

Monograph



Water Determination by Karl Fischer Titration

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1. Introduction

In addition to the determination of the pH, weighing and acid-base titration, the determination of the water content is one of the most frequently used methods in laboratories around the world. In addition to methods requiring complex apparatus, such as infrared reflection spectrometry, gas chromatography or microwave spectroscopy, two methods in particular have been able to establish themselves:

A – Drying methods (drying ovens, infrared lamps and infrared balances).

This method is commonly found in various standards, but suffers from the following disadvantages:

- In principle the loss on drying is determined, and not necessarily the water content. Apart from water, other volatile components of the sample and/or decomposition products are also determined. In order to obtain comparable results work must be carried out under strictly maintained predefined conditions (temperature and duration of the drying process).
- It takes a long time to obtain the analytical results (several hours in a drying oven). This can lead to bottlenecks, e.g. in the monitoring of manufacturing processes.

B – Titration methods

In contrast to drying, this is a specific method. If no side reactions occur only water will be determined. The method is rapid (normally a few minutes), can be validated and therefore fully documented. Since its introduction more than sixty years ago* its progress has been all-conquering and in many laboratories it is impossible to imagine life without it. The name Karl Fischer (1901–1958), KF for short, is as well known in most laboratories as that of Robert Wilhelm Bunsen (1811 – 1899) and Justus von Liebig (1803 – 1873).

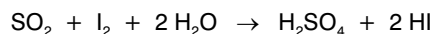
With the KF titration both free and bound water can be determined, e.g. surface water on crystals or the water contained inside them. The method works over a wide concentration range from ppm up to 100% and supplies reproducible and correct results.

* Karl Fischer
Neues Verfahren zur massanalytischen Bestimmung des Wassergehaltes von Flüssigkeiten und festen Körpern
[A new method for the volumetric determination of the water content of liquids and solids]

Angew. Chem. 48, (1935) 394 – 396

2. Reagents

When developing his new analytical method Karl Fischer took into account the well-known Bunsen reaction, which is used for the determination of sulfur dioxide in aqueous solutions:



This reaction can also be used for the determination of water if sulfur dioxide is present in excess and the acids so produced are neutralized by a base. The selection of pyridine, the base used by Karl Fischer, was completely at random: «pyridine was just standing in the rack». This led to the establishment of the classical KF reagent, a solution of iodine and sulfur dioxide in a mixture of pyridine and methanol.

Original formulation according to Karl Fischer

254 g iodine is dissolved in 5 liters of anhydrous methanol. This is treated with 790 g pyridine, mixed thoroughly and then 192 g liquid SO₂ is added.

1 mL KFR corresponds to approx. 3 mg H₂O

The titer of this combined reagent was not very stable – titer determinations had to be carried out virtually every day. Help was provided by the use of separate reagents. The titration solution consisted of 30 g iodine in 1 liter methanol. For the reaction solution 60 g SO₂ was introduced into a mixture of 300 mL each of methanol and pyridine. The titer of the titration solution prepared in this way (approx. 1.7 mg H₂O / mL) only decreased by approx 1.3% over a two-month period and could be regarded as being relatively stable.

However, for most applications it is advisable to work with a one-component reagent with a relatively stable titer. In order to obtain such a reagent the methanol was replaced by ethylene glycol monomethyl ether (Cellosolve).

Formulation as per European Pharmacopoeia 4 (2002)

220 g finely pulverized iodine is added to 700 mL each of ethylene glycol monomethyl ether and pyridine under vigorous stirring. When it has dissolved (approx. 30 min) the solution is cooled to –10 °C and then 190 g SO₂ is quickly introduced into the solution. Care must be taken that the temperature does not exceed 30 °C.

1 mL KFR corresponds to approx. 3.5...5 mg H₂O

The noxious odor and toxicity of pyridine was a source of annoyance for many users of the KF method. Work had to be carried out in the fume cupboard, which was helpful to the user but not to the environment. Research was carried out into the use of other bases in order to obtain pyridine-free reagents. During this work it was also found that the KF reaction only proceeded rapidly and stoichiometrically at a pH between 5 and 7.

Among the bases tested with varying success were diethanolamine, sodium acetate and sodium salicylate. The ideal substance was finally found: imidazole (C₃H₄N₂), which is similar to pyridine but odor-free and has a higher basicity (Eugen Scholz).

The latest trend is to replace the toxic methanol by the comparatively harmless ethanol.

Today there is general differentiation between single-component and separate reagents; in volumetry between the titrant and solvent, in coulometry between the anode and cathode solution.

Today a wide range of KF reagents and auxiliary solutions are offered by various manufacturers. They are intended for a particular application, i.e. custom-made:

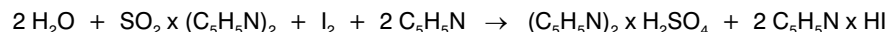
- Single-component and separate reagents for volumetry and coulometry.
- Pyridine-containing and pyridine-free reagents.
- Special reagents for water determination in aldehydes and ketones.
- Stable volumetric KF reagents with a titer of 1 mg H₂O/mL or 2 mg H₂O/mL for the determination of low water contents.
- Solvent additives for fats and oils, with halogenated hydrocarbons (usually unwanted) or without these (e.g. with decanol).
- Solvent additives for polar substances (e.g. salts, sugars).

- Buffer substances or buffer solutions for strongly alkaline or strongly acidic samples.
- Certified water standards from 0.1...10 mg/mL H₂O with a density of 1 g/mL.

This wide range of possibilities allows the user to determine the water content in practically any matrix. It is certainly no longer worth making up the reagents yourself!

3. Chemical reactions

Karl Fischer presented the following equation for water determination with his reagent:

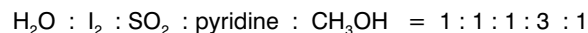


This gave a molar ratio of

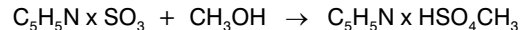
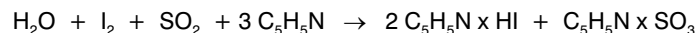


under the assumption that methanol only functions as a solvent and pyridine forms additive compounds with the acids.

However, this molar ratio was incorrect, as established by the studies of Smith, Bryant and Mitchell (Fischer had assumed an aqueous Bunsen reaction). The three authors determined the molar ratio:



In a first partial reaction water forms the (hypothetical) pyridine sulfur trioxide, which then further reacts with methanol:



The authors subsequently revised this equation by formulating iodine and SO₂ as pyridine adducts.

From the pH-dependency of the reaction constants Verhoef and Barendrecht later became aware that in the KF reagent it is not the SO₂ that functions as the reactive component, but rather the monomethyl sulfite ion that is formed from SO₂ and methanol:



They also established that pyridine does not take part in the reaction but only acts as a buffer substance (e.g. at the same pH the same reaction rate is achieved with sodium salicylate). Pyridine can therefore be replaced by another suitable base (RN). The added base results in a considerable displacement of the equilibrium to the right:



This means that the KF reaction in methanolic solution can now be formulated as follows:



Influence of the water content

The water content of the working medium influences the stoichiometry of the KF reaction. If it exceeds 1 mol/L (18 g/L) then the reaction behavior changes to favor the Bunsen reaction for aqueous solutions. This means that 2 H₂O are consumed for one I₂ or one SO₂. It is uneconomic to titrate such a high water content in a large volume of sample. In this case it is important to dilute the sample and/or to use a small amount of sample. If sepa-

rate KF reagents are used then the water capacity of the solvent must be taken into consideration, particularly for subsequent titrations. (The water capacity of these solvents is normally about 5...7 mg/mL, for a solvent volume of 25 mL this means max. 125...175 mg H₂O.)

Influence of the organic solvent

Theoretically non-alcoholic KF reagents can also be used, but in this case the stoichiometry also changes. In protic solvents, e.g. methanol or ethanol, the ratio H₂O : I₂ = 1 : 1, in aprotic solvents, e.g. DMF, the ratio H₂O : I₂ = 2 : 1. Intermediate values (uneven ratios) have been observed, e.g. with propanol, butanol and other long-chain alcohols. This has to do with the reactivity of the alcohol used. (In methanol about 100%, in propanol approx. 80% and in butanol only approx. 50% is present as sulfite ester.) With the KF reagents normally used an alteration in the stoichiometry is not to be expected, because:

- the titer determination and water determination are carried out in the same titration medium, and
- the alcohol fraction in the sample solution continuously increases during the course of the titration.

Kinetics of the KF reaction

Cedergren was (presumably) the first to thoroughly investigate the KF reaction sequence and establish that the reaction rate increases as the concentrations of SO₂, I₂ and H₂O increase. The reaction is first order referring to each individual component. For the rate constant K he used the equation:

$$-d[\text{I}_2] / dt = K [\text{I}_2] \times [\text{SO}_2] \times [\text{H}_2\text{O}]$$

to obtain the value:

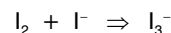
$$K = (1.2 \pm 0.2) \times 10^3 \times \text{I}^2 \times \text{mol}^{-2} \times \text{s}^{-1} \quad \log K = 3.08 \text{ } 0.08$$

Verhoef and Barendrecht confirmed the results of Cedergren, but at the same time found that the reaction constant K depends on the pH of the solution:

- Up to pH = 5 log K increases linearly with the pH.
- Between pH = 5.5 and 8 the reaction rate is constant (there is a plateau).
- Above pH 8 the reaction rate again increases slightly (side reactions probably occur).

From the increases in K under acidic conditions the authors conclude that it is not SO₂, but the sulfite base that is the reactive component.

The reaction rate is also strongly influenced as a result of the concentration of iodide ions. The iodine in the KF solution reacts with iodide to form triiodide; this strongly displaces the equilibrium to the right:



However, during the oxidation of the methyl sulfite the free iodine reacts far more quickly than the triiodide (Δ K approx. 10⁴). This reaction is also pH-dependent.

4. Volumetry and coulometry

The following are important for both methods:

- the KF reagent must be added as precisely, accurately, reproducibly and with as high a resolution as possible, and
- the titration cell must be as impervious as possible. It should be penetrated by as little atmospheric water as possible.
- The water adhering to the walls of the titration cell (inner water film) must be removed by swirling about the conditioned contents of the titration vessel.

Volumetry

It is only since the introduction of piston burets by Metrohm in the fifties of the previous century (sounds bizarre!) that it has been possible to carry out volumetric Karl Fischer titrations without requiring a cumbersome setup. The introduction of the Exchange Units (also by Metrohm) in the sixties brought further relief and improvements.

Metrohm Titrimos titrate with a resolution of 10'000 pulses per buret volume, Metrohm Titrandos even have a resolution of 20'000 pulses per buret volume. Normally piston burets with a volume of 5 mL, 10 mL or 20 mL are used for the titration; this means that the Titrimos have a resolution of 0.5 μL ...2 μL and the Titrandos' resolution is even 0.25 μL ...1 μL .

Although this resolution allows a high precision, this does not mean that titrations can be carried out down to the resolution limit. Even with impervious titration cells the introduction rate of atmospheric humidity can amount to a reagent consumption of 20 μL per min. The Metrohm titrators determine this value as the blank drift and automatically include it in the final calculation.

Higher (absolute) water contents are preferably determined by volumetric titration. Volumetry also has the advantages that solid or pasty samples can be introduced directly into the titration vessel and work can be carried out with a variety of suitable organic solvents specially adapted for use with the particular sample.

Of course it is also possible to determine small amounts of water volumetrically, e.g. in solvents. If an appropriate amount of sample and diluted KF reagents are used then the lower determination limit is approx. 50...100 ppm H_2O .

Despite great progress in the manufacture of KF reagents these do not have a stable titer. One of the minor disadvantages of volumetry is therefore that the titer has to be determined again and again.

Coulometry

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

Faraday's law applies:

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

m = mass of converted substance in g
M = molar mass in g/mol
Q = measured amount of charge in ampere-seconds
z = number of exchanged electrons (equivalence number, charge number)
F = electrochemical equivalent, 1 F = 96'485 coulomb/mol
(1 coulomb = 1 C = 1 ampere-second = 1 A s)

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

z = 2, M = 253.8 (I_2)

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

Requirements for coulometric titration are:

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

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

The same chemical processes take place as in a volumetric KF titration, i.e. 1 H_2O consumes 1 I_2 . As the iodine is generated electrolytically from the iodide in the KF solution this means that the coulometric determination of water is an absolute method – a titer does not need to be determined!

In order to generate iodine at the anode, Metrohm KF Coulometers work with variable current strengths and pulse lengths (100, 200 and 400 mA – with diaphragm-less cells with a constant current strength of 400 mA). Higher current strengths have not been able to establish themselves – side reactions occur and heat is produced. Working with variable pulse lengths allows precise «iodine addition» even in the region of the titration endpoint.

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

Coulometric water determination is primarily used for the determination of small amounts of water. Larger amounts of water require a lot of time and/or may exceed the water capacity of the KF reagent, which could lead to incorrect results. Metrohm KF Coulometers work in a determination range of 10 μg ...200 mg H_2O with a resolution of 0.1 μg H_2O .

5. Detection methods

In order to determine the end of the KF reaction – i.e. the titration endpoint at which all the H_2O has been converted – a detection or indication method is required. Titrimetric volumetric analysis stands and falls with the endpoint recognition. This means that the indication method assumes great importance. In addition to titrant addition it makes an important contribution to the reproducibility and, above all, the correctness of the results.

5.1 Visual or photometric indication

Karl Fischer himself only had the possibility of determining the titration endpoint visually. This method requires a high degree of routine and can normally only be used for uncolored sample solutions. When excess iodine is present the solution turns increasingly yellow to brown (with a large excess of iodine). This already indicates the difficulty of deciding the coloration point to which the titration is to be continued. In addition, this coloration differs in polar solvents (e.g. methanol) and nonpolar solvents (e.g. chloroform, DMF).

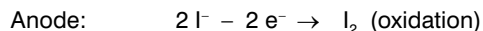
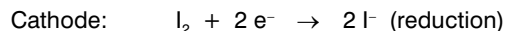
Further disadvantages of these methods are that they can hardly be automated or validated. They fell out of use rapidly as electrometric indication methods became available (toward the end of the nineteen forties).

5.2 Electrometric indication methods

In the meantime indication methods using two polarized (polarizable) electrodes have established themselves. Double Pt-wire or double Pt-ring electrodes are commonly used.

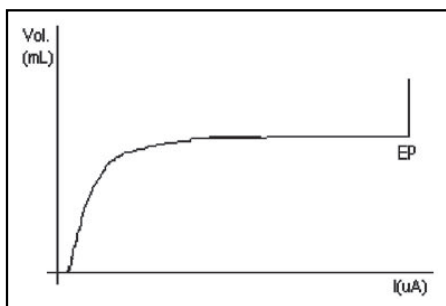
5.2.1 Biamperometric indication (U_{pol} or dead stop)

In this case a constant voltage of max. 500 mV is applied to the electrodes and the resulting current is measured. This method was first used mainly for aqueous iodometric titrations. The following reactions occur at the electrodes:



The relationship between the voltage, current and concentration of the depolarizer (iodine or triiodide) is similar to that found in polarography, i.e. initially only low voltages are required to produce a flow of current. Then the voltage increases steeply – as a function of the iodine concentration – and, when the limiting diffusion current has been achieved, the current increases only slightly. If the voltage is then further increased decomposition of either the solvent or conductive salt could occur.

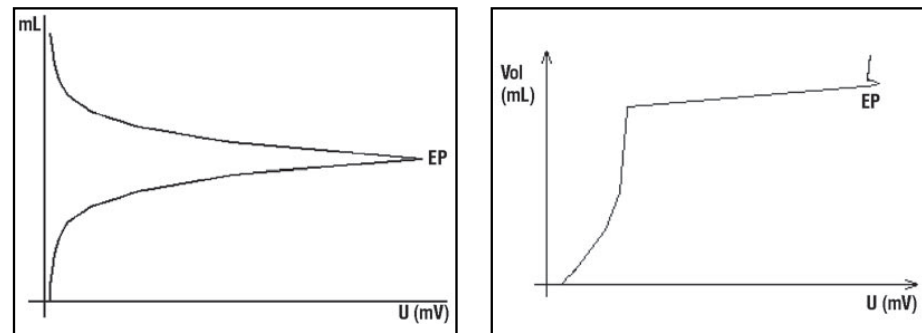
This means that a current flows for as long as iodine is present. When the iodine has been consumed (e.g. by titration with thiosulfate) the current falls abruptly to 0 (which is where the name «dead stop» comes from), the resistance between the electrodes increases strongly and the electrodes are again polarized. In KF titration the reverse occurs. If excess H_2O is present only a minimal current flows; this increases to a few μA when excess iodine is present. The «water loss» resulting from electrochemical conversion can be ignored. At 50 μA for 30 s it is theoretically approx. 1 μg H_2O . The illustration shows an example of a biamperometrically indicated titration curve:



Biamperometrically indicated titration curve

5.2.2 Bivoltametric indication (I_{pol})

In this case a small direct or alternating current is applied between the electrodes (AC is much more sensitive than DC, which is why AC is usually only used for coulometric titrations) and the resulting voltage is measured. The shape of the titration curve is similar to that obtained by biamperometry; however, the jumps are usually more marked and larger. If the sample solution and titrant are electrochemically active then peak-shaped or V-shaped titration curves are obtained. If only one partner is electrochemically active (the KFR with excess iodine) then L-shaped curves are obtained. Examples:



Examples of bivoltametrically indicated titration curves

The resulting voltages for excess iodine or water depend, of course, on the applied current (I_{pol}). Three examples (double Pt-wire electrode):

$I_{pol} = 50 \mu A$, U approx. 100 mV for excess iodine, approx. 680 mV for excess H_2O

$I_{pol} = 10 \mu A$, U approx. 5 mV for excess iodine, approx. 580 mV for excess H_2O

$I_{pol} = 1 \mu A$, U approx. 0 mV for excess iodine, approx. 350 mV for excess H_2O

The titration endpoint is determined by entering a switch-off voltage; reagent addition ceases when this limit is undercut. This «ideal endpoint» is best found experimentally. If too low a voltage is selected then the amount of excess iodine required to achieve the switch-off point will be too large. If it is too high then the titration will not start because no free iodine is required for this voltage to be achieved (decomposition of the solvent or electrolyte).

