	Coulomat AG Coulomat CG	Addition: syringe with needle Fill syringe from behind. Stirring time: 10 s
Standard titration parameters for all titrations: Ipol: 2 µA End point 100 mV Generation rate: normal Termination criterion: rel drift stop: 3 µg/min Online drift determination, Autostart						

Reagents

Coulomat AG-H:	anode reagent	HYDRANAL® Coulomat AG-H	Riedel No. 34843
Coulomat AG:	anode reagent	HYDRANAL® Coulomat AG	Riedel No. 34836
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840

All these applications can also be performed with a titration cell without diaphragm.

Reagent

Coulomat AD:	anode reagent	HYDRANAL® Coulomat AD	Riedel No. 34810

Comments on the applications

Nail varnish has a high viscosity and cannot be drawn into a syringe. Dispensing with a syringe is nevertheless possible. The nail varnish must be filled into the syringe from behind. For nail varnish remover and nail varnish containing acetone, special reagents for ketones and aldehydes must be used (see page 23).

8.3 Pharmaceuticals

Sample	**Sample weight**		**Result** ppm	**srel** %	**Reagents**	**Method**
	g	n				
massage oil	0.3	6	1059	0.21	Coulomat AG Coulomat CG	Addition: syringe with needle
eucalyptus oil	0.1	6	1267	0.39	Coulomat AG Coulomat CG	Addition: syringe with needle

Standard titration parameters for all titrations:
Ipol: 2 µA End point: 100 mV Generation rate: normal Termination criterion: rel. drift stop: 3 µg/min
Online drift determination, Autostart

Sample	**Batch No.**	**Bottle**	**Result** µg H_2O	**Reagents**	**Method**
lyophilized plasma	2B0A	1	771.3	Coulomat AG Coulomat CG	External dissolution in septum bottle with 5 mL Coulomat AG titrated to dryness Addition: syringe with long needle
		2	699.3		
		3	759.2		
		4	665.7		
	RR05	1	720.7		
		2	648.7		
		3	729.3		
		4	619.1		

Standard titration parameters for all titrations:
Ipol: 2 µA End point: 100 mV Generation rate: normal Termination criterion: rel. drift stop: 3 µg/min
Online drift determination, Autostart

Reagents

Coulomat AG:	anode reagent	HYDRANAL® Coulomat AG	Riedel No. 34836
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840

All these applications can also be performed with a titration cell without diaphragm.

Reagent

Coulomat AD:	anode reagent	HYDRANAL® Coulomat AD	Riedel No. 34810

Comments on the applications

Eucalyptus and massage oil

Direct titration presents no problems at all. Additional chloroform is not necessary.

Lyophilized plasma

External dissolution of the lyophilized material in methanol is not recommended because of its low water content. The correction for the blank value of the solvent is too high in comparison with the water content of the sample. The following method is used:

Approximately 5 mL anolyte are drawn from the anode compartment of the titration cell using a 10-mL plastic syringe with a long needle and then returned to the titration cell. The syringe is rinsed in this way until it is dry. Afterward, 5 mL anolyte are drawn into the syringe and injected through a septum stopper into the sample vial. The lyophilized material is suspended in the liquid by shaking (for about five minutes in an ultrasonic bath). The entire suspension is then drawn into the same syringe, injected into the titration cell and the water content determined.

Only dry air may be used for pressure compensation (aeration) when the sample is taken from the sample bottle with septum stopper.

8.4 Inorganic raw materials

Sample	Sample weight g	n	Result %	srel %	Reagents	Method
barium chloride dihydrate	0.03	7	14.77	1.9	Coulomat AG oven Coulomat CG	Drying with STROMBOLI oven sample changer: 220 °C, 80 mL air/min Titration time: 660 s
cetylpyridinium-chloride (CPC) monohydrate	0.06	7	4.89	1.6	Coulomat AG oven Coulomat CG	Drying with STROMBOLI oven sample changer: 180 °C, 80 mL air/min Titration time: 420 s
magnesium oxide	0.07	5	4.6	2.4	Coulomat AG oven Coulomat CG	Drying with DO307 sample oven: 250° C, 200 mL air/min Titration time: 400 s
sodium chloride	1.0	5	0.0360	4.2	Coulomat AG oven Coulomat CG	Drying with DO307 sample oven: 300° C, 200 mL Luft/Min Titration time: 600 s
lithium chloride	1.0	5	0.7088	3.4	Coulomat AG oven Coulomat CG	Drying with DO307 sample oven: 250° C, 200 mL air/min Titration time: 600 s
aluminum powder	3.0	6	0.0212	3.4	Coulomat AG oven Coulomat CG	Drying with DO307 sample oven: 280° C, 200 mL air/min Titration time: 900 s
aluminum oxide (Al_2O_3)	0.45	6	0.603	0.8	Coulomat AG oven Coulomat CG	Drying with STROMBOLI oven sample changer: 250 °C, 80 mL air/min Titration time: 360 s

Titration parameters for the titration with the DO307 drying oven
Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay time 60 s
Online drift determination, manual start

Titration parameters for the titration with the STROMBOLI drying oven:
Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay time 60 s
Manual start of the titration

Reagents

Coulomat AG oven:	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840

All these applications can also be performed with a titration cell without diaphragm.

Reagent

Coulomat AG oven:	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739

Comments on the applications

Many inorganic salts have low water contents and are thermally stable. They are therefore very suitable for coulometric KF titration using a drying oven.

Magnesium oxide

The high water content necessitates the use of a low sample weight. This requires a very homogeneous sample in order to obtain good reproducibility.