In all these indication methods there is an overtitrating (presence of excess iodine). In comparison to the visual methods, the electrometric methods have the advantage that the titration is always carried out to the same (slight) excess of iodine and in this way a better reproducibility and accuracy can be achieved.

6. Instruments

6.1 Volumetric Karl Fischer titration

Metrohm offers a large range of instruments for volumetric KF titration, starting with simple instruments for routine water determinations up to high-end instruments with numerous advantages. What all instruments have in common is that they are easy to operate and produce rapid, precise and reproducible results.

The Karl Fischer Titrinos and the Titrando with its Karl Fischer mode are automated titration systems that carry out the titration automatically, i.e. the titration rate and volume increments are controlled according to the signal measured by the indication system. In addition, the sample weight can be transmitted directly to the titration system via a connected balance. Results, curves, parameters and the configuration data can either be printed out or transferred to a PC database.

The titrators have both bivoltametric (I_{pot}) and biampereometric (U_{pot}) endpoint detection. For both types of detection the control parameters can be freely selected. This has the advantage that the control parameters can be optimized for difficult samples and special reagents, e.g. for the addition of solubility promoters. Good results are normally obtained with the default settings.

Slowly reacting reagents (e.g. those containing pyridine) require an additional stop delay when the endpoint is reached, i.e. the endpoint voltage or the endpoint current must be maintained for a few seconds when the endpoint has been reached. In the course of the development of new reagents and the improvement of the instruments this stop delay has been replaced by the drift-stop criterion. In addition to a predefined voltage (or current), a certain drift value must also be achieved. The drift is the amount of KF reagent per unit time that is consumed to keep the titration cell dry. In general, the drift value for titration cells titrated to dryness is in the order of a few $\mu\text{L}/\text{min}$. The aim of the absolute drift-stop correction is to achieve the drift value measured before the titration. In practice it has been shown that the achievement of an identical drift can considerably increase the titration time, which is why the use of a relative drift-stop criterion is recommended. If a relative drift stop is used then the titration will be stopped at a slightly higher drift than the initial drift.

If very small amounts of water are to be determined, or if a long titration time is necessary, then work should be carried out using an automatic drift correction. In this case the drift value is multiplied with the titration time and the value obtained is subtracted from the added volume.

In addition to the indication system, the resolution of the buret makes a contribution to the accuracy and reproducibility of the results. Metrohm standard burets add the reagent with a resolution of 10'000 steps per cylinder volume. For a 5 mL buret this means that in the region of the endpoint, addition will be carried out in 0.5 μL steps. If a Titrando is used in combination with an intelligent Exchange Unit you can store not only the current titer on the data chip of the Exchange Unit, but also carry out addition with the unique resolution of 20'000 steps per cylinder volume.

In principle all commonly available KF reagents can be used with the Metrohm KF titrators. However, please remember that these reagents do not have a stable titer and that the titer must be determined regularly. The interval between the titer determinations depends on the choice of reagent as well as on how impervious the titration cell is.

Leading reagent manufacturers offer certified water standards for determining the titer. It is also possible to determine the titer with water. In this case work has to be carried out with very small volumes and initially the handling takes some getting used to. This is why we recommend the use of certified standards; it is possible to back-weigh the added amount and volume dosing is no longer necessary. Solid substances such as di-sodium tartrate dihydrate can also be used, but care must always be taken that the substance is completely dissolved. Standard solutions are available with a water content of 10.0 ± 0.1 mg/g (for volumetric water determination), 1.0 ± 0.03 mg/g or 0.1 ± 0.005 mg/g (for coulometric determinations) and are offered in ampoules. When handling the standards proceed as follows:

Immediately after the ampoule is opened a syringe is approximately half-filled with the standard solution. The syringe is rinsed by inverting it and ejecting the complete contents (air and standard solution). This is to ensure that the inner walls of the syringe are completely wetted with the solution. The syringe is then filled with the whole of the remaining ampoule contents without entraining any air. After the needle has been wiped off the syringe is tared on a balance and the KF titrator is started. Part of the standard solution is then injected at one go. There are two ways of doing this:

- The standard solution is injected directly beneath the surface of the KF solution.
- It is injected without immersing the needle. The last drop is drawn back into the syringe.

The syringe is then pulled out and back-weighed. The sample weight can be transmitted directly from the balance to the KF titrator or entered manually.

Particular attention should also be given to the titration cell. Water is present everywhere: At a relative humidity of 60%, 0.5 mL air at 25 °C contain approx. 7 μg H_2O . This is why it is essential that the titration cell is impervious; it should be checked at regular intervals. Special attention should be paid to the sealing rings of the titration cell and the molecular sieve – check the drift! The titrator automatically conditions the titration cell before and between determinations. It is advisable to swirl the cell about from time to time in order to remove any water adhering to the walls. It is important that a constant drift value that is as low as possible is achieved.



841 Titrando with Touch Control, 803 KF Titration Stand and Reagent Organizer.

6.2 Coulometry

In contrast to volumetric Karl Fischer titration, in KF coulometry no titrant is added but the required iodine is generated directly in the iodide-containing electrolyte by electrochemical means («electronic buret»). There is a strictly quantitative relationship between the amount of electric charge and the amount of iodine generated. This relationship allows the extremely precise addition of the iodine.

Metrohm KF Coulometers work with variable current strengths and pulse lengths (100, 200 and 400 mA) for generating iodine at the anode. Higher current strengths have not proven themselves in practice – side reactions can occur and heat can be produced. Working with variable pulse lengths allows precise «iodine dosification» even in the region of the titration endpoint.

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

Coulometric water determination is primarily used for the determination of small amounts of water. Larger amounts of water require a lot of time and/or may exceed the water capacity of the KF reagent, which could lead to incorrect results. Metrohm KF Coulometers work in a determination range of 10 µg...200 mg H₂O with a resolution of 0.1 µg H₂O.

The iodine is produced by a generator electrode. There are two different types of generator electrodes:

A) Generator electrode without diaphragm

The generator electrode without diaphragm is easy to handle and easy to clean. Only a single reagent is required. However, care must be taken that only those reagents that are intended for generator electrodes without diaphragm are used. As no moisture can adhere to the diaphragm there is a further advantage – the electrode is rapidly ready for use. There is no cathode compartment in the generator electrode without diaphragm, as reduction takes place on a platinum surface.

B) Generator electrode with diaphragm

A generator electrode with diaphragm should be used whenever your samples contain ketones and aldehydes, as the special reagents used for them are only available for generator electrodes with diaphragms. An electrode with diaphragm should also be used for reagents with a low conductivity (the addition of chloroform, e.g., reduces the conductivity) and when measurements are to be made in the lower trace range. Reagents for coulometric water determination consist of an anolyte that is filled into the titration vessel and a catholyte that is filled into the cathode compartment. Both liquids should have about the same level in order to prevent pressure compensation from forcing the anolyte into the cathode compartment and vice versa.

The endpoint is determined by means of a double platinum electrode and is largely similar to that

As the coulometric KF method is an absolute method this means that no titer has to be determined. It must only be ensured that the reaction that generates the iodine takes place to 100%. Although this is the case with the reagents that are currently available, we still recommend that the whole system is checked from time to time with the aid of certified water standards with a water content of 1.0 ± 0.03 mg/g or 0.1 ± 0.005 mg/g. Handling the standards is described in 6.1 «Volumetric KF titration».

In coulometry, cells made completely of glass are used as titration cells, as cells with a plastic cover have a certain permeability to water vapor. This does not have much influence on volumetric KF titrations, as these are normally used to determine higher water contents than in KF coulometry. Care must also be taken that the cell is as impervious as possible.



756 Metrohm KF Coulometer



Generator cells for Metrohm KF Coulometers: on the left without, on the right with diaphragm

6.3 The Karl Fischer oven

Many substances only release their water slowly or at elevated temperatures. This means that they are not suitable for direct Karl Fischer titration. A further problem is the low solubility of certain samples in alcohols. In such cases traditional methods recommend complicated sample preparation procedures or the use of solubility promoters, which represent a health hazard. Other substances react with the KF reagents to release water or consume iodine; this falsifies the results.

The above-mentioned problems can be avoided by using a heating method. The substance under investigation is heated in an oven located upstream from the cell and the released water is transferred by a flow of dry carrier gas to the titration cell where it is determined by a Karl Fischer titration. As only the water enters the titration cell and the sample itself does not come into contact with the KF reagent this means that unwanted side reactions and matrix effects are ruled out.

Work is carried out with either a conventional tube oven or with an oven using the vial technique:

The 768 KF Oven is a conventional tube oven. A weighing spoon is used to transfer the sample to the sample boat, which is automatically transported into the oven at the start of the determination.

The 832 KF Thermoprep is a further development of the conventional Karl Fischer drying oven. The samples are no longer transported into the oven by using sample boats, but the vial technique is used. The samples are weighed out directly into vials that are then hermetically sealed and placed in the oven. A double hollow needle pierces the vial septum. A stream of dry carrier gas (air or inert gas) is introduced through the inlet needle and passes through the heated sample. The carrier gas containing the released moisture then passes through the outlet needle and via a heated transfer tube directly into the titration cell, in which the Karl Fischer water determination takes place. Depending on the water content of the sample the determination can be carried out volumetrically or, in the trace range, coulometrically. Working with vials means that the oven cannot be contaminated by the sample and, as a result, no carryover or memory effects can occur. In addition, the hermetic vial seals with PTFE-coated septa reliably prevent the water content from being falsified by atmospheric moisture.

6.4 Automation in Karl Fischer titrations

The use of a sample changer is well worth while for large numbers of samples. The advantages are not only to be found in the amount of time saved by the laboratory personnel: automated systems control the operating procedures and improve both the reproducibility and accuracy. In automated KF titration there is an additional difficulty; normal KF sample changers do not work in closed systems and penetration by atmospheric moisture cannot be prevented. For a water content $>1\%$ this interference can be corrected by the subtraction of a previously determined blank value. In principle, the use of such sample changers can only be recommended for volumetric determinations.

The predefined methods of the 824 Easy Sample Changer enable the problem-free and simple processing of a series of samples. The comprehensive Karl Fischer equipment allows the determination of water in both solids and liquids. The samples are weighed out into glass vessels and covered with aluminum foil. For the determination the 824 Easy Sample Changer transfers the particular sample to the titration station and moves the titration head to the working position. A remote signal starts the addition of the solvent and then the titration itself.

However, Metrohm also offers you the possibility of the automated determination of samples with a water content $<1\%$:

The 789 Sample Processor XL is the first sample changer in the world that supplies reliable and reproducible results in combination with the KF Coulometer. As in the oven technique, the samples are weighed out into vials, hermetically sealed with septa and placed on the sample rack. With the aid of a pipetting system adapted to the special conditions of the KF titration (minimization of the penetration of atmospheric humidity) a defined volume of the sample is transported to the coulometer cell where the water content is determined.

By using the 774 Oven Sample Processor the automation of the heating method is also possible. The principle corresponds to that of the 832 KF Thermoprep, with the exception that the sample vials are placed on the rack of the Oven Sample Processor. During the analysis the turntable positions the sample vial above the oven. The vial is then lowered automatically into the heating block.

In addition, the Oven Sample Processor offers the possibility of using temperature gradients. The recorded water release curve can be used to determine the optimum heating temperature for the particular sample. The curve also allows statements to be made

about the kinetics of water release as a function of the temperature. Depending on the water content of the sample, the titration can be carried out volumetrically or, in the trace range, coulometrically.



774 Oven Sample Processor with 756 KF Coulometer



Side view of the 774 Oven Sample Processor with coulometric KF cell



803 KF Titration Stand

6.5 Accessories for Karl Fischer titrations

A wide range of accessories makes it easier to carry out Karl Fischer titrations in the laboratory:

Use the 703 KF Titration Stand for stirring and manual exchange of the used titration solution. Solvents can be added and aspirated off with the built-in membrane pump without having to open the cell. This shortens the conditioning time considerably and minimizes reagent handling by the user. The 803 Ti Stand is similar to the 703 Ti Stand, but its functions and design are adapted to suit Titrandos.

With KF Coulometers and a Titrandos, reagent exchange is even easier to carry out by using a Dosino. All you have to do is define the time and the instrument will carry out the exchange automatically.

If special additional steps are necessary, such as titration of a heated solution or homogenization of the sample in the titration cell, then special accessories are available to suit your particular application. Some examples:



Weighing spoon for solid samples



Heatable cell for titrations at elevated temperatures

6.6 Software

All KF Titrinos and KF Coulometers are supplied including the Vesuv software; this allows the simultaneous collection and storing of the results from several instruments at the same time. Vesuv supports the verification of the titration data and curves stored in the database as well as export to a laboratory data system.

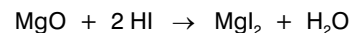
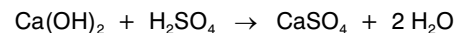
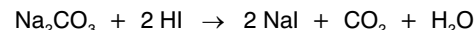
In automated systems we recommend the use of the **tiamo**™ titration software. In addition to a database, **tiamo** also offers you the possibility of controlling even complex systems from a PC. **tiamo** is also FDA-compliant. The Oven Sample Processor is automatically supplied with **tiamo**, but can also be used as a stand-alone system.

7. Side reactions

KF water determination is only specific if no side reactions take place with the KF reagents. This means that no water should be released in side reactions, nor should the sample consume or release iodine. Most (unwanted and interfering) side reactions can be suppressed by suitable measures. The most important interfering substances are:

7.1. Carbonates, hydroxides and oxides

During the KF titration methyl sulfuric acid and hydriodic acid are produced. Although these are attached to the base, they still form weak acids that react with the above-mentioned compounds to form salts and release water:

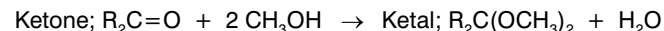
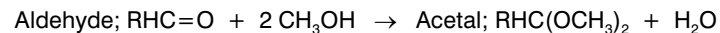


Not all oxides take part in an acidic reaction. In addition to alkali oxides and alkaline earth oxides, the following will react: Ag_2O , HgO , MnO_2 , PbO , PbO_2 and ZnO .

We recommend that the H_2O in these compounds is determined by the oven method.

7.2. Aldehydes and ketones

These two classes of compound combine with the methanol in the KFR to form acetals and ketals respectively with the release of water.



With aldehydes the reactivity decreases as the chain length increases. Aromatic aldehydes react more slowly than aliphatic aldehydes. Acetaldehyde reacts the quickest and causes the most problems. But there are always exceptions to any rule, formaldehyde and chloral do not form acetals and can be titrated without any problems.

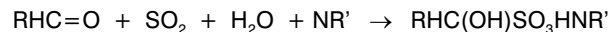
Ketones are less reactive than aldehydes. The reactivity also decreases as the chain length increases. Ketal formation is most rapid with acetone and cyclohexanone. The following are regarded as being stable (no ketal formation): diisopropyl ketone, benzophenone, deoxybenzoin, benzil, benzoin, camphor, alizarin, dibenzalacetone and dichlorotetrafluoroacetone.

Acetal and ketal formation is also influenced by the alcohol present. As the chain length increases the reactivity also decreases. This means that methanol is the quickest to react.

There are several ways of preventing acetal or ketal formation:

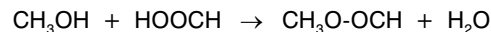
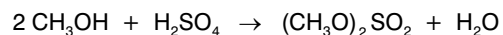
- By using KF reagents specially labeled for this purpose.
- By using methanol-free KF reagents. Methanol is replaced by a higher alcohol, e.g. 2-methoxyethanol.
- By making use of the different reaction rates and slowing down acetal or ketal formation so much that they do not interfere with the titration. This can be achieved by carrying out the titration at -10°C . This also freezes the bisulfite addition (see following section).

With aldehydes a second reaction – bisulfite addition – can also interfere. In this case H₂O is consumed, so that the water content determined could be too low.



7.3. Strong acids

Strong acids can react with the methanol contained in the KF reagent and release water:

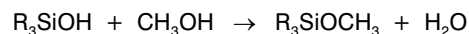


Among the organic acids the strongest esterification is shown by formic acid; acetic acid only undergoes partial esterification. Methanol esterifies the quickest. With propanol and/or 2-methoxyethanol slower reaction rates are achieved.

However, strong acids also lower the pH of the reaction solution so much that the KF reaction either no longer takes place or proceeds unsatisfactorily. The reaction mixture can be buffered by the addition of a base (e.g. imidazole) and the pH brought back to the optimal range again. If this measure is taken then no esterification occurs even with strong mineral acids (e.g. H₂SO₄ or HNO₃).

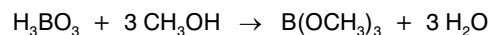
7.4. Silanols/Siloxanes

The terminal silanol groups esterify with the methanol contained in the KF reagents and release water. This means that methanol-free reagents must be used to determine the water content of these substances.



7.5. Boron compounds

Boric acid reacts with methanol with esterification and the release of water:



Boron trioxide (B₂O₃), metaboric acid (HBO₂) and borax / sodium tetraborate (Na₂B₄O₇) all react in the same way.

The esterification rate decreases as the chain length of the alcohol increases (methanol esterifies the quickest).

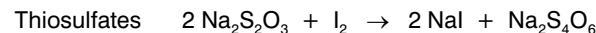
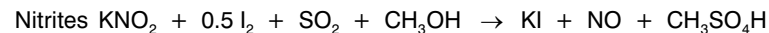
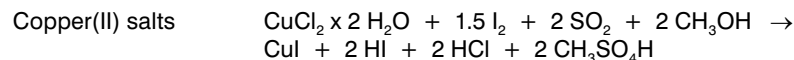
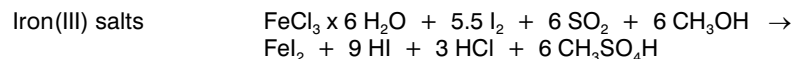
7.6. Metal peroxides

These form water with KF solutions and cannot be titrated directly. In some cases the oven method can be used (provided that the substances release their H₂O at <250 °C).

7.7. Reducing agents

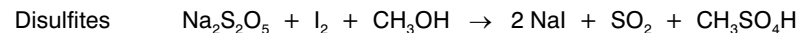
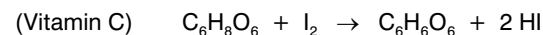
Reducing or oxidizing agents can react directly or indirectly with the iodine in the KF reagents and simulate a water content that is too high or too low, respectively.

0.5 mol H₂O / mol substance in the sample is simulated by:

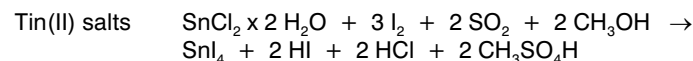
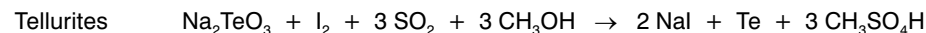
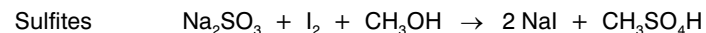
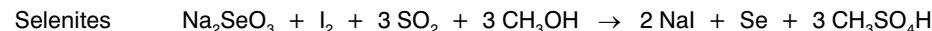
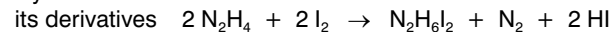


1 mol H₂O / mol substance in the sample is simulated by:

Ascorbic acid



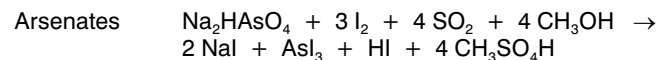
Hydrazine and



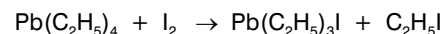
2 mol H₂O / mol substance in the sample is simulated by:



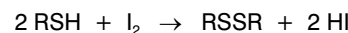
3 mol H₂O / mol substance in the sample is simulated by:



Petrochemical products may also contain interfering substances. The additive tetraethyl lead simulates a higher water content:



This same applies for mercaptans, which are oxidized to disulfides:



The water content of salts can usually be determined by the oven method. We recommend the following procedure for determining the water content of ascorbic acid and hydrazines:

The sample is dissolved in methanol and titrated against methanolic iodine solution. This oxidizes it and the KF water determination is no longer interfered with. In the same solution a titration can then be carried out with a combined KF solution. The H₂O content of the methanol used must be determined separately and subtracted from the result.

7.8. (Strong) Oxidizing agents

These release elemental iodine from the iodides in the KF reaction and simulate a water content that is too low.

7.8 a Dialkyl peroxides, diacyl peroxides and peresters form iodine. However, the reaction takes place slowly and can be «frozen» at low temperatures. The titration temperature to be used is product-specific and can be as low as –60 °C.

Hydroperoxides – e.g. H₂O₂ – do form iodine, but also an equivalent amount of H₂O. The KF titration is free from interference.

7.8 b Elemental chlorine and bromine also release iodine. In this case excess SO_2 is passed through the sample. This reduces these substances to chloride and bromide respectively, which no longer interfere.

7.8 c The water content of dichromates, chromates and permanganates is determined by the oven method.

8. Sample preparation techniques

Each sample preparation is preceded by sampling. Particularly with inhomogeneous samples – and there are a lot of them, even if it is not always obvious – this initial step plays a crucial role for the correctness and accuracy of the results. Correct sampling is therefore an essential requirement for the subsequent determination!

Many standardized methods provide detailed instructions concerning this subject. This may also apply for in-house instructions. If no instructions are available then the following points must be observed:

- The water content of the sample taken must be the same as the average water content of the original sample – i.e. the sample must be representative.
- Atmospheric moisture is an ever-present source of contamination, and not only in tropical countries.
- Hygroscopic samples have a large amount of water adhering to their surfaces.
- Samples that easily release water or become weathered have only a small amount of water on their surfaces.
- Liquids can release water if the water is not present in dissolved form but as a dispersion (precipitation or flotation, adherence to vessel walls – e.g. petrochemical products, margarine). The same applies for samples in which the solubility limit for water is undercut on cooling down.
- The more heterogeneous the water distribution in the sample, the larger the sample to be taken.
- Sampling must take place as quickly as possible and the water content of the sample must not change during transport and storage.

General

Many samples can be weighed out and/or injected directly into the titration vessel or titration cell, provided that they are soluble in the solvent used and do not undergo side reactions with the KFR.

In contrast, other samples require one or more preparation steps. The most important sample preparation techniques are described below. Further information can be found under the individual classes of substances.

It is very important that the sample preparation technique used does not introduce any additional water into the sample and that no water losses occur by heating the sample too strongly.

A) Dilution

For reasons of accuracy (sample size) we recommend that samples with a high water content (>40%) are diluted with an inert dry solvent before the determination. Metha-

nol can normally be used for this purpose. If the sample contains emulsified fats and/or oils then a dry mixture of 60% methanol and 40% decanol (or, if permitted, chloroform) should be used. The procedure is as follows:

Approx. 1 g sample is weighed out exactly into a dry Erlenmeyer flask fitted with a septum stopper. This is treated with approx. 20...25 g dry solvent (mixture), the flask is then sealed and the contents mixed. Part of the mixture is drawn off in a dry syringe and the syringe and its contents are tared. Some of the mixture is injected into the titration vessel and titrated. The amount of sample injected is determined by back-weighing the syringe. If a dry solvent is used then it is not absolutely necessary to take its blank value into account. Here is an example:

Sample weight	1.575 g
Methanol weight	22.725 g
Injected mixture	1.500 g
KFR titer	4.855 mg H_2O / mL
KFR consumption	6.255 mL

Calculation

Diluted sample	$22.725 \text{ g} + 1.575 \text{ g} = 24.300 \text{ g}$ (100%)
Sample fraction	$1.575 \text{ g} : 24.3 \text{ g} = 0.0648$
Injected sample	$0.0648 \times 1500 \text{ mg} = 97.22 \text{ mg}$
H_2O found	$6.255 \text{ mL} \times 4.855 \text{ mg/mL} = 30.37 \text{ mg}$
H_2O in sample	$30.37 \times 100 / 97.22 = 31.24\%$

The following samples can be treated in this way:

- Drilling and cutting oil emulsions
- Cosmetic lotions and emulsions
- Spirits
- Milk and cream, ready-to-use salad sauces, liquid spices.

B) Solvent extraction

This can take place in two different ways – external or during the titration in the titration vessel. It is usually carried out either warm or hot, less frequently at room temperature. If an external extraction is carried out then please remember that all the water can never be extracted, an average water content between the sample and the solvent is obtained. Example:

10 g sample with a water content of 10% is extracted with 50 mL methanol (density approx. 0.8 g/cm^3) with a water content of 100 ppm. The H_2O content of the mixture is $1004 \text{ mg} / 50 \text{ g}$, corresponding to $20.08 \text{ mg } \text{H}_2\text{O} / \text{g}$ or $2.008\% \text{ H}_2\text{O}$.

This also means that the larger the ratio between the sample and dry solvent, the less water will be extracted from the sample. The blank value of the solvent must, of course, be taken into consideration when calculating the water content.

Better values are obtained if the extraction is carried out directly in the titration vessel and the water is titrated immediately. A titration vessel equipped with a heating jacket and a reflux condenser is used and the titration is carried out, for example, at $50 \text{ }^\circ\text{C}$. Work can be carried out with or without an extraction time (set at the titrator) as required. (If an extraction time is used then please note that a sufficiently long stop delay must be observed for the EP.)

This method is primarily used for cereal flour.

C) Homogenization

In liquids water can float, adhere to the inner walls of the sample bottle or be deposited on the bottom. This occurs particularly when the sample is taken at a high temperature and allowed to cool down to room temperature before the analysis. The water can again be distributed homogeneously by immersing the bottle in an ultrasonic bath.

The separated water can also be dissolved again by the addition of an exactly weighed-out amount of a solubility promoter (e.g. isopropanol), whose water content has been accurately determined (blank value). This method is suitable for pastes and viscous liquids.

Solids are usually inhomogeneous and must be thoroughly comminuted and homogenized. The procedure depends on the constitution of the sample:

Coarse particles, hard and tough

Ball mill or analytical mill (closed) with water cooling. This method is suitable for coffee, cereals, semolina, pasta, beans, lentils, pills, spices* and tea*.

* Followed by high-frequency comminution.

Coarse, fatty

Grating and high-frequency comminution, e.g. for nuts, seeds and almonds.

Coarse, soft, inhomogeneous

Comminute with a meat grinder or knife, then high-frequency comminution. Suitable for dried fruits, meat and sausages, fruit and vegetables.

Pasty, inhomogeneous

Homogenization with a blender, then possibly high-frequency comminution. For jam, mustard, precooked spinach.

Suspensions

High-frequency comminution, e.g. for fruit and vegetable juice, fruit pulp, concentrates and tomato puree.

High-frequency comminution is the only method that can guarantee that even plant samples are thoroughly homogenized. In this method the cells are disrupted and the water present inside the cells is extracted. Comminution is usually carried out externally in a dry Erlenmeyer or round-bottom flask with the addition of a suitable solvent (mostly methanol).

Comminution in the titration vessel is also possible; the mixing head is commonly used as a stirrer (remove the magnetic stirrer bar from the titration vessel).

D) Heating method

The sample is either heated in a dry stream of gas (air or nitrogen) or a dry stream of gas is passed through the heated sample; in each case the released water is transferred to the titration vessel and immediately titrated. The heating temperature should be set as high as possible – just high enough so that the sample does not decompose and no interfering secondary constituents distill over. The heating temperature and duration must be optimized in preliminary tests. The appropriate blank values must be subtracted.

This method is used for samples that cannot be extracted (or cannot be completely extracted) with a suitable solvent or that undergo side reactions with the KFR. Examples are:

- Plastics, minerals, carbonates and metal oxides, carbon powder
- Petrochemical products containing additives (motor oils, lubricating oils and greases)
- Starting materials for pharmaceutical products, certain freeze-dried samples.

9. Water determination in raw materials / basic chemicals

9.1 Inorganic salts

Salts may contain adherent or enclosed moisture. In the determination of the adherent water the procedure must ensure that the salt does not dissolve. The working medium is methanol/chloroform 1:3 and the titration must be carried out quickly.

There are two methods for the determination of the total water content:

- In a solvent mixture in which the salt dissolves completely. A mixture of methanol/formamide 2:1 is suitable. Carrying out the titration at an elevated temperature (e.g. 50 °C) often helps to accelerate the dissolution of the sample and release of water.
- By the heating method (oven method). A dry stream of gas transfers the released water to the titration cell.

9.1.1 Halides

Alkali halides crystallize out without any water of crystallization, but usually contain enclosed water that is only released slowly. In such cases it is advisable to set an extraction time at the titrator. Examples are: NaCl, KCl, NH₄Cl, KI, CsI and KF. Glacial acetic acid is used as the working medium for KHF₂.

In contrast, alkaline earth halides usually crystallize out as hydrates, in which the water can be determined without any problems. Examples are: MgCl₂ x 6 H₂O, CaCl₂ x 2 H₂O, BaCl₂ x 2 H₂O and SrCl₂ x 6 H₂O. CaF₂ is insoluble, only the adherent water is determined.

The following can also be titrated without any problems: AlCl₃ x 6 H₂O, FeCl₂ x 4 H₂O, MnCl₂ x 4 H₂O, CoCl₂ x 6 H₂O, CdCl₂ x 2.5 H₂O, SnCl₄ x 5 H₂O, KF x 2 H₂O and NaClO₄.

Other halides which present problems for direct titration are:

- CuCl₂ x 2 H₂O. As a result of the following side reaction «only» 1.5 H₂O can be found:
$$\text{CuCl}_2 \times 2 \text{H}_2\text{O} + 1.5 \text{I}_2 + 2 \text{SO}_2 + 2 \text{CH}_3\text{OH} \rightarrow \text{CuI} + 2 \text{HCl} + 2 \text{HI} + 2 \text{HSO}_4\text{CH}_3$$
- FeCl₃ undergoes a reduction reaction (iodine consumption)
- SnCl₂ is a strong reducing agent (iodine consumption)
- TiCl₃ and VCl₃ are also strong reducing agents.

For these halides the heating method, or an azeotropic distillation with toluene or xylene is indicated. In KClO₃ the water is also determined by the heating method (300 °C).

9.1.2 Sulfur compounds

Sulfates often crystallize out as hydrates, which dissolve relatively easily in methanol. Example are: $\text{Na}_2\text{SO}_4 \times 10 \text{H}_2\text{O}$, $\text{MgSO}_4 \times 7 \text{H}_2\text{O}$, $\text{MnSO}_4 \times 4 \text{H}_2\text{O}$, $\text{NiSO}_4 \times 6 \text{H}_2\text{O}$, $\text{ZnSO}_4 \times 7 \text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \times 18 \text{H}_2\text{O}$, $\text{KAl}(\text{SO}_4)_2 \times 12 \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \times 6 \text{H}_2\text{O}$.

The following sulfates must be analyzed by the heating method, as they either release no water at all or not all their water:

$\text{CaSO}_4 \times 2 \text{H}_2\text{O}$, $\text{MnSO}_4 \times \text{H}_2\text{O}$ and $\text{ZnSO}_4 \times \text{H}_2\text{O}$.

$\text{CuSO}_4 \times 5 \text{H}_2\text{O}$ undergoes a side reaction on direct titration, apparently only 4.5 H_2O can be found (see also CuCl_2).

Hydrogen sulfates (e.g. KHSO_4) are very acidic. Larger amounts of sample must be neutralized (addition of imidazole).

Sodium sulfite (Na_2SO_3), sodium disulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) react quantitatively with iodine. These substances are dissolved in pyridine/methanol and first titrated with iodine solution. The pyridine-sulfur dioxide components are then added and the water titrated.

Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) does not react with iodine in methanolic solution. The water in this salt can be determined.

Soluble sulfides are oxidized by the KF reagent to form sulfur. As the reaction does not proceed stoichiometrically, water determination by the Karl Fischer method is not possible.

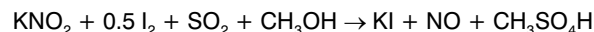
9.1.3 Nitrogen compounds

Nitrates are normally easy to analyze. Examples are:

NH_4NO_3 , KNO_3 , $\text{Co}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$, $\text{HgNO}_3 \times \text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \times 9 \text{H}_2\text{O}$.

The water in KCN is determined by the heating method (280...300 °C) and that in potassium hexacyanoferrate in methanol/formamide 2:1.

Nitrites react with the iodine in the KF reagent and cannot be titrated:



9.1.4 Phosphorus compounds

Phosphates normally present no problems. As tertiary phosphates have a strongly alkaline reaction, they must first be neutralized (addition of salicylic acid). Secondary calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ is insoluble. Its water content must be determined by the heating method. The same applies for sodium polyphosphates (280...300 °C). A few more examples:

NaH_2PO_4 , K_2HPO_4 , Na_3PO_4 , $\text{MgHPO}_4 \times 3 \text{H}_2\text{O}$, $\text{MgNH}_4\text{PO}_4 \times 6 \text{H}_2\text{O}$, CaHPO_4 and potassium hexafluorophosphate.

Hypophosphites do not react with the KF reagent and can be analyzed.

9.1.5 Further compounds

- Alkali silicates cannot be titrated directly. They react like alkali hydroxides and release water on neutralization – heating method.
- Selenites, tellurites, arsenates, arsenites, borates and tetraborates undergo side reactions and cannot be titrated directly. See section 7.

9.2 Inorganic oxides, peroxides and per salts

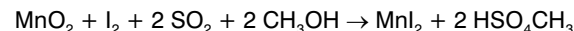
9.2.1 Oxides

Many oxides react with the acids produced during the titration of the water with KF reagent. However, the reaction rate depends very much on the structure of the oxide. Mineral oxides often react slowly and incompletely. Examples are:

Na_2O , K_2O , MgO , CaO , Cu_2O , ZnO , HgO and Ag_2O .

Lead dioxide (PbO_2) and red lead (Pb_3O_4) react with the KF reagent, although incompletely as the oxide particles are enclosed by the lead iodide formed.