Barium chloride dihydrate

The recovery of the two molecules of water of crystallization was very good. The theoretical value is 14.737%

Cetylpyridinium chloride (CPC) monohydrate

A drying temperature of 180 - 200 °C must be used with STROMBOLI. Above 200 °C, CPC is no longer thermally stable. The theoretical value is 5.028%

Sodium chloride, lithium chloride, aluminum powder, aluminum oxide

The coulometric titration using the drying oven presents no problems at all.

8.5 Organic raw materials

Sample	**Sample weight**		**Result** ppm	**srel** %	**Reagents**	**Method**
	g	n				
naphthalene	0.1	6	33.5	10.2	Coulomat AG Coulomat CG	External dissolution in methanol 0.4 g dissolved in 25 mL methanol Addition: 5 mL aliquot with syringe
4-chlorotoluene dried (1)	0.8	6	30.7	1.7	Coulomat AG Coulomat CG	Addition: syringe with needle
benzyl alcohol dried (1)	0.4	6	1273	0.16	Coulomat AG Coulomat CG	Addition: syringe with needle
phenol	1.0	6	173.7	1.8	Coulomat AG Coulomat CG	External dissolution in methanol 17 g dissolved in 60 mL methanol Addition: 1 mL aliquot with syringe:
acetophenone dried (1)	0.3	6	2830	0.46	Coulomat AK Coulomat CG-K	Addition: syringe with needle
benzaldehyde dried (1)	0.4	6	242.6	0.9	Coulomat AK Coulomat CG-K	Addition: syringe with needle
salicylic acid	0.4	6	115.8	2.9	Coulomat AG Coulomat CG	External dissolution in methanol 30 g dissolved in 60 mL methanol (immediately titrated) Addition: 3 mL aliquot with syringe
methyl benzoate dried (1)	0.9	6	49.1	2.0	Coulomat AG Coulomat CG	Addition: syringe with needle
benzamide	0.3	6	117.5	3.6	Coulomat AG Coulomat CG	External dissolution in methanol 16 g dissolved in 50 mL methanol Addition: 1 mL aliquot with syring:e
n-butylamine	0.2	6	1.14%	0.8	Coulomat AG mit 20 g benzoic acid Coulomat C	Addition: syringe with needle
aniline	0.1	1	not possible	--	Coulomat AG mit 20 g benzoic acid Coulomat C	
Standard titration parameters for all titrations: Ipol: 2 µA End point: 100 mV Generation rate: normal Termination criterion: rel. drift stop: 3 µg/min Online drift determination, Autostart						

(1) dried over molecular sieves 3Å

Reagents

Coulomat AG:	anode reagent	HYDRANAL® Coulomat AG	Riedel No. 34836
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840
Coulomat AK:	anode reagent	HYDRANAL® Coulomat AK	Riedel No. 34820
Coulomat CK:	cathode reagent	HYDRANAL® Coulomat CG-K	Riedel No. 34821

All these applications can also be performed with a titration cell without diaphragm.

Reagents

Coulomat AD:	anode reagent	HYDRANAL® Coulomat AD	Riedel No. 34810
Coulomat AK:	anode reagent	HYDRANAL® Coulomat AK	Riedel No. 34820

Comments on the applications

Naphthalene

Since naphthalene is not very soluble in methanol, only a small sample amount can be used. The coulometric determination with external dissolution presents no problems at all.

4-Chlortoluolene, benzyl alcohol, benzoic acid methylester

The coulometric titration presents no problems.

Phenol

Phenol is dissolved externally in methanol.

Acetophenone

Ketones react with methanol with the formation of water to form a ketal. To prevent this, methanol-free anolyte and catholyte are used.

With these reagents the titration of acetophenone can be performed without difficulty and with very good reproducibility.

Benzaldehyde

Aldehydes react with methanol with the formation of water to form an acetal. To prevent this, methanol-free anolyte and catholyte are used. Another side reaction, the bisulfite addition, occurs in which water is consumed. The titration is started with <AUTOSTART> immediately after adding the sample. The weight is entered at the titrator during or after the titration. These side reactions can be suppressed by predosing approx. 80% of the titrant.

Salicylic acid and benzamide

Salicylic acid and benzamide are dissolved in methanol and titrated by external dissolution.

The salicylic acid solution must be analyzed immediately because if it is allowed to stand (more than 3 hours) an increasing amount of water is measured (e.g. 250 ppm after 24 hours). This is due to the slow formation of the ester of salicylic acid.

n-Butylamine

n-butylamine is titrated coulometrically with addition of benzoic acid. The values show an increasing tendency within a series, which leads to poorer reproducibility.

Aniline

Aniline does not give a stable end point with methanol as solvent. In spite of the use of methanol- free reagents and neutralization with benzoic acid, a coulometric titration was not possible (no end point).