Manganese dioxide (MnO_2) also reacts with the KF reagent:

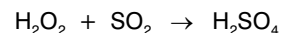


As a result of this reaction, the water in the above-mentioned oxides is best determined by the heating method.

Insoluble oxides, e.g. annealed iron(III) oxide or aluminum oxide are inert. They do not react with the KF reagents.

9.2.2 Peroxides / per salts

Hydrogen peroxide and its addition products react with the sulfur dioxide of the KF reagent in the following way:



This means that neither water nor iodine is consumed or formed. The water determination is not influenced. However, as sulfuric acid is formed with H_2O_2 this should be neutralized (addition of imidazole).

Metal peroxides and per salts behave similarly. However, if the peroxides contain oxides, hydroxides or carbonates then these will react with the KF reagent. See also 9.2.1 and 9.3.

In metal peroxides and addition compounds the water content is determined by the heating method. Examples are:

Na_2O_2 , BaO_2 , MgO_2 , ZnO_2 , CaO_2 , as well as $\text{Na}_2\text{CO}_3 \times \text{H}_2\text{O}_2$, $\text{NaBO}_2 \times \text{H}_2\text{O}_2 \times 3 \text{H}_2\text{O}$ and $\text{Na}_4\text{P}_2\text{O}_7 \times \text{H}_2\text{O}_2$.

For peroxodisulfates (persulfates) the following instructions with separate reagents apply:

A 1:1 mixture of formamide and KF solvent is cooled to approx. –20 °C and titrated until dry. A high-frequency mixer (e.g. Polytron or Ultra-Turrax) is used as the «stirrer». The mixture is titrated to dryness, 1...1.5 g sample is added and the titration with iodine solution is started. Extraction time 2 min. The water in $\text{K}_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is determined by this method.

9.3 Inorganic hydroxides and carbonates

During the KF titration methyl sulfuric acid and hydriodic acid are formed. Although these are attached to the base, they still form weak acids that react with the above-mentioned compounds to form salts and release water – see section 7, «Side reactions». This is why the water in hydroxides and carbonates is determined by the heating method. Examples:

NaOH , KOH , $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, Na_2CO_3 , NaHCO_3 , CaCO_3 , MgCO_3 and K_2CO_3 .

An exception is chalk/lime (CaCO_3). In this case the water can be determined by a direct volumetric titration in methanol – but only if the solution is changed after each determination, as otherwise the side reaction occurs.

9.4 Inorganic acids

These present no problems for the water determination, provided that they are first neutralized (esterification and chiefly «pH displacement»). At least an equivalent amount of imidazole (or pyridine) is added to the methanol. This method is used for determining water in HCl , HNO_3 , H_2SO_4 and H_3PO_4 .

HBr and HF are absorbed in pyridine and titrated. Transparent plastic vessels are used for HF and the titration endpoint is determined visually or photometrically (HF attacks glass).

9.5 Organic salts

For carboxylic acid salts the same principles apply as for inorganic salts – see section 9.1. This means that the determination of the soluble salts presents no difficulties, as they do not displace the pH of the KF system.

Formamide considerably improves the dissolving capacity for polar substances and accelerates the extraction of moisture from solids and the reaction procedure. The KF titration becomes faster. However, it also influences the KF stoichiometry if more than 50% V/V is added. Solutions with a methanol/formamide ratio of 2:1 are ideal. The determination is also accelerated if the titration is carried out at a higher temperature (e.g. at 50 °C).

The water content of organic salts is normally determined volumetrically. Examples of substances that have been investigated are:

Sodium acetate, sodium tartrate, trisodium citrate, tripotassium citrate, potassium sodium tartrate, sodium glutamate, magnesium aspartate hydrochloride, magnesium di-aspartate, EDTA disodium salt, calcium folinate, calcium gluconate, calcium glycerophosphate, calcium sorbate, potassium acetate, sodium benzoate, sodium propionate, sodium salicylate, barium acetate, ammonium oxalate, potassium oxalate, cadmium acetate and magnesium acetate.

The water in zinc diamylthiocarbamate is determined coulometrically by the heating method (120...140 °C, sample weight 2...3 g).

Sodium methylate has a strongly alkaline reaction. 5 g benzoic acid is dissolved in 30 mL methanol (in the titration cell), titrated to dryness and then approx. 2 g sample is added.

9.6 Organic peroxides

The most important requirement for the analysis of organic peroxo compounds is a sufficiently large excess of SO_2 in the KF system. If this is not the case then the KF reaction is prevented by the lack of SO_2 . As strong acids could also be formed, there must be a large enough supply of bases present (buffering).

This is why the water in these compounds is generally determined volumetrically with separate reagents.

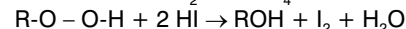
Organic peroxides react at different rates and undergo different reactions with the KF reagents. Nevertheless, they can still be titrated if work is carried out at low temperatures so that any possible side reactions can be «frozen».

General procedure:

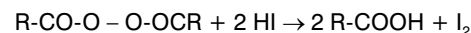
25...30 mL KF solvent is placed in the titration vessel, cooled to –20 °C to –60 °C and titrated to dryness with iodine solution. The sample is added and its water content is titrated at the same (low) temperature.

A few more reaction equations:

Alkyl peroxides



Diacyl peroxides



Dialkyl peroxides

react slowly and do not normally influence the KF titration.

- Benzoyl peroxide / dibenzoyl peroxide, –40 °C, 0.3 g sample
- Butylhydroperoxide / tert. butylhydroperoxide, –20 °C, 0.1 g sample
- Dicyclohexylperoxidicarbonate, –40 °C, 0.2 g sample
- Diethylhexylperoxidicarbonate, –60 °C, 3 g sample
- Methyl ethyl ketone peroxide / butanone peroxide, –20 °C, 0.3 g sample

9.7 Organic bases

All organic bases are nitrogen compounds. They include aliphatic and aromatic amines, heterocyclenes, amides and imines.

They can be divided into three groups according to their behavior:

Weak bases, strong bases and substances that cause chemical interference.

Weak bases with pK_B values >8 normally present no problems. They behave like hydrocarbons and can be titrated like them (take solubility in methanol into account, it may be necessary to add propanol or decanol as a solubility promoter). Examples are:

Pyridine, picoline, quinoline, imidazole, benzimidazole, benzothiazole, nicotine, N',N'-dimethylaniline and diphenylamine.

Strong bases with pK_B values <8 can cause difficulties by increasing the pH of the KF system. This could delay the titration or even make it impossible. For this reason they should first be neutralized. This is done by adding an excess of benzoic acid (e.g. 5 g), titrating to dryness and then adding the sample (even large excesses of benzoic acid do not interfere with the titration). Examples of substances that have been analyzed are:

- Propylamine, butylamine, hexylamine, methoxypropylamine, TRIS, aminoethanol, cyclohexylamine, pipentylamine, dicyclohexylamine, diethanolamine, triethylamine, diethylethanolamine, triethanolamine, dimethylcyclohexylamine.
- Diaminoethane, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dimethylaminopropylamine, hexamethylenediamine.
- Pyrrolidine, piperidine, methylpiperidine, piperazine, morpholine.

- Aniline, toluidine, anisidine, aminophenol, naphthylamine, methylaniline, dimethylaniline, diethylaniline, diphenylamine.
- Methylimidazole, triazine, triazole, carbazole, hydroxyquinoline, aminopyridine and aminobenzothiazole.

Long-chain amines usually do not dissolve completely in methanol. Help is provided by adding trichloroethylene and titrating at an elevated temperature.

Chemical interference is caused by: 1,2-diaminoethane (titration only possible with a 10-fold excess of acetic acid), aniline, m-toluidine, aminophenol, 1,2-diaminopropane and 1,2-phenylenediamine. These substances are analyzed in methyl glycol with a methanol-free titrant.

The water content cannot be titrated (because of unknown influences or side reactions) in pyrrole, methylpyrrole, indole and N',N'-diethyl-p-phenylenediamine.

In contrast, there are no problems with acid amides. Examples:

Formamide, N,N-dimethylformamide, chloracetamide, dimethylacetamide and urea.

It is chiefly the volumetric determination of the water content that has proven itself in practice. In coulometric titrations the interference is more noticeable. «Poisoned»* anodes are often observed. This unwanted effect increases if benzoic or salicylic acid is added, but is also observed with chlorinated hydrocarbons.

* The anode is passivated by a coating – unhindered current flow can no longer be guaranteed and the instrument produces an error message (voltage no longer sufficient to achieve the necessary current strength).

9.8 Organic acids

The water determination in carboxylic acids can usually be carried out without any problems. Stronger acids must be neutralized before the titration (e.g. by adding imidazole to the solution) so that the pH of the KF system does not decrease too much.

Acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid and bromoacetic acid tend toward esterification – water is formed. For these acids a solvent such as methyl glycol is used and they are titrated with a methanol-free titrant.

Most organic acids can be titrated volumetrically or coulometrically – with the exception of propionic acid, which shows a clear esterification in coulometric titration. As the chain length increases the tendency to esterification also increases.

Long-chain carboxylic acids/fatty acids are not sufficiently soluble in methanol at room temperature. To improve their solubility the titration can be carried out at elevated temperature (e.g. at 40...50 °C) or with the addition of a solubility promoter (propanol, chloroform), e.g. for stearic and palmitic acids.

The following organic acids have been titrated:

Propionic acid, butyric acid, 2-ethylhexanoic acid, mandelic acid, cinnamic acid, lactic acid, malonic acid, maleic acid, fumaric acid, tartaric acid, citric acid, benzoic acid, salicylic acid, naphthalenecarboxylic acid, indolecarboxylic acid, nicotinic acid, malic acid, pyruvic acid, levulinic acid and sulfanilic acid.

Formic acid is an exception. In addition to esterification, there is also an iodine oxidation by the KF titrant. This is why reagents for ketones and aldehydes are required. The maximum sample volume is 1 mL as side reactions occur with larger amounts of sample.

Terephthalic acid is sparingly soluble and its water content is best determined by the heating method (200 °C). The same applies for most amino acids (heating temperature 140...160 °C) (if insoluble substances are titrated in suspensions then only the surface water will be determined).

10. Water determination in cosmetics and pharmaceuticals

10.1 Cosmetics

10.1.1 Products containing oils and fats

Apart from fat, oils and emulsifiers, these fat(oil)-in-water emulsions contain a considerable amount of water (40...95%). This large amount of water means that a direct titration of such substances is not advisable – the small sample weight means that the weighing error would be too large. This is why such samples are first diluted. Because of the fat and oil fraction this is done by using a solvent mixture of methanol/chloroform 2:1.

Approx. 2 g sample is weighed out into a dry Erlenmeyer flask fitted with a septum stopper (for creams either directly from the tube or via a syringe without needle). Approx. 50 g methanol/chloroform 2:1 is added together with a magnetic stirrer bar. The flask is sealed, the contents are shaken vigorously and the flask is then placed on the magnetic stirrer for 5...10 min. A blank sample containing 50 g of the solvent mixture is prepared in a second flask.

25 mL methanol is placed in the titration vessel and titrated to dryness. The blank value of the solvent mixture is determined first by taking approx. 5 mL from the «blank value» flask with a dry syringe (with needle) and determining the blank value of approx. 2 mL of this solution. The syringe is weighed before and after sample addition in order to determine the exact sample weight. The blank value is calculated in mg H₂O / 2 g.

The sample solution is then treated in exactly the same way.

Calculation example:

$$\% \text{ water} = (\text{EP1} - \text{C30}) \times \text{C01} \times \text{C02} \times \text{C03} / \text{C00}$$

where

EP1 = mL KF solution for the sample

C00 = sample weight in g

C01 = titer of KF solution (mg H₂O / mL)

C02 = 100 (for %)

C03 = 25 (dilution factor, 2 g to 50 g)*

C30 = blank value (mg H₂O / 2 g)*

* Strictly speaking, this is not quite correct but, because of the large amount of water in the sample, it is not relevant.

The water content of the following samples has been determined in this way:

Hand creams, foot balsam, body lotion, salves, face lotion, night cream, day cream, complexion lotion, moisturizer, sun cream, sun lotion and hair cream.

10.1.2 Liquid soaps, shower gels, bath liquids, shampoos, hair gels

These also contain large amounts of water. They can be analyzed without any problems as their pH is neutral to slightly acidic. However, in such cases we also recommend a di-

lution as is described in detail in section 10.1.1. Dry methanol on its own is quite sufficient – the addition of chloroform for such oil-containing products is not necessary.

10.1.3 Products containing alcohol

These include eau de Cologne, after shaves, hair tonic and face lotions and can be analyzed directly. The amount of sample depends on the water content and type of titration (volumetric or coulometric).

10.1.4 Sprays

The water content of deodorant sprays, foot sprays and hair sprays can be determined as follows:

25 mL methanol (water content max. 0.01%) is placed in the titration vessel and titrated to dryness with a dilute KF reagent (titer e.g. 2 mg H₂O / mL). A thin piece of tubing is attached to the dosing valve and the spray can is shaken vigorously. The valve is then pressed for about 3 s to rinse the tubing. The spray can is then weighed and approx. 1.5...3.5 g spray is added to the mixture and its water content titrated (the exact sample weight is obtained by back-weighing the spray can).

10.1.5 Dental care and mouth rinse products

Mouth rinses contain a lot of water. They are best analyzed as described under 10.1.1 by dilution with methanol and volumetric titration.

Toothpastes often contain abrasive pigments (e.g. CaCO₃) that could react with the KF reagents. Their water content can be determined in the following way:

Approx. 1 g sample and approx. 40 mL methanol are weighed out into a dry Erlenmeyer flask fitted with a septum stopper. A magnetic stirrer bar is added, the flask is sealed, shaken vigorously and placed on the magnetic stirrer for 5 min. The solution is then allowed to settle out and approx. 5 mL of the supernatant liquid is removed with a dry syringe. Approx. 3 mL of this is then injected into the conditioned titration vessel. A blank sample is treated in the same way. The sample weight is determined by back-weighing the syringe. The calculation of the water content is described in 10.1.1.

Denture sterilizing tablets (for false teeth) contain hydrogen carbonates (bicarbonates), which react with the KF reagents with the release of water. We have determined their water content by the heating method (70 °C*, nitrogen as carrier gas). A few tablets were crushed in a mortar, mixed and 0.2...0.5 g of the powder was used for the analysis.

* At higher temperatures the hydrogen carbonates (bicarbonates) react with other constituents to release water.

10.1.6 Other products

Body powders and make-ups can contain talcum or oxides that react with the KF reagents with the release of water. Tests on these products with the heating method have shown that interference occurs; so we have used the extraction method with methanol as described for toothpaste in 10.1.5.

Lipsticks and lip salves contain paraffins that are insoluble or only sparingly soluble in methanol. We have determined their water content in the following way:

Approx. 0.2 g sample and approx. 25 mL of a 1:1 methanol/chloroform mixture are weighed out into a dry Erlenmeyer flask fitted with a septum stopper. The flask is sealed and the sample dissolved by warming to approx. 30 °C. The water is determined in 5...10

mL of this mixture (removed with a dry syringe that is weighed before and after injection). The titration cell contains 20 mL methanol/chloroform 2:1. A blank sample is treated in the same way, for calculation please refer to 10.1.1.

The water content of solid soaps (toilet soap, hand soap) is determined volumetrically with separate reagents at elevated temperature. 25 mL of the solvent is placed in the titration cell, warmed to 40 °C and titrated to dryness. Approx. 0.5 g soap shavings are added and their water content is titrated at the same temperature. The instrument is programmed for an extraction time of 5...15 min (the sample must be dissolved).

Mascara and mascara remover are diluted with a 2:1 mixture of methanol/chloroform and the water content determined as per 10.1.1.

Nail polish and nail polish remover could contain ketones. They are placed directly in the titration vessel and volumetrically titrated with special reagents just like ketones. See section 15.6.

Baby oils and almond oil contain very little water. Their water content is best determined coulometrically. The addition of a solubility promoter (decanol or chloroform) to the anode solution is recommended (see section 15.6).

10.2 Pharmaceuticals

For many years now the KF titration has been stipulated as the standard method for determining the water content of pharmaceutical ingredients. The most important standards for us are:

- European Pharmacopoeia (Pharm.Europe) 4th Edition & Supplements 2002
- U.S. Pharmacopoeia, USP 25 NF-20, 2002, and USP 26 NF 21, 2003

Both of these contain detailed information about the sample size / sample weight, the titration method (>95% direct volumetric titration), the range of water content permitted and the reagents to be used. By their nature the given methods are also validated methods; this means that the use of modern, pyridine-free reagents is somewhat severely limited: if modern reagents are used then the users must validate the methods themselves and prove that the same results are obtained. In order to avoid unnecessary work it is advisable to consult the manufacturer of the reagents. These remarks apply in particular to Pharm.Europe, which describes the use of a pyridine-containing reagent for KF volumetry that is no longer commercially available – i.e. the users must prepare it themselves! In this respect the USP is considerably less restrictive. Although it also describes a pyridine-containing reagent, it nevertheless also permits the use of commercially available reagents containing other solvents or bases than pyridine or other alcohols than methanol.

Pharm.Europe describes 442 substances for which the water content has been determined by the Karl Fischer method, the *USP* describes 285 substances. There is no point in listing all 727 substances here – they are all described in our method collection *Pharm PAC 6.6042.003* (English version).