8.6 Solvents

Sample	**Sample weight**		**Result** ppm	**srel** %	**Reagents**	**Method**
	g	n				
toluene	0.5	5	227.1	1.8	CombiCoulomat frit	Addition: syringe with needle
toluene dried (1)	3.0	3	1.42	14.5	Coulomat AG Coulomat CG	Addition: syringe with needle
n-hexane sample I dried (1)	1.0	6	10.5	7.2	Coulomat AG Coulomat CG	Addition: syringe with needle
n-hexane sample II dried (1)	2.0	8	4.6	9.1	Coulomat AG Coulomat CG	Addition: syringe with needle
cyclohexane	1.5	4	23.6	7.1	Coulomat AG Coulomat CG	Addition: syringe with needle
isopropyl alcohol	0.2	6	787.6	0.3	Coulomat AG Coulomat CG	Addition: syringe with needle
ethylene glycol	6.0	8	588.4	0.4	Coulomat AG Coulomat CG	Addition: syringe with needle
ethylene chloride dried (1)	0.6	6	38.2	3.2	Coulomat AG Coulomat CG	Addition: syringe with needle
diethyl ether dried (1)	0.5	6	40.0	4.0	Coulomat AG Coulomat CG	Addition: syringe with needle
acetaldehyde	0.5	1	not possible	--	Coulomat AK Coulomat CG-K	Sample cooled to 0 °C. Addition: sysringe with needle
acetone	0.7	6	118.0	0.7	Coulomat AK Coulomat CG-K	Addition: syringe with needle
acetone dried (1)	2.0	6	21.3	6.6	Coulomat AK	Addition: syringe with needle
isobutyl methyl ketone	0.4	6	717.0	0.2	Coulomat AK Coulomat CK	Addition: syringe with needle
Ethyl acetate dried (1	0.5	6	34.9	1.2	Coulomat AG Coulomat CG	Addition: syringe with needle
dimethylformamide dried (1)	0.4	6	347.3	1.0	Coulomat AG Coulomat CG	Addition: syringe with needle
Standard titration parameters for all titrations: Ipol: 2 µA End point: 100 mV Generation rate : normal Termination criterion: rel drift stop: 3 µg/min Online drift determination, Autostart						
(1) dried over molecular sieves 3Å						

Reagents

Coulomat AG:	anode reagent	HYDRANAL® Coulomat AG	Riedel No. 34836
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840
Coulomat AK:	anode reagent	HYDRANAL® Coulomat AK	Riedel No. 34820
Coulomat CK:	cathode reagent	HYDRANAL® Coulomat CG-K	Riedel No. 34821
CombiCoulomat frit:	anode and cathode reagent	Apura CombiCoulomat frit	MERCK No. 1.09255

All these applications can also be performed with a titration cell without diaphragm.

Reagents

Coulomat AD:	anode reagent	HYDRANAL® Coulomat AD	Riedel No. 34810
Coulomat AK:	anode reagent	HYDRANAL® Coulomat AK	Riedel No. 34820
CombiCoulomat fritless:	anode and cathode reagent	Apura CombiCoulomat fritless	MERCK No. 1.09257

Comments on the applications

Dried solvents contain only very low concentrations of water, sometimes only traces, so that KF coulometry can be particularly recommended.

Toluene and n-hexane

Toluene and n-hexane sample II were dried for 24 hours over molecular sieves 3Å.

n-hexane sample I was dried for 1 hour over molecular sieves 3Å.

These examples show that the METTLER TOLEDO DL32/39 KF coulometer also yields reproducible results in trace analysis.

e.g. 4.6 ppm ± 0.4 ppm; 1.5 ppm ± 0.2 ppm.

Cyclohexene, isopropyl alcohol, ethylene glycol, ethylene chloride, diethylether, ethyl acetate

These samples present no problems for coulometric titration.

Acetone, isobutyl methyl ketone

Ketones react with methanol with the formation of water to ketals. To prevent this, methanol-free anolyte and catholyte are used.

Acetaldehyde

The boiling point of acetaldehyde is 15 °C. The sample was cooled to about 0 °C so that it could be added with a syringe.

Coulometric determination is not possible because the acetaldehyde is oxidized at the anode with the formation of water.

Dimethylformamide

Dimethylformamide can be easily analyzed by KF coulometry. This can also be expected for other acid amides.

8.7 Petroleum products

Sample	**Sample weight**		**Result**	**srel**	**Reagents**	**Method**
	g	n	ppm	%		
gasoline super grade	0.6	13	769.3	0.5	Coulomat A Coulomat CG	Addition: syringewith needle
kerosene	2.5	7	36.1	1.4	Coulomat A Coulomat CG	Addition: syringe with needle
gasoline dried over molecular sieves 3Å	0.5	6	43.4	2.5	Coulomat A Coulomat CG	Addition: syringe with needle
hydraulic oil	0.5	6	579.8	2.0	50 mLCoulomat AG 50 mL Chloroform Coulomat CG	Addition: syringe with needle
turbine oil	3.0	3	33.5	1.0	50 mLCoulomat AG 50 mL Chloroform Coulomat CG	Addition: syringe with needle
transformer oil	10.0	5	30.4	1.9	50 mLCoulomat AG 50 mL Chloroform Coulomat CG	Addition: syringe with needle
brake fluid	0.3	7	1081.2	0.38	Coulomat AG Coulomat CG	Addition: syringe with needle
silicone oil	0.5	6	103.5	1.7	Coulomat A Coulomat CG	Addition: syringe with needle
paraffin granules	3.0	6	31.0	15.9	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven: 150 °C, 200mL air/min Drying time: 900 s
motor oil	1.0	5	316.5	4.5	Coulomat AG oven Coulomat CG	Drying with STROMBOLI oven sample changer: 170 °C, 80 mL N_2/min Drying time: 700 s
crude oil	3.0	5	202.0	6.6	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven: 130 °C, 200mL air/min Drying time: 1200 s
carbon black	0.8	5	3582.7	1.5	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven: 200 °C, 200mL air/min Drying time: 900 s

Standard titration parameters for all direct titrations:
Ipol: 2 µA End point: 100 mV Generation rate: normal Termination criterion: rel. drift stop: 3 µg/min
Online drift determination, Autostart

Titration parameters for titrations with the DO307 drying oven
Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay time 60 s
Online drift determination, manual start of the titration

Titration parameters for titrations with the STROMBOLI drying oven:
Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay time 60 s
Manual start of the titration

Reagents

Coulomat A:	anode reagent	HYDRANAL® Coulomat A	Riedel No. 34807
Coulomat AG:	anode reagent	HYDRANAL® Coulomat AG	Riedel No. 34836
Coulomat AG oven:	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840

All these applications can also be performed with a titration cell without diaphragm.

Reagents

Coulomat AD:	anode reagent	HYDRANAL® Coulomat AD	Riedel No. 34810
Coulomat AG oven:	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739

Comments on the applications

Gasoline, kerosene, petrol

Since Coulomat A already contains chloroform, these samples can be titrated without the addition of chloroform. After 2-3 samples, the solubility power of the solvent is exhausted and an emulsion is formed. But even under these conditions, coulometric titration yields correct results with good reproducibility.

Turbine and hydraulic oils

With chloroform addition, these oils can be titrated directly as an emulsion. These heavy oils do not emulsify as well as gasoline of petrol. The titration time is longer and the reproducibility is poorer.

Transformer oil

This oil can be titrated directly as an emulsion. The very low water content necessitates the use of a large sample weight.

Brake fluid

This sample is soluble in the anolyte. Direct titration is no problem.

Silicone oil

Silicone oil can be titrated directly in Coulomat A as an emulsion without additional chloroform. It emulsifies very well. The titration time is short and the reproducibility good.

Paraffin

Paraffin can only be dissolved in the methanol/chloroform mixture at temperatures of about 50 °C. For instrumental reasons, coulometric determinations at higher temperature are not possible. The drying oven is therefore employed.

If air is used as purge gas, the drying temperature must not exceed 180 °C. At 200 °C, oxidation begins after about 10 minutes and water is evolved.

The poor reproducibility is mainly due to the inhomogeneity of the sample granules.

Motor oil

Motor oil contains additives such as zinc dialkyldithiophosphate and calcium and magnesium sulfonate to improve its properties. These additives make up a total of 5-7%.

Direct titration with chloroform addition is possible, but the values obtained are too high because side reactions occur with the additives.

Water determination using the drying oven at 140 – 180 °C gives reliable values. Nitrogen must be used as purge gas otherwise the additives decompose at these temperatures. This leads to results that are too high and poorly reproducible.

Crude oil

Direct titration with chloroform addition gives wrong results:

- the sample is merely emulsified, but the water is not completely released.
- water content that is too low (mean value of 6 samples = 128.9 ppm, RSD = 0.7%)
- black deposits in the titration cell necessitates cleaning of the cell.

The drying oven is therefore used. The crude oil sample is injected with a syringe through a septum directly into the glass boat of the DO307 drying oven.

Carbon black

Coulometric determination using the drying oven is no problem.

8.8 Plastics

Sample	Sample weight		Result	srel	Reagents	Method
	g	n	ppm	%		
polyethylene granules	0.8	3	1858	3.1	Coulomat AG oven Coulomat CG	Drying with STROMBOLI oven sample changer: 200 °C, 80 mL air/min Drying time: 1200 s
polypropylene granules	2.0	6	148.3	5.4	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven: 180 °C, 200mL air/min Drying time: 600 s
polypropylene film	0.5	3	2743	1.2	Coulomat AG oven Coulomat CG	Drying with STROMBOLI oven sample changer: 170 °C, 80 mL air/min Drying time: 600 s
polystyrene granules	2.0	6	322.2	2.4	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven: 160 °C, 200 mL air/min Drying time: 900 s
PVC film	0.1	6	638.1	2.2	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven: 150 °C, 200 mL air/min Drying time: 300 s
Titration parameters for the titrations with the DO307 drying oven: Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay time 60 s Online drift determination , manual start of titration Titration parameters for the titrations with the STROMBOLI drying oven: Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay time 60 s Manual start of the titration						

Reagents

Coulomat AG oven:	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840

All these applications can also be performed with a titration cell without diaphragm.

Reagent

Coulomat AG oven:	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739

Comments on the applications

Polyethylene, polypropylene, polystyrene granules

If air is used as purge gas, the oven temperature must not exceed 180 °C. At 220 °C, polyethylene and polypropylene begin to oxidize and water is evolved.

When the sample cools, it may stick to the glass boat or vial. When using the DO307, place a piece of aluminum foil in the glass boat. This allows you to remove it more easily afterward.

PVC and PP film

A 3 cm^2 piece is cut from the film so that it easily fits in the glass boat of the drying oven. The sample must not touch the sides of the oven otherwise it might stick.

8.9 Agrochemicals

Sample	**Sample weight** g	n	**Result** ppm	**srel** %	**Reagents**	**Method**
rose fungicide solution	0.5	6	828.6	0.36	CombiCoulomat frit with 20% decanol	Addition: syringe with needle
Standard titration parameters for the titration: Ipol: 2 µA End point: 100 mV Generation rate: normal Termination criterion: rel drift stop: 3 µg/min Online drift determination, Autostart						

Reagent

CombiCoulomat frit:	anode and cathode reagent	apura CombiCoulomat frit MERCK No. 1.09255

This application can also be performed with a titration cell without diaphragm.

Reagent

CombiCoulomat fritless:	anode and Cathode reagent	apura CombiCoulomat fritless MERCK No. 1.09257

Comments on the applications

This sample is only soluble with the addition of 1-decanol. If the sample merely emulsifies, lower values are obtained.