With methanol in the titration cell we have determined the water content of the following substances by direct volumetric titration:

Pyrazolone, ciprofloxacin hydrochloride, effortil, folic acid, nicotinic acid and scopolamine hydrobromide.

And in methanol at 50 °C:

Glucose, hyaluronic acid Na salt, lysine acetylsalicylate, acetylsalicylic acid, Ca folinate and lactose monohydrate.

The water content of the following substances has been determined in a solvent mixture, in some cases after heating to 50 °C:

Mannitol and sorbitol (methanol/formamide 2:1), *erythromycin* (pyridine), *isomalt, glucosylmannitol/glucosylsorbitol* (methanol/formamide 1:1, ground-up sample), *Mg aspartate, Mg lactate, Ca glycerophosphate, coffeine* (methanol/formamide 2:1, 50 °C), *glycerol monostearate and suppositories* (methanol/chloroform 2:1, dilute titrant with 2 mg H₂O/mL), *lanolin* (methanol/chloroform 1:1), *serine phosphoric acid* (methanol/formamide 2:1, 50 °C) and *herb extracts* (methanol/formamide 2:1).

With some products or substances side reactions can occur if the titration is carried out directly in methanol (pH alteration of the KF system, oxidation by iodine, poor solubility in methanol, etc.). If such samples cannot be determined by the heating method then we suggest the following procedures:

Salves and creams are first diluted with methanol/chloroform.

Approx. 1.5 g sample is weighed out into a dry Erlenmeyer flask fitted with a septum stopper. Approx. 50 g methanol/chloroform 1:1 is added together with a magnetic stirrer bar, the flask is sealed and vigorously shaken. It is then placed on the magnetic stirrer for 5 min. 25 mL methanol/chloroform 2:1 is placed in the titration cell and titrated to dryness. Sample solution is removed through the septum stopper with a dry syringe and approx. 1 mL is injected into the titration vessel. The sample weight is obtained by differential weighing of the syringe. A blank value for the solvent mixture is determined in the same way. Please refer to section 10.1.1 for the calculation.

In *lozenges* we have determined the water in the same way as in salves. 3 g comminuted sample is dissolved in 20 g formamide under gentle heating and approx. 1 g is titrated with the separate KF reagents for aldehydes and ketones.

Bismuth subnitrate is treated in the same way (5 g sample in approx. 50 g methanol, 2...3 g of the separated out supernatant solution is titrated).

Of the highly viscous *pentanol* approx. 1 g is diluted with approx. 10 g methanol and approx. 2 g of the mixture is titrated with the separate KF reagents for aldehydes and ketones.

For *amoxicillin, penicillin G, dobutamine hydrochloride monohydrate, arginine aspartate and norepinephrine hydrochloride*, 30 mL methanol + 5 g salicylic acid is placed in the titration cell and titrated to dryness; the sample is then added and its water content determined.

For *S-carboxymethyl-L-cysteine* 20 mL of a 1:1 mixture of methanol/formamide is placed in the titration vessel with 5 mL KF buffer solution and titrated to dryness. Approx. 1 g sample is added and its water content is determined.

With *adenosine-5'-triphosphoric acid disodium salt imidazole* (approx. 3 g) is added to the methanol in the titration cell in order to stabilize the pH of the KF system.

Vitamin C (ascorbic acid) and *ascorbates* are oxidized by the iodine in the KF reagents and an increased water content is simulated. The following procedure – with separate reagents – is proposed for these substances:

25 mL methanol is placed in the titration vessel and the sample is dissolved in it. The vitamin C or ascorbate is then titrated with methanolic iodine solution (the titrant consump-

tion does not need to be noted down). 10 mL working medium (SO₂ plus base in methanol) is added and the water content is titrated with the same titrant. The blank value of 25 mL methanol + 10 mL working medium (without sample) is determined and taken into account in the calculation.

Lindane contains free chlorine and its water content must also be determined with separate KF reagents:

25 mL working medium (SO₂ + base in methanol) is placed in the titration vessel and approx. 2 g sample is added. The solution is stirred for 5 min and the water content is then determined by titration with iodine solution. The blank value for 25 mL working medium (without sample) must then be determined separately and taken into account in the calculation.

For *N-acetylcysteine* 20 mL methanol + 5 mL KF buffer solution + 1 g N-methylmaleinimide is placed in the titration vessel and titrated to dryness with KF solution. Approx. 1 g sample is added, the solution is stirred for 5 min and the water content is then titrated.

The water content of many substances/samples can be analyzed by the heating method (oven method). For tablets we recommend comminuting a mixed sample to powder. Application Bulletin No. 280 contains detailed working instructions using the 774 Oven Sample Processor. Dry nitrogen should normally be used as the carrier gas. The oven temperature should be set so that the sample does not decompose while still releasing its water as quickly as possible (use a temperature ramp in a preliminary test). Some examples for which this method has been used are given below:

Starch-containing tablets (150 °C), *gelatin capsules* (120 °C), *antibiotic tablets* (180 °C, separate KF reagents for aldehydes and ketones – contain glutaraldehyde), *effervescent tablets* (90 °C), *Ca methyltetrahydrofolate* (120 °C), *N-(omega)nitro-L-arginine* (160 °C), *starch-stearic-acid mixtures* (140 °C), *Fe fumarate and Fe gluconate* (140 °C), *rubber stoppers* (250 °C), *lyophilizates and vaccines* (70...140 °C), *foil-packed tablets* (130 °C), *amino acid mixtures* (140 °C), *serotonin* (200 °C), *dry cimicifugin extracts* (90 °C) and *multivitamin tablets* (120 °C).

Application Bulletin No. 282 describes water determination using the heating method (774 Oven Sample Processor) in great detail for the following substances:

Bupivacaine hydrochloride (200 °C), *carbidopa* (150 °C), *quinidine sulfate* (180 °C), *quinine hydrochloride* (135 °C), *quinine sulfate* (130 °C), *cyproheptadine hydrochloride* (150 °C), *cysteine hydrochloride monohydrate* (150 °C), *dihydralazine sulfate-2.5-hydrate* (120 °C), *ethacridine lactate monohydrate* (180 °C), *histidine hydrochloride monohydrate* (200 °C), *levothyroxin sodium* (150 °C), *metamizole sodium* (150 °C), *metixene hydrochloride* (180 °C), *morphine hydrochloride* (180 °C) and *niclosamide monohydrate* (130 °C).

11. Water determination in foodstuffs and semi-luxuries

This group includes substances that have a very wide range of structures. They vary from well-defined compounds (e.g. table sugar, alcoholic drinks) up to complex cellular structures (e.g. dry fruit, meat products), in which some of the water is bound sorptively at the surface and some in capillaries between the particles. Water may also be completely enclosed in cells from which it is very difficult to «release» it. As a result a wide range of sample (pre-)treatment techniques must be used, which is why we have divided this section into 11 subsections.

With foodstuffs it can be assumed that chemical side reactions (formation of water) hardly occur. Substances such as aldehydes and mercaptans are, if at all, only present in small amounts and their share in the normally high water content can be ignored.

In most foodstuffs the water is distributed inhomogeneously. This is why the sample must be selected so that it represents the average composition. A large amount of sample is, if necessary, comminuted and mixed and the water is determined in a smaller amount of sample.

11.1 Beverages

The KF titration itself represents no difficulties for this class of substances. However, please remember that the water content may reach 40...98%. This high water content means that sample addition directly into the titration vessel may not be advisable – the small sample weight means that the weighing error would be too large. This is why it is best to dilute the sample with dry methanol.

Approx. 2 g sample is weighed into a dry Erlenmeyer flask with septum stopper. Approx. 50 g methanol is added, the flask is then sealed and the contents are thoroughly mixed. A blank containing 50 g methanol is prepared in the same way in a second flask.

25 mL methanol is placed in the titration vessel and titrated to dryness. The blank value of the solvent (methanol) is determined first by removing approx. 5 mL solution from the «blank» flask with a dry syringe and determining the blank value on approx. 2 mL. The exact sample weight is determined by weighing the syringe before and after injection. The blank value is calculated in $\text{mg H}_2\text{O} / 2 \text{ g}$.

The dilute sample solution is treated in exactly the same way.

Example of the calculation:

$$\% \text{ water} = (\text{EP1} - \text{C30}) \times \text{C01} \times \text{C02} \times \text{C03} / \text{C00}$$

EP1 = mL KF solution for the sample

C00 = sample weight in g

C01 = titer of the KF solution ($\text{mg H}_2\text{O} / \text{mL}$)

C02 = 100 (for %)

C03 = 25 (dilution factor, 2 g to 50 g)*

C30 = blank value ($\text{mg H}_2\text{O} / 2 \text{ g}$)*

* Strictly speaking, this is not quite correct but, because of the large amount of water in the sample, it is not relevant.

The water content of the following samples has been determined in this way:

Cognac, fruit juice, vegetable juice, gin, kirschwasser, liqueurs, syrup, spirits, grape juice, wine and whiskey.

11.2 Fats and oils

The coulometric method is to be preferred for fats and oils because of their low water content. The volumetric method should be used for butter and margarine, which can have a water content of 15...19%.

Coulometric method

The titration cell is filled with KF reagent (in the anode compartment possibly 70 mL anolyte plus 30 mL 1-decanol). The cell contents are first titrated to dryness (conditioned) until a constant drift is achieved (typically $<10 \mu\text{g H}_2\text{O}/\text{min}$).

A dry syringe (whose needle is not too thin) is filled three times with sample and these portions are rejected. It is then filled again, approx. 0.5 to 1 g sample is injected into the titration cell and the water content is titrated. Solid fats are melted first.

The water content of the following samples has been determined in this way:

Deep-frying oil, cooking fat, olive oil, peanut oil, sunflower oil, rapeseed oil and safflower oil.

Volumetric method

A 2:1 mixture of methanol/1-decanol is used to dissolve the sample completely.

In butter and margarine the water is not uniformly distributed so they must be homogenized before the determination. However, they must not be heated above 25 °C as otherwise phase separation could occur.

Approx. 30 mL solvent mixture is placed in the titration vessel and titrated to dryness (conditioned) until a constant drift of approx. 10...20 $\mu\text{L}/\text{min}$ is achieved. The homogenized sample is filled into a dry syringe (without needle). Approx. 0.3 g sample is placed in the titration vessel and the water content is titrated.

We have used this method to determine the water content of certified, table and cooking butter, as well as in various brands of margarine.

Special instructions apply to lecithin. Formamide is added to prevent the electrodes from being coated.

30 mL of a 2:3:1 mixture of methanol/chloroform/formamide is placed in the titration vessel and titrated to dryness (conditioned). The sample is filled into a dry syringe (without needle). Approx. 0.3 g sample is placed in the titration vessel and the water content is titrated.

11.3 Dairy products, protein-containing products, meat products

Formamide is a relatively good solvent for protein. It is used in a mixture with methanol. Solvent mixtures containing methanol/chloroform or methanol/1-decanol are used for samples containing fats. Samples that do not release their water readily are titrated at 50 °C. The volumetric method is to be preferred because of the usually high water content and risk of contaminating the coulometry cell.

Butter

In butter the water is not uniformly distributed – it must be homogenized before the determination. The water determination in butter is described in detail in section 11.2.

Milk (unskimmed milk), cream and yogurt

Milk and yogurt tend to demix. This is why they must be homogenized before the water determination. The high water content means that the sample must be diluted with dry methanol. The determination is described in detail in section 11.1.

Curd cheese and cottage cheese

These are filled into a syringe without needle and approx. 0.1 g is placed in the conditioned titration vessel (approx. 30 mL methanol).

Cheese

It is difficult to extract the water from these samples. The sample is divided up as finely as possible and approx. 0.2 g is used for the determination.

Approx. 30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel, warmed to 50 °C and titrated to dryness. The sample is added and its water content is titrated at the same temperature (do not titrate too quickly as all the water must be extracted).

Powdered milk

Releases the water slowly and is also titrated at 50 °C. In order to distribute the fats better (in unskimmed milk powder) a 1:1 solvent mixture of methanol/chloroform or methanol/1-decanol is used.

30 mL of the solvent mixture is placed in the titration vessel, warmed to 50 °C and titrated to dryness. Approx. 1 g sample is added and its water content is titrated at the same temperature.

Yeast (fresh and dried)

In this sample the water is distributed heterogeneously and is partly enclosed in the cells.

A large amount of sample is premixed. The titration is carried out at 50 °C. A high-frequency mixer (e.g. Polytron or Ultra-Turrax) is used directly in the titration vessel as the «stirrer».

Fresh yeast: sample weight approx. 0.1 g, solvent: methanol

Dried yeast: sample weight approx. 0.5 g, solvent: methanol/formamide 2:1

Mayonnaise

Does not dissolve very well in methanol so a 1:1 solvent mixture of methanol/chloroform or methanol/1-decanol is used.

30 mL of the solvent mixture is titrated to dryness in the titration vessel (conditioned). Approx. 0.3 g sample is added from a syringe without a needle and the water content is titrated.

Egg yolk, egg white and gelatin

In order to extract the water as quickly as possible the titration is carried out at 50 °C and in a 2:1 mixture of methanol/formamide.

30 mL solvent mixture is heated to 50 °C and titrated to dryness (conditioned). Max. 0.1 g of egg yolk sample is added with a syringe or approx. 0.5 g egg white powder or gelatin is added to the titration vessel and the water content is determined at the same temperature.

Meat and meat products

As well as proteins and fats, these products contain relatively large amounts of water that is enclosed in cells. In such samples the water content can be determined as follows:

Approx. 2 g sample (cut up with a knife) is weighed out into to a dry flask. Approx. 50 g of a 5:1 mixture of methanol/chloroform is added and the mixture is comminuted with a

high-frequency mixer (e.g. Polytron or Ultra-Turrax) for approx. 3...5 min. A blank determination is made on the solvent mixture in exactly the same way.

Approx. 1 g of the supernatant liquid is used for the titration. Please refer to section 11.1 for the calculation of the water content.

We have used this method to determine the water content of smoked fish (trout, salmon), pork and sausages.

11.4 Honey, molasses, sugar

Sugars are not very soluble in methanol, which is why their water content is usually titrated in methanol-formamide mixtures. In some cases a titration at 50 °C results in increased solubility and shorter titration times. However, some products decompose at even this low temperature – high-bias results are obtained or the endpoint is not reached.

For saccharose, apart from the total water content, the adherent moisture is often of interest. As in this case the sample must not dissolve, work is carried out in a solvent mixture of 1:4 methanol/chloroform.

Honey

Approx. 30 mL methanol is placed in the titration vessel and titrated to dryness (conditioned). A syringe without needle is used to add approx. 0.2 g sample and its water content is titrated.

Molasses

Only dissolves slowly in methanol, which is why a solvent mixture of 2:1 methanol/formamide is used at 50 °C.

30 mL mixture is placed in the titration vessel, heated to 50 °C and titrated to dryness (conditioned). Approx. 0.2 g sample is added with a syringe without needle and its water content is titrated at the same temperature.

Various types of sugar

For these sugars we recommend the following solvents, titration conditions and sample weights:

D(-)-Fructose	30 mL methanol/formamide 2:1, room temperature, 2 g
D(-)-Mannite	30 mL methanol/formamide 2:1, 50 °C, 2 g
D(+)-Galactose	30 mL methanol/formamide 2:1, 50 °C, 3 g
D(+)-Glucose, monohydrate	30 mL methanol, 50 °C, 0.3 g
D(+)-Lactose	30 mL methanol/formamide 2:1, room temperature, 0.5 g
D(+)-Saccharose	for adherent water: 25 mL methanol/chloroform 1:4, room temperature, 5 g (titrate quickly, stop delay 10 s). for total water: 30 mL methanol/formamide 2:1, 50 °C, 1 g.

Table sugar/ crystal sugar

see above, saccharose.

11.5 Candies and sweetmeats

These substances also do not dissolve very well in methanol, so that most samples are dissolved in 30 mL methanol/formamide mixture and titrated at 50 °C. Sample preparation consists of comminution: hard substances in a mortar or mill, soft substances are cut up finely with a knife.

The following samples can be analyzed in this way (comminution, solvent, titration conditions, sample weight):

<i>Candies</i>	mortar, methanol/formamide 2:1, 50 °C, 0.5 g
<i>Fruit gums</i>	knife, methanol/formamide 2:1, 50 °C, 0.3 g
<i>Candied fruits</i>	knife, methanol/formamide 2:1, 50 °C, 0.2 g
<i>Caramel</i>	knife, methanol/formamide 4:3, 50 °C, 0.3 g
<i>Chewy candies</i>	knife, methanol/formamide 2:1, 50 °C, 0.5 g
<i>Licorice straps</i>	mortar or knife, methanol/formamide 2:1, room temperature; hard 0.5 g, soft 0.1 g
<i>Toffee</i>	knife, methanol/formamide 2:1, room temperature, 0.5 g

The following products are cut into small pieces with a knife and placed in the titration vessel. A high-frequency mixer is used as the «stirrer» (e.g. Polytron or Ultra-Turrax):

<i>Jelly babies</i>	methanol/formamide 4:3, room temperature, 0.2 g
<i>Marzipan</i>	methanol/formamide 2:1, 50 °C, 0.3 g

Special instructions apply for chewing gum and jams:

Chewing gum

5 g of finely chopped sample is weighed out into a dry Erlenmeyer flask fitted with a septum stopper. 50 g dry methanol and a magnetic stirrer bar are added and the flask is sealed with the stopper. The water is extracted by stirring on a magnetic stirrer for 3...5 h. A blank determination on the methanol used is carried out in the same way in a second flask.

A dry syringe is used to take, for example, 5 mL of the extract and the water content is determined in part of this. Examples of the calculation are given in sections 11.1 and 11.3.

Jams

The sample is first homogenized in a blender and taken up in a dry syringe without needle.

30 mL of a 2:1 mixture of methanol/formamide is warmed to 50 °C in the titration vessel and titrated to dryness (conditioned). Approx. 0.1 g sample is added and the water content is titrated at the same temperature.

11.6 Chocolate, coffee, cocoa

These samples are not soluble in methanol. Some of them contain considerable amounts of fats and sugars. For this group it is very important that the samples are comminuted as finely as possible. This considerably accelerates the release of the water. The best comminution is obtained with a laboratory mill fitted with a cooling jacket in order to prevent overheating and loss of water. The titration is usually carried out at elevated temperature in a methanol-formamide mixture. The volumetric method is generally recommended for determining the water content.

Chocolate

The sample is finely chopped up with a knife or grated into small flakes. Two methods are proposed for determining the water content:

- 30 mL methanol is warmed to 50 °C in the titration vessel and titrated to dryness (conditioned). Approx. 1 g sample is added and the water content is titrated at the same temperature.
- 30 mL of a 1:1 mixture of methanol/chloroform is placed in the titration vessel and titrated to dryness. Approx. 1 g sample is added and its water content is titrated.

Cocoa beans

are ground up finely before the analysis. 30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness. Approx. 0.5 g sample is added and the water content is titrated at the same temperature.

Cocoa powder

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness. Approx. 0.5 g sample is added and the water content is titrated at the same temperature.

Instant coffee

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel and titrated to dryness (conditioned). Approx. 1 g sample is added and the water content is titrated.

Roasted coffee

is ground up as finely as possible before the analysis. The titration vessel is equipped with a reflux condenser and 30 mL dry methanol is placed in it, heated to boiling (approx. 65 °C) and titrated to dryness (conditioned). Heating is stopped, approx. 1 g sample is added and its water content is titrated at the boiling point. Stop delay 20 s.

Raw coffee

is ground up as finely as possible before the analysis. 30 mL of a 3:1 mixture of methanol/chloroform is placed in the titration vessel and titrated to dryness (conditioned). A high-frequency mixer (e.g. Polytron or Ultra-Turrax) is used as the «stirrer». Approx. 0.5 g sample is added and its water content is titrated – the high-frequency mixer is used as the stirrer.

Cappuccino powder

Separate reagents must be used for such samples. 25 mL of the working medium (methanol, SO₂ and base) is placed in the titration vessel and titrated to dryness. Approx. 0.25 g sample is added and its water content titrated with the iodine solution.

11.7 Nuts, dried fruits, dried vegetables, tobacco products

In plants the largest portion of the water is enclosed in cells and is therefore difficult to extract. Thorough sample comminution and titration at an elevated temperature are the basic requirements for obtaining good results. Because of the risk of contaminating the coulometric titration cell and because special solvents have to be used, we recommend the volumetric method.

Dried fruits

are best comminuted and mixed at the same time in a meat grinder.

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel and titrated to dryness (conditioned). A high-frequency mixer (e.g. Polytron or Ultra-Turrax) is used as the «stirrer». Approx. 0.2 g sample is added and its water content is titrated – the high-frequency mixer is used as the stirrer. Examples:

Apricots, pears, dates*, figs, plums*, raisins and sultanas.

* destoned

Nuts, almonds and kernels

are finely ground up in a cooled laboratory mill. 30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness. Approx. 0.5 g sample is added and its water content is titrated at the same temperature.

Examples: walnuts, peanuts (roasted), hazelnuts, Brazil nuts, pine nuts, sunflower seeds and almond kernels.

Dried vegetables

must also be finely comminuted (mortar or cooled laboratory mill). 30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel, warmed to 50 °C and titrated to dryness. Approx. 0.25 g sample is added and its water content is titrated at the same temperature.

Tobacco

Exactly the same procedure as for dried vegetables.

Pipe tobacco / cigarette tobacco

is cut up into small pieces with a knife or scissors. 30 mL methanol/formamide is placed in the titration vessel and titrated to dryness. A high-frequency mixer (e.g. Polytron or Ultra-Turrax) is used as the «stirrer». Approx. 0.2 g sample is added and its water content is titrated – the high-frequency mixer is used as the stirrer.

11.8 Fruit and vegetables

By their very nature, fresh fruit and vegetables contain a lot of water. Most of it is enclosed in cells and must be «released» from them. The best way of doing this is with a high-frequency mixer (e.g. Polytron or Ultra-Turrax).

In order to obtain a representative sample a reasonable amount of the sample (e.g. 10 g) is grated, cut up with a knife and mixed. 2 g is then weighed out into a dry flask. 50 g dry methanol is added, the sample is comminuted with the high-frequency mixer for 3...5 min and allowed to settle. A blank determination is carried out by treating 50 g methanol in exactly the same way in a second flask. The blank value is determined first.

25 mL methanol is titrated to dryness in the titration vessel. Approx. 5 mL sample solution is drawn up into a dry syringe. Approx. 2 mL is added to the titration vessel and its water content determined. The sample weight is determined by weighing the syringe before and after injection.

The calculation of the water content is described in detail in section 11.1.

11.9 Cereal products, flour, starch

Most of the water in these products is bound in cells and is difficult to extract. Coarse material is ground up in a cooled laboratory mill. Extraction of the water at an elevated temperature and the addition of formamide accelerates this process and reduces the titration time.

Barley, semolina, corn, rice, rye, soybean grist, wheat and wheat grist

These products are ground up in a cooled laboratory mill to give a fine powder (flour).

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.3 g sample is added and its water content is titrated at the same temperature.

Potato, corn and rice starch, soybean and wheat flour

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). 0.3...0.5 g sample is added and its water content is titrated at the same temperature.

Starch syrup

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). The sample is drawn into a dry syringe without needle and approx. 0.2 g is added to the titration vessel. The water content is titrated at the same temperature.

Plant gums (pectin, guar gum)

If not already present in powder form these substances are ground up in a cooled laboratory mill. The analysis is the same as that described for cereals. Sample weight approx. 0.2 g.

Muesli, breakfast cereals, oat flakes, popcorn

The samples are first pre-comminuted (e.g. with a knife) so that they can be further reduced in size by the cutter of the high-frequency mixer (e.g. Polytron or Ultra-Turrax), which is used simultaneously as the stirrer.

30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel and titrated to dryness (conditioned). Approx. 0.2 g sample is added and its water content is titrated – the high-frequency mixer is used as the stirrer.

11.10 Bakery products and pasta

Sample preparation depends on the consistency of the sample. Hard samples are ground up carefully and as finely as possible (cooled laboratory mill). Softer samples are cut up into smaller pieces.

These samples generally only release their water sluggishly. Some samples may decompose (with release of water) when titrated at an elevated temperature.

In the literature there are few references about the determination of the water content of these samples by the Karl Fischer method, either because of the expected (or experienced) difficulties or because of lack of interest.

Pasta (noodles, spaghetti, etc.)

are ground up as finely as possible in a cooled laboratory mill.

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.5 g sample is added and its water content is titrated at the same temperature.

Breadcrumbs, rusks

Exactly the same procedure as for pasta. Sample weight approx. 1 g.

Bread, cakes

These are cut up finely with a knife and mixed. 3 g sample is weighed out into a dry Erlenmeyer flask fitted with a septum stopper. 50 g dry methanol and a magnetic stirrer bar are added, the flask is sealed and the contents stirred on a magnetic stirrer for 15...30 min. The suspension is then allowed to settle. A blank determination is carried out by treating 50 g methanol in exactly the same way in a second flask.

25 mL methanol is placed in the titration vessel and titrated to dryness (conditioned). Approx. 5 mL extract is removed from the flask with a dry syringe, approx. 2...3 mL is added to the titration vessel and the water content is titrated. The exact sample weight is obtained by weighing the syringe before and after injection.

An example of a water content calculation can be found in section 11.1.

Cookies, crackers

The samples are first pre-comminuted (e.g. with a knife) so that they can be further reduced in size with the cutter of the high-frequency mixer (e.g. Polytron or Ultra-Turrax), which is used simultaneously as the stirrer.

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.5 g sample is added and its water content is titrated at the same temperature (the high-frequency mixer is used as the stirrer).

Sponges, pastries

These are ground up in a cooled laboratory mill.

Not all the water can be extracted at room temperature. At 50 °C some samples (depending on their composition and types of sugar they contain) tend to decompose. This decomposition becomes apparent when the titrator cannot reach an endpoint or when results are obtained that are unbelievably high. Samples that do not decompose can be analyzed as follows:

30 mL of a 2:1 mixture of methanol/chloroform is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.5 g sample is added and its water content is titrated at the same temperature.

Potato chips

We have determined the water content of these samples by using the heating method (oven method) at an oven temperature of 140 °C and with nitrogen as the carrier gas. The chips were first slightly reduced in size.

11.11 Spices, other foodstuffs, animal feed

Spices

The Karl Fischer method provides a more accurate and more selective alternative to the frequently used drying method. Not only can even the water enclosed within the cells be determined (after appropriate sample preparation), but also only the water is determined and not the sum of all volatile constituents. Studies have also shown that essential oils do not interfere with the KF titration.

A requirement for good water extraction is that the plant material is comminuted as finely as possible (cooled laboratory mill, mortar) and that the cells are split up.

50 mL methanol or 50 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel and titrated to dryness (conditioned). A high-frequency mixer (e.g. Polytron or Ultra-Turrax) is used as the «stirrer». 0.2...0.4 g sample is added, the titrator is started with an extraction time of 180 s and the water content is titrated.

As an alternative to this method, good results have also been obtained by titration at an elevated temperature (50 °C or in boiling methanol, without high-frequency mixer).

Examples of samples that have been analyzed: basil, ginger, coriander, marjoram, nutmeg, rosemary, black and white pepper, thyme.

Condiments (powdered, to be used for sprinkling) are analyzed as follows:

30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.3 g sample is added and its water content is titrated at the same temperature.

Other foodstuffs

Potato flour, instant mashed potatoes

30 mL of methanol is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.3 g sample is added and its water content is titrated at the same temperature.

Baby food

30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 1 g sample is added and its water content is titrated at the same temperature.

Instant soups, packaged soups

30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.3 g sample is added and its water content is titrated at the same temperature.

Animal feed

Canned food for dogs and cats

The samples are first passed through the meat grinder. Approx. 2 g of the comminuted sample is weighed out into a dry flask. 50 g of a 4:1 mixture of methanol/chloroform is added. The contents are mixed with a high-frequency mixer (Polytron or Ultra-Turrax) for

2...3 min and allowed to settle. A blank determination is made on the solvent mixture in exactly the same way.

25 mL of methanol is placed in the titration vessel and titrated to dryness (conditioned). Approx. 1 g extract is added from a syringe and the water content is titrated. An example of the calculation is given in section 11.1.

Fish meal

30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.5 g sample is added and its water content is titrated at the same temperature.

Dog biscuits

The samples are ground up in a cooled laboratory mill.

30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.2 g sample is added and its water content is titrated at the same temperature.

Dog flakes

The samples are first cut up with a knife so that they can be further reduced in size by the cutter of the high-frequency mixer (e.g. Polytron or Ultra-Turrax), which is used simultaneously as the stirrer.

30 mL of a mixture of methanol/formamide is placed in the titration vessel and titrated to dryness (conditioned). Approx. 0.2 g sample is added and its water content is titrated.

12. Water determination in biological samples

Most of the water is enclosed in cells and can only be extracted slowly. The complete water content can never be found by using a drying oven method. This is why the KF method has also proved to be an accurate and rapid absolute method for such samples. In order to achieve the correct result quickly, the titration is often carried out at an elevated temperature. The addition of formamide normally accelerates both the extraction of the water and the KF reaction. However, the formamide fraction must not exceed 50% as otherwise the stoichiometry of the KF reaction changes.

Dried plant material is ground up in a cooled laboratory mill. 20 mL methanol and 10 mL formamide are placed in the titration vessel, warmed to 50 °C and titrated volumetrically to dryness. 0.1...0.2 g of the comminuted sample is added and its water content is titrated at the same temperature.

Fresh plants are cut up with a knife. 50 mL methanol is placed in an external flask (Erlenmeyer or round-bottom). 1...2 g of the cut-up plant material is added and the cells are disrupted with a high-frequency mixer (e.g. Polytron or Ultra-Turrax) for 5...10 min. The water content of part of this mixture (e.g. 5 mL) is determined volumetrically.

Meat and serum samples contain, in addition to a lot of water, protein that does not dissolve in methanol. Comminution with a high-frequency mixer has again proved itself in practice here. The sample is passed through a meat grinder and approx. 2 g is added to 50 g of a 4:1 mixture of methanol/chloroform and comminuted with a high-frequency mixer (e.g. Polytron or Ultra-Turrax) for 2...3 min. The water content of approx. 1 g of the ex-

tract is titrated volumetrically at room temperature. An example of the calculation is given in section 11.1.

In biological *standard reference materials* a knowledge of the total water content is extremely important. Changes in the water content influence the shelf life of the materials as well as the results of other analyses, as these refer to the dry weight. In an interesting publication – Rückold, S., Grobecker, K.H., Isegard, H.D.; Fresenius J. Anal. Chem. 370, (2001) 189–193 – the authors demonstrate that the true water content can only be found with the KF method. Drying methods yield incorrect results.

There are two possible ways of carrying out the KF titration (both provide identical values):

- the heating method (oven method) at 130 °C, and
- titration in methanol at 50 °C (where «drift stop» must be used as the switch-off criterion).

The following standard reference materials have been compared:

- *tuna muscle* CRM 669, lyophilized, powdered
- *plankton* CRM 414, freeze-dried, powdered
- *cod muscle* CRM 422, freeze-dried, powdered

In *proteins* and *gelatins* the water content can be determined as follows:

20 mL methanol and 10 mL formamide are placed in the titration vessel, warmed to 50 °C and titrated volumetrically to dryness. The comminuted* sample is then added and its water content titrated volumetrically at the same temperature.

* The smaller the particles, the faster the determination.

In *collagen* we have determined the water content by the heating method at 160 °C.

Lyophilizate and *vaccines* are also analyzed best by the heating method (70...120 °C).

Freeze-dried immunglobulin G is analyzed by the same method as that used for proteins (see above). Reference: Kluss, Mester, Ärtzl. Lab. 23, (1977) 339–343.

The *steroid hormones pregnenolone acetate, androstenedion enolether* and *D.H.A. bromohydrin* have been analyzed by the following method using the separate special reagents for aldehydes and ketones **:

20 mL working solution and 2 mL chloroform are placed in the titration vessel and titrated to dryness. The titer of the KF titrant is then determined three times with 10 µL dist. H₂O. Approx. 200 mg sample is then added and its water content determined. After each titration, time is allowed for a constant drift to be achieved (approx. 5 min) before a new sample is added. The solution must be replaced after 5 samples have been analyzed.

** These reagents were selected because of unidentified side reactions – the interferences then vanished.

13. Water determination in petrochemical products

13.1 Hydrocarbons

The water determination in such products is relatively simple. They normally contain only little water, so that the coulometric method is commonly used. In order to improve the solubility of long-chain hydrocarbons a solubility promoter (propanol, decanol or chloro-

form) should be added. Interference from double bonds occurs practically never. Examples of substances whose water content has been determined:

Pentane, hexane, dimethylbutane, methylbutadiene, benzene, toluene, xylene, ethyltoluene, dimethylstyrene, octane, dodecane, tetradecene, icosane, octacosane, petroleum ether, gasoline, cyclohexane, methylcyclohexane, cycloheptane, vinylcyclohexane, cyclododecane, decylcyclohexane, dicyclopentadiene, dimethylnaphthalene, trimethylstyrene, biphenyl, acenaphthene, fluorene, methylenepheneanthrene, allocymol and norbornadiene.

13.2 Hydraulic, insulating, transformer and turbine oils

The water content of these products is virtually always determined coulometrically (cell with diaphragm). As they do not dissolve very well in the anode electrolyte, chloroform or trichloroethylene is added to it (70 mL electrolyte solution + 30 mL solubility promoter).

The following procedure is appropriate for the very low water contents of these products:

During conditioning the titration cell is swirled about manually from time to time in order to remove the water adhering to the cell walls. It is very important that as low a drift value and, above all, as constant a drift value as possible are achieved.

A dried syringe is filled with sample at least three times; the first two fillings are rejected. 2...5 mL sample is then injected into the titration cell.

Depending on the sample, after a few additions two phases may start to form in the anode compartment. In this case stirring is stopped and the upper, oil-containing phase is aspirated off. If the drift becomes instable and starts to increase then both electrolytes (anode and cathode compartments) must be exchanged.

13.3 Motor oils, lubricating oils and greases

These practically always contain additives that undergo side reactions with the KF reagents and simulate a water content that is too high. This is why the heating method (oven method) is used for these samples – oven temperature 120...160 °C, depending on the product.

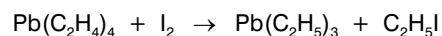
13.4 Mineral oil (crude oil, heavy crude)

The water in these products is not distributed homogeneously so that they must be homogenized before being analyzed (ultrasonic bath or high-frequency mixer). They also contain tars that contaminate the electrodes and the titration cell. For this reason volumetric titration is preferred and a solubility promoter is added to the methanol in the titration cell:

- Crude oil in general 10 mL methanol + 10 mL chloroform + 10 mL toluene
- Heavy crude 10 mL methanol + 10 mL chloroform + 20 mL toluene.