8.10 Surfactants

Sample	**Sample weight** g	n	**Result** ppm	**srel** %	**Reagents**	**Method**
non-ionic surfactant nonyl phenyl ethylene glycol	0.25	6	718.4	0.58	CombiCoulomat frit	Addition: syringe with needle
Standard titration parameters for the titration: Ipol: 2 µA End point: 100 mV Generation rate: normal Termination criterion: rel. drift stop 3 µg/min Online drift determination, Autostart						

Reagent

CombiCoulomat frit:	anode and cathode reagent	apura CombiCoulomat frit MERCK No. 1.09255

This application can also be performed with a titration cell without diaphragm.

Reagent

CombiCoulomat fritless:	anode and cathode reagent	apura CombiCoulomat fritless MERCK No. 1.09257

Comments on the application

This titration worked without any problems.

8.11 Paper and cement

Sample	Sample weight		Result %	srel %	Reagents	Method
	g	n				
photocopy paper white	0.03	6	4.88	1.0	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven: 140 °C, 200mL air/min Drying time: 600 s
photocopy paper ecological	0.06	6	4.98	0.51	Coulomat AG oven Coulomat CG	Drying with DO337 drying oven: 140 °C, 200mL air/min Drying time: 900 s
newspaper	0.04	6	7.04	0.53	Coulomat AG oven Coulomat CG	Drying with DO337drying oven: 140 °C, 200mL air/min Drying time: 900 s
insulating paper	0.05	6	6.41	0.6	Coulomat AG oven Coulomat CG	Drying with DO337drying oven: 140 °C, 200mL air/min Drying time: 900 s
cement	0.4	6	0.820	2.2	Coulomat AG oven Coulomat CG	Drying with DO307 drying oven: 300 °C, 200mL air/min Drying time: 1200 s
Titration parameters for the titration parameters with the DO307drying oven Ipol: 2 µA, End point: 100 mV, Generation rate: normal, Termination criterion: fixed titration time; delay 60 s Online drift determination, manual start of the titration						

Reagent

Coulomat AG oven:	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739
Coulomat CG:	cathode reagent	HYDRANAL® Coulomat CG	Riedel No. 34840

All these applications can also be performed with a titration cell without diaphragm.

Reagent

Coulomat AG oven:	anode reagent	HYDRANAL® Coulomat AG oven	Riedel No. 34739

Comments on the applications

Paper

Cut the paper into pieces of approx. 4-8 cm^2 and place them in the glass boat of the drying oven using tweezers. Store the paper in a closed container under constant conditions. The ambient conditions (humidity) have a strong influence on the water content of the samples.

Cement

No problem using the drying oven at 300 °C.

These applications can also be performed with the STROMBOLI oven sample changer.

8.12 Hazards and disposal

8.12.1 Reagents for coulometry

These reagents contain iodide, sulfur dioxide, buffer (imidazole) and solvents (methanol, chloroform, tetrachloromethane, 2-methoxyethanol).

Safety precautions

Easily inflammable. Irritates the skin. Poisonous when inhaled or swallowed.
Keep the container tightly sealed. Keep it away from sources of ignition. Avoid contact with eyes and the skin.

Disposal

As an organic solvent.

8.12.2 Safety data of the KF components and auxiliary solvents

Iodine	Poison class CH: 2 (very strong toxin) oxidative effect
Diethylene glycol monomethyl ether	Poison class CH: 4 (harmful) Flash point: 87 °C
2-methoxyethanol **(Ethylene glycol monomethyl ether)**	Poison class CH: 2 (very strong toxin) Flash point: 46 °C inflammable; can cause child deformity; health hazard if inhaled, swallowed or in contact with the skin; irritates the respiratory organs
Methanol	Flash point: 11 °C Poison class CH: 3 (strong toxin) easily inflammable; poisonous if inhaled or swallowed
o-Xylene	Flash point: 28 °C Poison class CH: 4 (harmful) inflammable; dangerous to the health if inhaled
Chloroform	Flash point: not combustible Poison class CH: 1* (very strong toxins) dangerous to the health if inhaled, carcinogenic, mutagenic, teratogenic
1-Decanol	Flash point: 95 °C Poison class CH: F (not subject to toxicity classification) irritates the eyes and skin.
Formamide	Flash point: not combustible Poison class CH: 3 (strong toxin) irritates the eyes and skin; can cause child deformity
Toluene	Flash point: 6 °C Poison class CH: 4 (harmful) easily inflammable; dangerous to the health if inhaled

8.13 Literature on the applications

8.13.1 Foodstuffs

HADORN, H.: Ringversuche zur Wasserbestimmung in Lebensmitteln nach Karl Fischer
Mitt. Gebiete Lebensm. Hyg. 71, 220-235 (1980)

HADORN, H.: Ringversuche zur Wasserbestimmung in Lebensmitteln nach Karl Fischer
Mitt. Gebiete Lebensm. Hyg. 71, 220-235 (1980)

ZÜRCHER, K.; HADORN, H.: Störungen bei der Wasserbestimmung nach Karl Fischer
Mitt. Gebiete Lebensm. Hyg. 72, 177-182 (1981)

ZÜRCHER, K.; HADORN, H.: Wasserbestimmung nach Karl Fischer an verschieden Lebensmitteln
Deutsche Lebensmittel Rundschau 77, 343-355 (1981)

ZÜRCHER, K.; HADORN, H.: Wasserbestimmung in Lebensmitteln nach der Methode Karl Fischer
1. Teil: Deutsche Lebensmittel Rundschau 74, 249-259 (1978)
2. Teil: Deutsche Lebensmittel Rundschau 74, 287-296 (1978)

SCHOLZ, E.: Wasserbestimmung in Lebensmitteln
Deutsche Lebensmittel Rundschau 79, 302-306 (1983)