13.5 Gasoline, motor fuels

Chemical interference is caused by mercaptans, which are oxidized by iodine and simulate a water content that is too high. Tetraethyl lead also reacts with iodine:



In order to eliminate interference by mercaptans, Francis and Persing (Talanta 25, 1978, 282–283) recommend complexing them with N-maleinimide in the presence of pyridine. A further method consists of determining their content separately by potentiometric titration with AgNO_3 and taking it into account when calculating the water content (1 ppm mercaptan sulfur (S) corresponds to approx. 0.5 ppm H_2O).

Examples of products:

Lead-free gasoline, aviation gasoline, kerosene, diesel fuel

The water content of these products is usually determined by coulometric titration. In volumetric titrations, solubility promoters (chloroform, toluene) should be added to the methanol.

14. Water determination in plastics

Most plastics dissolve only slowly or not at all in organic solvents, which is why we recommend the use of the heating method (oven method). As some substances are sensitive to oxidation at 100...300 °C we recommend using dry nitrogen as the carrier gas. The nitrogen is dried by molecular sieve (possibly after preliminary drying with silica gel). In this way a residual moisture of <10 $\mu\text{g H}_2\text{O/L}$ can be achieved.

Plastic samples with a very low water content are extraordinarily hygroscopic and immediately pick up water from the atmosphere. This is why they should be analyzed immediately after the container has been opened.

Water is normally very strongly bound in plastics. Because of their usually very low water content, we recommend coulometric titration. In each determination approx. 500...3000 $\mu\text{g H}_2\text{O}$ should be released (amounts of water that are too low increase the standard deviation, amounts of water that are too high could condense in the tubing).

The heating temperature should be about 100...300 °C and can be optimized for the particular classes of plastics by applying a temperature ramp. It should be as high as possible in order to shorten the analysis time.

The gas flow is set to 100...500 mL/min (5...30 L/h) – on 774 and 832 instruments to 40...60 mL/min. Lower gas flows lower the amount of external moisture (drift) and improve water uptake in the titration cell. Larger amounts of gas may prevent the risk of condensation in the tubing. However, it is better to heat the tubing.

As the analysis takes a relatively long time (5...20 min), the whole apparatus must be maintained at equilibrium. It is important that the drift is kept as constant as possible for the whole time, as it is used as a correction value for the subsequent determinations. The gas flow must also be kept constant as a matter of course.

Approximate oven temperatures for the various types of plastics are given in the following table.

Heating method for plastics

Type	Oven temperature/°C
ABS	160
Caprolactam	100...120
Epoxy resin	120
Melamine resin	160
Nylon 6 / Nylon 66	160...230
Phenol-formaldehyde resins	200
Polyacrylamide	200
Polyamide	160...230
Polycarbodiimide	150
Polycarbonate	140...160
Polyester	140...240
Polyether	150
Polyethylene	200
Polyethylene terephthalate	180...200
Polyimide	160
Polyisobutylene	250
Polymethylmethacrylate	180
Polyoxymethylene	160
Polypropylene	160...200
Polystyrene	120
Polyurethane	180
Polyvinyl acetate	170
Polyvinyl butyral (PVB)	150
PTFE	250
Rubber stoppers	250
Silicone rubber	250
Soft PVC	140...160
Styrene acrylate	170
Teflon	250
Terephthalic acid esters	150
Urea-formaldehyde resin	100

In β -caprolactam the water content can also be determined by direct volumetric titration. The solvent is methanol (max. 0.01% H₂O); a dilute KFR with a titer of 2 mg H₂O/mL is used as the titrant. 2.5...5 g sample is added to the titration vessel from a dry syringe (without needle). Coulometric titration cannot be recommended (cell contamination).

15. Water determination in paints, lacquers, solvents

15.1 Alcohols

There are no problems in determining the water content of these substances. In order to improve the solubility of long-chain alcohols (e.g. stearyl alcohol) some propanol can be added to the methanol. Both coulometric and volumetric methods are suitable. We recommend volumetric titration for higher water contents. The water content of the following alcohols has been determined:

Methanol, ethanol, propanol, isopropanol, butanol, glycerol, pentanediol, hexanol, methylpentanol, cyclohexanol, methylpentanediol, heptanol, hexanetriol, dimethylpentanol, octanol, ethylhexanol, nonanol, geraniol, dodecanol, benzyl alcohol, phenoxyethanol, phenylpropanol, stearyl alcohol, cetyl alcohol, ethylene glycol, sorbitol and mannitol.

15.2 Halogenated hydrocarbons

The water determination usually presents no problems. Coulometry is normally preferred because of the low water content. The addition of chloroform is only necessary for long-chain compounds.

As a result of their manufacturing processes, chlorinated hydrocarbons may contain free chlorine, which releases iodine and produces low-bias results. However, the chlorine can be added to double bonds and then no longer interferes. Procedure:

20 mL of the sample containing chlorine is treated with 2 mL 1-tetradecene in a dry Erlenmeyer flask, the flask is sealed, its contents mixed and then allowed to stand for 10 min. The chlorine-free sample can then be titrated. The water content of the 1-tetradecene is determined separately and included in the calculation as the blank value.

The water content of the following halogenated hydrocarbons has been determined:

Dichloromethane, chloroform, carbon tetrachloride, trichloroethane, dichloroethane, bromoform, iodomethane, tetrachloroethane, dibromomethane, tetrabromoethane, iodoethane, allyl chloride, cyclohexyl chloride, difluorobenzene, chlorobenzene, dichlorobenzene, chlorotoluene, benzyl chloride, benzyl bromide, iodonaphthene, chlorooctane, bromodecane, bromotetradecane, bromohexadecane and chlorobenzhydryl chloride.

15.3 Phenols

This class contains substances that can be titrated in different ways. Some can be titrated without any problems, while others undergo side reactions which, however, can be suppressed under optimized working conditions. In volumetric titration combined reagents are normally used. Not all phenols can be titrated coulometrically. Side reactions occur more frequently with coulometry and in some cases coating of the anode makes the determination impossible. The side reactions normally result in an increased iodine consumption (oxidation of the substance), which simulates a too high water content. This iodine consumption is pH-dependent and in some cases can be suppressed by the addition of salicylic acid. However, the addition of salicylic acid has no effect with some phenols, recovery rates of 120...140% being obtained for added water. For this reason we recommend that, for critical phenols, the determination is verified by spiking the titrated sample solution with water.

Phenols that can be determined *coulometrically* and *volumetrically* without problems are:

Phenol, cresol, fluorophenol, chlorophenol, dichlorophenol and nitrophenol.

Only *volumetrically* with combined KF reagents:

Bromophenol, catechol, naphthol, hydroxyquinoline, guaiacol, resorcinol, dimethylphenol and trimethylphenol.

For *pyrogallol* and the *aminophenols* the maximum sample weights are 1 g and 0.1 g respectively.

15.4 Esters

These normally cause no problems. They can be titrated both coulometrically and volumetrically. In some cases the addition of a solubility promoter (chloroform or propanol) is recommended to improve the solubility.

Examples:

Acetoacetic acid ethyl ester, acetic acid ethyl ester, acrylic acid ethyl ester, carbazinic acid methyl ester, ethyl propionate, ethylhexyl nitrate, amyl acetate, butyl acetate, glycerol monostearate, levulinic acid ethyl ester, bromoisobutyric acid ester, hydroxybenzoic acid methyl ester, salicylic acid methyl ester and terephthalic acid dimethyl ester.

15.5 Ethers

These substances cause no problems. Ethers behave like hydrocarbons. KF coulometry is mainly suitable for short-chain ethers. In some cases the addition of a solubility promoter (chloroform or propanol) is recommended to improve the solubility. Examples:

Diethyl ether, dioxan, diethyleneglycol monomethyl ether, diethyleneglycol diethyl ether, polyethylene glycol(s), anisole, fluoranisole, iodanisole, guaethole, resorcinol dimethyl ether, didecyl ether, diheptyl ether and trioxan.

15.6 Aldehydes and ketones

Because of their side reactions (acetal and ketal formation with the release of water, and sulfite addition to aldehydes with take up of water – see section 7.2), aldehydes and ketones were for a long time the problem children for KF titration. Many attempts were made to suppress these side reactions (titration in alcohol-free media, at low temperatures, etc., etc.). In the meantime it is possible to use specially developed reagents to determine the water content in such samples with a relatively satisfactory degree of accuracy.

Individual aldehydes react at different rates – acetaldehyde reacts the quickest. The reaction rate decreases as the chain length increases, and aromatic aldehydes react more slowly than aliphatic ones. Chloral and formaldehyde are exceptions. They do not form acetals and their water content can be titrated without interference.

Ketones are not as reactive as aldehydes. The reaction rate also decreases as the chain length increases. The quickest ketal formation takes place with acetone and cyclohexanone. The following ketones are regarded as being stable:

Diisopropyl ketone, benzophenone, deoxybenzoin, benzil, benzoin, camphor, alizarin, dibenzalacetone and dichlorotetrafluoroacetone.

The volumetric method is preferred for aldehydes and ketones, as the corresponding time-proven KF reagents are available. The following working procedure has proved to be effective:

25...50 mL of the special working medium is placed in the titration vessel and titrated to dryness with the special titrant until a stable endpoint is achieved (conditioning). The titration itself is then started, the sample is added immediately and titration is continued until a stable endpoint has again been achieved (e.g. drift).

Their differing reactivities mean that, depending on the sample, different sample weights must be used. If these lie under 10 mL or 10 g then they are given in parentheses behind the individual substances. In addition to those mentioned above, the water content of the following substances has been determined:

Aliphatic aldehydes such as acetaldehyde (2), propionaldehyde (2), butyraldehyde (5), crotonaldehyde (5), caprylaldehyde (5), glycolaldehyde (1), chloral, chloral hydrate (0.5), paraldehyde, cyclohexanecarbaldehyde (5), diphenylacetaldehyde, acetaldehyde diethylacetal and bromoacetaldehyde diethylacetal.

Aromatic aldehydes such as benzaldehyde (5), bromobenzaldehyde (2), salicylaldehyde, hydroxybenzaldehyde (5), anisaldehyde, dimethylaminobenzaldehyde and phenylglyoxal (0.5).

Aliphatic ketones such as acetone, methyl-n-propyl ketone, methyl isobutyl ketone, ethyl isobutyl ketone, allylacetone, octanone, decanone, dihexyl ketone (5), cyclohexanone, trifluoroacetone and hexachloroacetone (5).

Aromatic ketones such as acetophenone, fluoroacetophenone, dihydroxyacetophenone (5), aminoacetophenone, benzyl methyl ketone, benzyl acetone, benzophenone (5) and benzoin (2).

Heterocyclic ketones such as acetylpyridine, pyrrolidone, methyl pyrrolidone, benzoylpyridine and acetylindol (2).

Diketones such as diacetyl (1), acetylacetone, hexanedione, cyclohexanedione (1), benzoylacetone, benzil and dibenzoylmethane.

Ketocarboxylic acids must be buffered, as otherwise the pH of the KF system drops too much. Imidazole is added to the working medium.

Examples are:

Pyruvic acid (1), oxobutyric acid (1), levulinic acid, benzoylpropionic acid (5), acetylbenzoic acid (5) and benzoylbenzoic acid.

15.7 Paints and lacquers

Paints contain pigments that are mostly insoluble in organic solvents and KF reagents. Latex paints clump with methanol and then do not release their water completely. Some paints and lacquers contain ketones and must be titrated in the absence of methanol (side reaction). With some adhesives and paints chloroform must be added as the solubility promoter. In addition, paints and/or lacquers may contain reactive amines that would increase the pH of the KF system too much. In this case the sample solution is treated with salicylic acid in order to stabilize the pH. Some inorganic pigments react with the KF reagent to release water. This mainly concerns Ag_2O , Pb_3O_4 (red lead) and ZnO . In contrast, Al_2O_3 and TiO_2 cause no such problems.

For all these reasons we recommend that the determination of the water content of these products is carried out only by the volumetric method (contamination of the coulometric titration cell, special reagents are not always available).

The water in paints is usually not distributed uniformly. They must therefore be homogenized before the sample is taken and before it is injected into the titration vessel.

Aqueous dispersion paints

Those of these paints that contain polyvinyl acetate, acrylate or mixed polymers of polyvinyl chloride or acrylates present no problems. 20 mL methanol and 10 mL formamide are placed in the titration vessel and titrated to dryness. Approx. 0.1 g sample is added from a syringe and its water content is titrated.

Latex paints

Latex paints clump together in methanol. For most of these samples the method described in ASTM D 4017-96 has proven itself in practice. A high-frequency mixer (e.g. Polytron or Ultra-Turrax) is used for stirring and homogenization. Sufficient methanol is placed in the titration vessel to completely immerse the mixing head and then titrated to dryness. 0.1...0.15 g sample is added from a dry syringe and its water content titrated under the following conditions:

Extraction time 60 s, stirring speed «minimum», stop delay 20 s.

Paste paints with a water content of <0.5% have been analyzed as follows:

Approx. 20 g sample is weighed out into a dry Erlenmeyer flask. A magnetic stirrer bar and approx. 70 g of a 1:1:1 solvent mixture of methanol, p-xylene and chloroform are added. The flask is sealed immediately and stirred on the magnetic stirrer for 1 h. The suspension is allowed to settle and approx. 5 g of the sample extract is injected into the titration vessel (containing methanol titrated to dryness). As an alternative to the magnetic stirrer, the flask can also be placed in an ultrasonic bath for 20 min. The blank value of the solvent mixture must also be determined and taken into account in the calculation.

Insoluble *paint pigments* are analyzed as follows:

Approx. 2 g of the previously comminuted sample is weighed out into a dry Erlenmeyer flask and treated with approx. 75 g dry methanol. The flask is sealed, its contents are mixed briefly and the flask is then placed in an ultrasonic bath for 20 min. 1...2 g sample extract is then injected into the titration vessel (the blank value must also be determined and taken into account in the calculation).

Lacquers that contain ketones as the solvent are titrated with the special reagents for aldehydes and ketones (see section 15.6)

A *multi-component lacquer* based on polyols, isocyanate hardener and diluting agent has been analyzed as follows:

20 mL pyridine and 1 mL 1-ethylpyridine are placed in the titration vessel and titrated to dryness. A syringe is used to add 1...3 g sample whose water content is titrated.

Adhesives can also have their water content analyzed.

For *polyurethane adhesives*, titration in methanol is quite adequate. For polyurethane-chlorinated-rubber adhesives and cyanacrylate adhesives (fast-setting adhesives) 10 mL methanol and 20 mL chloroform are placed in the titration vessel.

16. Water determination in gaseous samples

The Karl Fischer titration is an elegant method for determining water in gaseous samples. As such samples normally have a low water content, coulometric titration is to be preferred. If the volumetric method is used then a solvent mixture made up of equal amounts by volume of methanol and ethylene glycol should be used as the absorption solution.

Particular attention must be given to sampling. It is often advisable to set up the titrator directly at the sampling point or to introduce the sample directly into the detached but conditioned titration vessel.

General procedure

It is best to introduce the gas directly into the titration cell through a capillary that is immersed as deeply as possible in the KF solution. A flow meter is installed in the gas line and the flow rate adjusted with a control valve. The gas flow should be between 50 mL/min and a maximum of 250 mL/min (3...15 L/h).

In order to achieve a stable equilibrium the gas line must be thoroughly purged with the gas sample (10...30 min). This is done by installing a three-way stopcock in the line and not passing the gas sample through the titration cell during the purging phase.

The time during which the sample is passed into the titration cell must be measured in order to be able to subsequently carry out the necessary calculation of the water content.

The amount of sample depends primarily on the water content, the method used (coulometric or volumetric titration) and the required accuracy. With larger amounts of sample please remember that the methanol that evaporates must be topped up from time to time. If the samples are liquid samples from a pressurized (sample) container then the samples must always be taken in the liquid form – i.e. from the liquid phase by inverting the container – as the gas phase always has a lower water content because on evaporation the majority of the water remains in the liquid phase.

The water content is normally calculated in $\mu\text{g/L}$ or mg/L :

Gas volume = flow-through time x gas flow

Example: 15 min at 100 mL/min results in 1.5 liter gas sample

Water content, coulometry = A / V

Water content, volumetry = $(A \times t) / V$

A = Titrator reading ($\mu\text{g H}_2\text{O}$ or mL KFR)

t = Titer of KF solution ($\text{mg H}_2\text{O/mL}$)

V = Gas volume

If the water content is to be calculated in % then the mass of the gas introduced into the titration vessel must be known. This can be obtained by differential weighing (sample container before and after removing the gas) or by calculation.

The molar mass of a gas occupies a volume of 22.4 L at 273 K. However, as work is normally carried out at higher temperatures, the thermal expansion of the sample must be taken into account.

Example:

The water content in 0.75 L methane was determined at 22 °C. 240 $\mu\text{g H}_2\text{O}$ were read off at the KF Coulometer.

$M(\text{CH}_4) = 16.043 \text{ g/mol}$

Weight of methane sample = $0.75 \times 16.043 \times 273 / 22.4 / 295 = 0.497 \text{ g} = 497 \text{ mg}$

This 497 mg CH₄ contains 0.24 mg (240 µg) H₂O

The water content of the sample is therefore $0.24 / 497 = 0.048 \cdot 10^{-2} = 0.048\%$

The water content of the following gaseous samples has been determined by this general method:

Butane, natural gas, freons, carbon dioxide, methane, propane, oxygen, nitrogen.