KREISER, W.R.; MARTIN, R.A.: Comparison of Accuracy, Precision and Speed of Three Methods for Determining Moisture in Milk Chocolate
J.Assoc.Off.Anal.Chem. 60, 303-306 (1977)

RADAR, B.R.: Determination of Moisture in Dried Vegetables
J.Assoc.Off. Anal.Chem. 50, 701-703 (1967)

RÜEGG, M. et al: Die Bestimmung des Wassergehaltes in Milch und Milchprodukten mit der Karl Fischer Methode.
Mitt. Gebiete Lebensm. Hyg. 77, 131-138 (1986)
Mitt. Gebiete Lebensm. Hyg. 77, 139-146 (1986)
Mitt. Gebiete Lebensm. Hyg. 77, 446-451 (1986)
Mitt. Gebiete Lebensm. Hyg. 77, 535-543 (1986)
Mitt. Gebiete Lebensm. Hyg. 78, 309-316 (1987)

SCHNEIDER, F.; EMMERICH, A.; TICMANIS, U.: Die Bestimmung der Oberflächenfeuchte von Zucker, Zucker 28, 349-536 (1975)

STRANGE, T.E.: Collaborative Study of Moisture in Cheese by Gas Chromatographie and by Karl Fischer Titration
J.Assoc.Off.Anal.Chem.55, 507-510 (1972) und
J.Assoc.Off.Anal.Chem.53, 865-868 (1970)

THUNG, S.B.: Comparative Moisture Determination in Dried Vegetables by Drying after Lyophilisation or by the Karl Fischer Method.
J. Sci. Food. Agric. 15, 236-244 (1964)

"Sugar Analysis" published 1979 by ICUMSA

International Standard FIL/IDF 23: 1964 Wasserbestimmung in Butteröl mit der Karl Fischer Methode.
Michwirtschaft 21, 137-139 (1966)

ISO/DIS 5381. Starch Hydrolysis Products. Determination of Water Content
(Modified Karl Fischer Method).

8.13.2 Pharmaceuticals

CACHET, T., HOOGMARTENS, J.: Determination of water in erythromycin by Karl Fischer titration
J.Pharm.Biomed.Anal. ISSN 0731-7085; 6, 5, 461-472, 1988

MÜLLER, M.: Determination of water in erythromycin by Karl Fischer Titration
Deutsche Apoth. Ztg: ISSN 0011-9857; 127, 41, 2034-2036, 1987

LINDQUIST, J.: Determination of water in penicilins using fast Karl Fischer reagents
J.Pharm.Biomed.Anal. ISSN 0731-7085; 2, 1, 37-44, 1984

Use of a simple Karl Fischer apparatus for water determination in lyophilized radiopharmaceutical kits
Appl. Radiat.Isot, ISSN 0883-2889; 38, 11, 992-993, 1987

8.13.3 Chemicals and solvents

BRYANT, W.M.D., MITCHELL, J.: Analytical Procedures Employing Karl Fischer Reagent (Determination of Water of Hydration in Salts in Inorganic Oxides and Related Components) J.Am.Chem.Soc: 63, 2924-2930 (1941)

SCHOLZ, E.: Wasserbestimmung in Carbonsäuren
Fresenius Z. Anal. Chem. 312, 423-426 (1982)

SCHOLZ, E.: Titration of Aldehydes und Ketones
Anal. Chem. 57, 2965-2971 (1985)

SCHOLZ, E.: Wasserbestimmung in Phenolen
Fresenius Z. Anal. Chem. 330, 8, 694-697 (1988)

ISO 3699-1976 Anhydrous Hydrogen Fluoride for Industrial Use - Determination of Water Content - Karl Fischer Method

ISO/DIS 7105 Liquefied Anhydrous Ammonia for Industrial Use - Determination of Water Content - Karl Fischer Method

ISSN 0192-2971, ASTM-Standard, D-1364-87, 1987
Test method for water in volatile solvents (Karl Fischer Titration)

8.13.4 Petroleum oils and plastics

MUROI, K.: Determination of Water in Plastic Materials by Karl Fischer Method
Bunseki Kagaku 11, 351, 1962

PRAEGER, K., DINSE, H.D.: Experiences in the Determination of Small Amounts of Water in Polyethylene and Polyamide
Faserforsch. Textiltechn. 21, 37-38 , 1970

ASTM-Standard, D-4377-88, 1988
Test method for water in crude oils (Karl Fischer Titration)

ASTM Designation: D 789-81 Standard Specification for Nylon Injection Molding and Extrusion Materials

DIN 51777 Teil 1 Test von Mineralöl, Kohlenwasserstoffen und Lösungsmitteln
Wasserbestimmung nach Karl Fischer. Direkte Methode

DIN 53715 Wasserbestimmung von pulverförmigen Kunststoffen nach Karl Fischer

ISO/DIS 5381 Flüssige Petroleum Produkte - Wasserbestimmung nach Karl Fischer

SHARMA, H.D., SUBRRAMANIAN N.: Determination of Water in Ion-Exchange Resins by Karl Fischer.
Anal. Chem. 41, 2063-2064, 1969
Anal. Chem. 42, 1278-1290, 1970

VAN ACKER. P., DE COTE, F., HOSTE, J.: Determination of Water in Strong Base Anion-Exchange Resins by the Karl Fischer Titration
Anal. Chim. Acta. 73, 198-203, 1974

8.13.5 Paints, surfactants, cellulose, minerals

ASTM D 4017-81 Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method

ASTM D 1348-61 Standard Test Method for Moisture in Cellulose

ISO 4317-1977 Surface-Active Agents - Determination of Water - Karl Fischer Method

FUJINO, H., MUROI, K.: Determination of Water Content in Electric Insulation Papers by Karl Fischer Method. Bunseki Kagaku 30, 624, 1981

LINDNER, B., RUDERT, V.: Verbesserte Methode zur Bestimmung von gebundenem Wasser in Mineralien, Gesteinen und anderen Feststoffen
Fresenius Z. Anal. Chem. 248, 21 - 24 (1969)

RECHENBERG, W.: Bestimmung des Wassergehaltes in Zement
Zement-Kalk-Gips 29, 512 - 516 (1976)

FARZANEH, A., Troll G.: Quantitative Methode zur Bestimmung von Wasser in Mineralien, Gesteinen und anderen Feststoffen
Fresenius Z. Anal. Chem. 287, 43 - 45 (1977)

9 Appendix

9.1 Literature references

[1] FISCHER, K. : Neues Verfahren zur massanalytischen Bestimmung des Wassergehaltes von Flüssigkeiten und festen Körpern. Angew, Chem. 48, 394 - 396 (1935)

[2] EBERIUS, E.: Wasserbestimmung mit Karl Fischer Lösung; 2. Auflage, Verlag Chemie Weinheim (1954)

[3] VERHOFF,J.C., BARENDRECHT E.: Mechanism and reaction rate of the Karl Fischer titration reaction. Part I. Potentiometric measurements. J. Electronal. Chem. 71, 305-315 (1976)

VERHOFF,J.C., BARENDRECHT E.: Mechanism and reaction rate of the Karl Fischer titration reaction. Part II. Rotating ring disk electrode measurement. J. Electronal. Chem. 75, 705-717 (1976)

VERHOFF,J.C., BARENDRECHT E.: Mechanism and reaction rate of the Karl Fischer titration reaction. Part V. Analytical implications. Anal. Chim. Acta. 94, 395-403 (1977)

VERHOFF,J.C., KOK W.Th.: Mechanism and reaction rate of the Karl Fischer titration reaction.
Part III. Rotating ring disk electrode measurement - comparison with the aqueous system.
J. Electronal. Chem. 86, 407-415 (1978)

VERHOFF,J.C., COFINO W.P.: Mechanism and reaction rate of the Karl Fischer titration reaction.
Part IV. First and second order catalytic currents at a rotating disk electrode.
J. Electronal. Chem. 93, 75-80 (1978)

[4] SCHOLZ. E., Karl-Fischer Reagentien ohne Pyridin. Fresenius Z.
Anal. Chem., 303, 203 - 207 (1980)

SCHOLZ. E., Karl-Fischer Reagentien ohne Pyridin Genauigkeit der Wasserbestimmung
Fresenius Z. Anal. Chem., 306, 394 - 396 (1981)

SCHOLZ. E., Karl-Fischer Reagentien ohne Pyridin. Einkomponenten Reagentien.
Fresenius Z. Anal. Chem., 309, 30-32 (1981)

SCHOLZ. E., Karl-Fischer Reagentien ohne Pyridin. Neue Eichsubstanzen
Fresenius Z. Anal. Chem., 309, 123-125 (1981)

SCHOLZ. E., Karl-Fischer Reagentien ohne Pyridin. Zweikomponenten Reagentien mit Imidazol
Fresenius Z. Anal. Chem., 312, 460-464 (1982)

[5] SEUBERT, A: Diplomarbeit an der Universität Hanover (1988)

9.2 Other literature used

BUNSEN, R.W., Liebigs Ann. Chem. 86. 265 (1853)
HYDRANAL®-Praktikum Auflage 2001 Wasserreagentien für die Karl Fischer titration
Sigma-Aldrich Laborchemikalien GmbH D- 30918 Seelze Deutschland

SCHOLZ. E., Karl Fischer titration, Springer Verlag Berlin 1984
Wasserbestimmung durch Karl Fischer titration

WIELAND, G., Theorie und Praxis
GIT Verlag GmbH, Darmstadt

9.3 Norms

EN ISO 10101:	Erdgas - Bestimmung des Wassergehaltes nach Karl Fischer
ISO 3699:	Anhydrous hydrogen fluoride for industrial use - Determination of water content - Karl-Fischer-method
DIN 51777:	Test von Mineralöl, Kohlenwasserstoffen und Lösungsmitteln - Wasserbestimmung nach Karl Fischer.
DIN 53515:	Wasserbestimmung von pulverförmigen Kunststoffen nach Karl Fischer

9.4 ASTM standards

E-700:	Water in Gases using Karl Fischer Reagent
D803-97	Standard Test Method for testing tall oil
D890-98	Standard Test Method for water in liquid naval stores
D1064-00	Standard Test Method for Water in organic liquids by coulometric Karl Fischer Titration
D1123-99	Standard Test Method for Water in engine coolant concentrate by Karl Fischer Reagent Method
D1348-94(1998)	Standard Test Method for moisture in cellulose
D1364-95(1999)	Standard Test Method for water in volatile solvents (Karl Fischer Titration Reagent Method)
D1533-00	Standard Test Method for Water in insulating liquids by coulometric Karl Fischer Titration
D1631-99	Standard Test Method for water in phenol and related materials by the iodine reagent method
D2072-92(1998)	Standard Test Method for water in fatty nitrogen components
D2575-70(1998)	Standard Method for testing polymerized fatty acid
D3401-97(2001)	Standard Test Method for water in halogenated organic solvents and their admixtures
D4017-02	Standard Test Method for Water in paints and paint materials by Karl Fischer Method
D4377-00	Standard Test Method for Water in Crude oil by potentiometric Karl Fischer Titration
D4672-00	Standard Test Methods for polyurethane raw materials determination of water content of polyols
D4895-98	Standard Specification for polytetrafluoroethylen (PTFE=) resin produced from dispersion
D4928-00	Standard Test Method for Water in crude oil by coulometric Karl Fischer Titration
D5460-93(1998)	Standard Test Method for rubber compounding materials in rubber additives
D5530-94(1998)	Standard Test Method for Total Moisture of Hazardous Waste Fuel by Karl Fischer Titration
D6304-00	Standard Test Method for determination of water in petroleum products, lubricating oils, and additives by coulometric Karl Fischer Titration

Mettler-Toledo GmbH,
Analytical,
CH-8603 Schwerzenbach, Switzerland
Phone +41-1-806 77 11, Fax +41-1-806 73 50
Internet: http://www.mt.com

AT Mettler-Toledo GmbH., A-1100 Wien
Tel. +43-1-604 19 80, Fax +43-1-604 28 80
AU Mettler-Toledo Ltd., Port Melbourne, Victoria 3207
Tel. +61-3-9644 5700, Fax +61-3-9645 3935
BE N.V. Mettler-Toledo s.a., B-1932 Zaventem
Tel. +32-2-334 02 11, Fax +32-2-334 03 34
CH Mettler-Toledo (Schweiz) AG, CH-8606 Greifensee
Tel. +41-1-944 45 45, Fax +41-1-944 45 10
CN Mettler-Toledo (Shanghai) Ltd., Shanghai 200233
Tel. +86-21-6485 0435, Fax +86-21-6485 3351
CZ Mettler-Toledo, spol, s.r.o., CZ-12000 Praha 2
Tel. +420-2-25 49 62, Fax +420-2-2424 7583
DE Mettler-Toledo GmbH, D-35353 Giessen
Tel. +49-6-41 50 70, Fax +49-6-41 507 128
DK Mettler-Toledo A/S, DK-2600 Glostrup
Tel. +45-4327 0800, Fax +45-4327 0828
ES Mettler-Toledo S.A.E., E-08038 Barcelona
Tel. +34-93-223 76 00, Fax +34-93-223 02 71
FR Mettler-Toledo s.a., F-78222 Viroflay
Tel. +33-1-3097 1717, Fax +33-1-3097 1616
HK Mettler-Toledo (HK) Ltd., Kowloon
Tel. +852-2744 1221, Fax +852-2744 6878
HR Mettler-Toledo, d.o.o., HR-10000 Zagreb
Tel. +385-1-230 41 47, Fax +385-1-233 63 17
HU Mettler-Toledo, KFT, H-1139 Budapest
Tel. +36-1-288 40 40, Fax +36-1-288 40 50
IT Mettler-Toledo S.p.A., I-20026 Novate Milanese
Tel. +39-2-333 321, Fax +39-2-356 29 73
JP Mettler-Toledo K.K., Tokyo 143-0006
Tel. +81-3-5762-0606, Fax +81-3-5762-0756
KR Mettler-Toledo (Korea) Ltd., Seoul (135-090)
Tel. +82-2-518 20 04, Fax +82-2-518 08 13
KZ Mettler-Toledo CA, 480009 Almaty
Tel. +7- 3272-608 834, Fax +7-3272-608 835
MY Mettler-Toledo (M) Sdn. Bhd. 47301 Petaling Jaya
Tel. +60-3-703 27 73, Fax +60-3-703 17 72
MY Mettler-Toledo (S.E.A.), 47301 Petaling Jaya
Tel. +60-3-704 17 73, Fax +60-3-703 17 72
MX Mettler-Toledo S.A. de C.V., México C.P. 06430
Tel. +52-5-547 57 00, Fax +52-5-541 22 28
NL Mettler-Toledo B.V., NL-4000 HA Tiel
Tel. +31-3-4463 8363, Fax +31-3-4463 8390
PL Mettler-Toledo, Sp. z o.o., PL-02-929 Warszawa
Tel. +48-22-651 92 32, Fax +48-22-651 71 72
RU Mettler-Toledo C.I.S. AG, 10 1000 Moscow
Tel. +7-095-921 92 11, Fax +7-095-921 63 53
SE Mettler-Toledo AB, S-12008 Stockholm
Tel. +46-8-702 50 00, Fax +46-8-642 45 62
SG Mettler-Toledo (S) Pte. Ltd., Singapore 139944
Tel. +65-7786 779, Fax +65-7786 639
SK Mettler-Toledo, SK-82104 Bratislava
Tel. +421-7-4342 7496, Fax +421-7-4333 7190
SI Mettler-Toledo, d.o.o., SI-1236 Trzin
Tel. +386-61-162 18 01, Fax +386-61-162 17 89
TH Mettler-Toledo (Thailand) Ltd., Bangkok 10310
Tel. +66-2-719 64 80, Fax +66-2-719 64 79
TW Mettler-Toledo Pac Rim AG, Taipei
Tel. +886-2-2579 5955, Fax +886-2-2579 5977
UK Mettler-Toledo Ltd., Leicester, LE4 1AW
Tel. +44-116-235 70 70, Fax +44-116-236 63 99
US Mettler-Toledo, Inc., Columbus, OH 43240
Tel. +1-614-438 4511, Fa

For all other countries:
Mettler-Toledo GmbH
PO Box, VI-400, CH-8606 Greifensee, Schweiz
Telefon +41-1-944 22 11, Fax +41-1-944 31 70

Printed in Switzerland on 100% chlorine-free
paper, for the sake of our environment.