And here are a few special samples:

Ammonia, liquid

Work under a fume hood! 10 g dry ethylene glycol is placed in a dry Erlenmeyer flask and cooled to approx. –80 °C. 25...50 mL sample is added and mixed, then the ammonia is allowed to evaporate (let the flask reach room temperature slowly). Use a dry syringe to inject approx. 5 mL ethylene glycol into the titration vessel and determine its water content. A blank determination on the ethylene glycol used is carried out in exactly the same way and taken into account in the calculation.

Chlorine

This would consume water by oxidizing the iodide contained in the KF reagent to iodine and simulate a water content that is too low.

The sample is passed through a mixture containing equal volumes of pyridine, sulfur dioxide and methanol and the water content of an aliquot of the mixture is determined. (Sulfur dioxide reduces the chlorine to inert chloride.) The blank value of the solvent mixture must be determined separately.

The same remarks apply to liquid and gaseous bromine.

Hydrogen chloride

Approx. 50 mL pyridine (max. 0.01% H₂O) is placed in a dry Erlenmeyer flask and approx. 5 g of the sample is introduced. The mixture is allowed to cool down, made up to 100 mL with methanol and mixed. In this way the precipitated pyridinium salts are redissolved. The water content of an aliquot of this solution is determined. Take the blank value into account!

Direct introduction of the sample into the titration cell cannot be recommended because of heat production and salt formation. In addition, gaseous HCl can react with methanol and release water; this would simulate a too high water content.

Ethylene oxide, propylene oxide

The sample is added from the liquid side of a pressure-resistant gas pipet. The addition can be carried out rapidly as the sample quickly dissolves in the KF reagent. The cell is titrated to dryness until a stable drift has been established. The sample is then added and its water content determined. Max. 20 g sample can be titrated in 30 min, after which time the reagent must be replaced. As the addition of the sample takes some time, a minimum titration time of 5 min should be programmed at the instrument.

Hydrogen sulfide

H₂S is oxidized to sulfur by the iodine in the KF reagent. As this reaction does not take place stoichiometrically, water determination by the Karl Fischer method is not possible!

Methyl chloride

The boiling point of methyl chloride is –23 °C. A low-temperature volumetric titration can be carried out with two-component reagents. Methanol is precooled in the titration cell to –30 °C and titrated to dryness. The sample is then added and its water content titrated at this low temperature.

Sulfur dioxide, liquid

The sample is added from the liquid side of a pressure-resistant gas pipet. It can be carried out rapidly as the sample quickly dissolves in the KF reagent. The cell is titrated to dryness until a stable drift has been established. The sample is then added and its water content determined. As the addition of the sample takes some time, a minimum titration time of 5 min should be programmed at the instrument.

Vinyl chloride

The sample is added from the liquid side of a pressure-resistant gas pipet. It can be carried out rapidly as the sample quickly dissolves in the KF reagent. The cell is titrated to dryness until a stable drift has been established. The sample is then added and its water content determined. As the addition of the sample takes some time, a minimum titration time of 5 min should be programmed at the instrument.

17. Water determination in special samples

Metrohm has been manufacturing KF titrators for half a century and during this time has accumulated a vast amount of application knowledge from which you can profit as a customer. In the preceding sections we have described the water determination in more than 800 substances. This section contains further substances that we think could be of interest to you. If you cannot find your product or substance in the index just contact Metrohm.

17.1 Surfactants

25 mL methanol is placed in the titration vessel and titrated to dryness (conditioned). 0.3...0.5 g sample is added and the water content titrated. The following have been analyzed:

Betaines, benzalkonium chloride, cetylpyridinium chloride, didecylmethylimidazolium chloride, Hyamine 1622 and nonylphenol.

For *dodecylbenzenesulfonic acid* (and its mixtures with residual sulfuric acid) the following applies:

30 mL methanol plus 5 g imidazole are placed in the titration vessel and titrated to dryness (conditioned). Approx. 1 g sample is added and its water content titrated.

Sodium dodecyl sulfate (sodium lauryl sulfate) and soaps can be titrated at elevated temperatures:

30 mL of a 2:1 mixture of methanol/formamide is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 0.5 g (possibly comminuted) sample is added and its water content titrated at the same temperature.

For *coco fatty acid aminoxide* and *tallow fatty acid amine* the working medium must be buffered:

25 mL of a 4:1 mixture of methanol/chloroform is placed in the titration vessel, treated with approx. 5 g benzoic acid and titrated to dryness (conditioned). 1...2 g sample is added and its water content titrated.

With the heating method (oven method) we have determined the water content of sodium polyphosphate (300 °C), soap flakes and washing powder (120 °C).

Remark:

If the sample contains a lot of water then it should be diluted with dry methanol. The method and calculation are given in section 10.1.

17.2 Technical products

- Coal powder, coal dust, carbon black and carbon powder for spectroscopy have been titrated coulometrically by the heating method at a temperature of 200...270 °C. Sample weight 0.3...1 g. The 768 Drying Oven should be used for voluminous, very fine particles.
- Aerosil, a very voluminous and light form of SiO₂, can be analyzed in two different ways:
 - a) In methanol, sample weight approx. 0.2 g
 - b) By the heating method in a 768 Drying Oven (200 °C), sample weight approx. 50...100 mg, coulometric titration.
- In glass fiber wool and powdered glass only the adherent water is determined. Determination takes place by coulometric titration. Glass fiber wool; approx. 1 g, 180...200 °C. Glass powder; approx. 0.5 g, 280...300 °C.
- Nitrating acid (mixture of H₂SO₄ and HNO₃)
50 g pyridine is weighed out into a dry Erlenmeyer flask fitted with a septum stopper. Approx. 1 g sample is carefully added with the flask being swirled about, the flask is then sealed and the contents are mixed.
25 mL methanol is placed in the titration vessel and titrated to dryness (conditioned). 4...5 g sample solution is injected into the titration vessel (sample weight by weighing the syringe before and after injection) and the water content titrated. A blank determination is carried out on the pyridine and taken into account in the calculation.
- Gypsum, plaster of Paris
Gypsum (CaSO₄ x 2 H₂O) does not release its water completely. It must be titrated coulometrically by the heating method at 200 °C. Sample weight approx. 50...100 mg.
Plaster of Paris contains approx. 0.5 mol H₂O. 25 mL methanol is placed in the titration vessel, heated to 50 °C and titrated to dryness (conditioned). Approx. 1 g sample is added and its water content titrated at the same temperature.
- Regulated set cement
25 mL methanol is placed in the titration vessel, heated to 50 °C and titrated to dryness. Approx. 0.2 g sample is added and its water content titrated at the same temperature.
- Water glass
30 mL methanol is placed in the titration vessel, treated with approx. 7 g salicylic acid and titrated to dryness (conditioned). Approx. 0.1 mL sample is added from a dry syringe (sample weight by differential weighing) and its water content is titrated. For this sample a high-frequency mixer (e.g. Polytron or Ultra-Turrax) is used instead of a magnetic stirrer.

17.3 Inorganic compounds

- In sulfur hexafluoride (SF₆) we have determined the water content coulometrically according to section 16, «Water determination in gaseous samples».
 $M(\text{SF}_6) = 146.05 \text{ g/mol}$
- The water content of the following salts has been determined by the heating method (sample weight, oven temperature):

Potassium cyanide (KCN)	1 g	280...300 °C
Lithium cobaltite (LiCoO ₂)	0.5...1 g	100 °C
Magnesium stearate	0.1 g	140...160 °C
Sea salt	0.5 g	150 °C.
- The following have been titrated volumetrically at elevated temperature:
Ammonium hydrogen fluoride (NH₄HF₂). 0.3 g in 30 mL methanol/formamide 2:1 plus approx. 3 g imidazole.
Sodium hypophosphite monohydrate (NaH₂PO₂ x H₂O). 0.3 g in methanol/formamide 2:1.
The solvent mixture is placed in the titration vessel, warmed to 50 °C and titrated to dryness. The sample is added and its water content titrated at the same temperature.
- Antimony(III) chloride (SbCl₃). 30 mL working solution (for aldehydes and ketones) is placed in the titration vessel and titrated to dryness. Approx. 1 g sample is added and its water content titrated.

17.4 Agriculture

- In fertilizers (fertilizer granulate, artificial fertilizers) it is the adherent water which is of primary interest, but the total water content may also have to be determined.
Adherent water: 30 mL of a 1:2 mixture of methanol/chloroform is placed in the titration vessel and titrated to dryness (conditioned). Approx. 0.5...1 g sample is added and its water content titrated (titrate quickly). Replace the solvent mixture after each determination.
Total water: 30 mL methanol plus approx. 7 g salicylic acid are placed in the titration vessel, heated to 50 °C and titrated to dryness (conditioned). Approx. 0.5 g sample is added and its water content titrated at the same temperature. Stop delay 15 s.
- The water content of urea can be determined without any problems.
25 mL methanol is placed in the titration vessel and titrated to dryness (conditioned). Approx. 2 g sample is added and its water content titrated. The solvent must be replaced after each determination.
- In the pesticides dimethoate and/or domethoate (dissolved in cyclohexanone) the water content has been determined as follows: 30 mL working medium (for aldehydes and ketones) is placed in the titration vessel and titrated to dryness (conditioned). Approx. 2 g sample solution (exact weight by differential weighing) is added from a dry syringe and its water content titrated.

17.5 Leather, paper, textiles

The water content of these products depends to a large extent on their storage conditions and atmospheric moisture. Practically all the information found in the literature uses an external extraction with dry methanol for the KF water determination that can take up to one hour. The water content of an aliquot of the extract is then determined. Water deter-

mination by the Karl Fischer method always yields higher H₂O contents than the drying oven method, which can never determine all the water.

We have chosen the heating method for most samples and have achieved reliable values with it together with shorter analysis times.

Wherever necessary the sample is cut up into small pieces with a knife or scissors. Sample weight. 0.1...0.3 g, oven temperature 150 °C.

Examples of samples that have been analyzed:

Cotton, cellulose, insulating paper, cardboard, adhesive tape, linen, blueprinting paper, paper, compressed wood and transformer board (190 °C), viscose and wood pulp.

For *leather, silk and wool* proceed as follows (cut the sample into small pieces):

A reflux condenser is attached to the titration vessel, 50 mL methanol is added, heated to boiling (approx. 65 °C) and titrated to dryness (conditioned). It is allowed to cool down slightly, approx. 0.2...0.5 g sample is added and its water content is titrated at the boiling temperature.

In *ink* (dissolved in tripropylene glycol monoethyl ether) the water content has also been determined:

25 mL methanol is placed in the titration vessel and titrated to dryness (conditioned). Approx. 3 g sample (exact weight by differential weighing) is added from a dry syringe and its water content titrated.

17.6 Pharmaceuticals

As already mentioned in section 10.2 «Water determination in drugs», H₂O can be determined by the Karl Fischer method in a great number of raw materials. A few examples are given here:

Cefalexin, penicillin and penicillin-G-potassium have been analyzed as follows:

30 mL methanol plus approx. 5 g salicylic acid is placed in the titration vessel and titrated to dryness (conditioned). 1...3 g sample is added and its water content titrated.

In *serotonin* the water content has been titrated coulometrically by the heating method. Sample weight 25...75 mg, oven temperature 200 °C, nitrogen as carrier gas.

Sodium nitroferricyanide and *pyrazolone* are titrated in methanol.

25 mL methanol is placed in the titration vessel and titrated to dryness (conditioned). The sample is added (nitroferricyanide 0.1...0.2 g, pyrazolone 0.2...0.4 g) and its water content determined. With pyrazolone the solvent must be replaced after three determinations.

2-Methyl-5-mercaptothiadiazole has an interfering side reaction under normal KF conditions. The water content of this substance can be determined as follows:

30 mL working medium (reagent for aldehydes and ketones) and approx. 5 g salicylic acid are placed in the titration vessel and titrated to dryness (conditioned). Approx. 2 g sample is added and its water content titrated.

17.7 Organic compounds

These substances were not mentioned in section 9, or not in detail:

General procedure

The solvent is placed in the titration vessel and titrated to dryness (conditioned). The sample is then added and its water content is titrated.

Solvent 30 mL methanol

Polyvinyl pyrrolidone sample weight approx. 0.1...0.2 g
Tributyltin chloride sample weight approx. 1...2 g
Vinyl acetate sample weight approx. 3 g (titrate very quickly)

Solvent 30 mL methanol/1-decanol 1:2

2-Methyl-1,3-butadiene sample weight approx. 5 mL (titrant 2 mg H₂O/mL)
2,5-Norbornadiene sample weight approx. 5 mL (titrant 2 mg H₂O/mL)
Dicyclopentadiene sample weight approx. 5 mL

Solvent 30 mL methanol plus 5 g salicylic acid

Mercaptopurine sample weight approx. 0.3 g
N-Methyl pyrrolidone sample weight approx. 2 g

Solvent 30 mL methanol plus 3 g imidazole

Chlorotoluene sulfurylchloride sample size approx. 5 mL (titrant 2 mg H₂O/mL)

Solvent 30 mL working medium (for aldehydes and ketones)

N-Vinyl-2-pyrrolidone sample weight approx. 5 g
Panthenol sample weight approx. 0.5 g (use syringe without needle)
Lemon oil sample size approx. 1 mL (titrate at -10 °C).

Methanesulfonic acid chloride normally contains (interfering) free chlorine that must first be reduced. The titration itself takes place in methanol.

Approx. 50 g sample is weighed out into a dry Erlenmeyer flask fitted with a septum stopper and treated with 5 g of a solution containing 5 g SO₂ and 10 g imidazole in 100 mL methanol. The flask is sealed, its contents mixed and allowed to stand for 5 min for the reaction to take place completely. The water content of an aliquot (taken with a dry syringe) is titrated. A blank determination must be carried out on the reaction solution and taken into account in the calculation.

In the following three substances the SH group interferes. It is added to N-ethylmaleinimide. The water content can then be determined without interference.

Ethyl thioglycolate and thioglycolic acid

Solvent: 30 mL methanol + 3 g imidazole + 1 g N-ethylmaleinimide. Titrate to dryness, add approx. 0.3 g sample, allow to react under stirring for 5 min and then titrate the water content.

Thiokol

Solvent: 30 mL 2-chloroethanol + 3 g imidazole + 1 g N-ethylmaleinimide. Titrate to dryness, add approx. 0.3 g sample from a dry syringe without needle, allow to react under stirring for 5 min and then titrate the water content.

17.8 Miscellaneous

Finally a few samples or substances that were not mentioned (or only mentioned in general) in previous sections.

The heating method (oven method) has been used to determine the water content of the following (oven temperature, sample weight, remarks):

Aspartame (tablets) 130 °C, approx. 0.4 g (contains carbonate, decomposes at higher temperatures)

<i>Bleaching powder</i>	150 °C, approx. 0.25 g (contains hypochlorite and carbonate)
<i>Cyclamate (tablets)</i>	140 °C, approx. 1 g (contains carbonate, decomposes at higher temperatures)
<i>Detoxification powder</i>	190 °C, approx. 0.2 g (contains hypochlorite and carbonate)
<i>Rubber stoppers</i>	180...250 °C, approx. 0.3 g (cut into small pieces, determine optimal oven temperature – sample must not decompose).

Bitumen emulsions contain tars that leave sticky deposits on the electrodes and in the titration vessel. Work is therefore carried out with a special solvent mixture:

30 mL of a 1:1 mixture of 1-decanol/xylene is placed in the titration vessel and titrated to dryness (conditioned). Approx. 0.1 g sample is added from a dry syringe and its water content is titrated.

With *fruit fibers* (from citrus fruits) the water is extracted externally:

5 g sample is weighed out into a dry Erlenmeyer flask fitted with a septum stopper. 80 g dry methanol is added, the flask is sealed, its contents briefly mixed and then it is placed in an ultrasonic bath for 10...15 min to extract the water. The suspension is allowed to settle and the water content is determined in an aliquot of the extract (dry syringe, approx. 2 g). A blank determination is carried out on the methanol and taken into account in the calculation.

For *Lanolin* 30 mL methanol/1-decanol is placed in the titration vessel and titrated to dryness (conditioned). Approx. 0.5 g sample is added (syringe without needle) and its water content is titrated.

In polystyrene foam the water content cannot be determined by the heating method (becomes voluminous and blocks the release of water). Proceed as follows:

Approx. 10 g sample and 40 g p-xylene are weighed out into a dry Erlenmeyer flask fitted with a septum stopper. A magnetic stirrer bar is added, the flask is sealed and placed on a heated magnetic stirrer until the sample has dissolved. After cooling down 20 g methanol is added under stirring – this precipitates the polystyrene again. It is allowed to settle and the water content of an aliquot of 4...5 g (dry syringe) is titrated coulometrically. A blank determination is made in the same way and taken into account in the calculation. The solvents used must be as dry as possible.

Silicone oils only contain traces of water. They are titrated coulometrically. The anode solution contains 20% toluene.

A dry syringe is filled three times with sample solution and the contents are rejected. Approx. 0.5 g of the fourth filling is injected into the titration cell and its water content titrated.

In *silanols/siloxanes* the OH groups react quantitatively with «normal» KF reagents, so that a working medium for aldehydes and ketones is used:

30 mL working medium is placed in the titration vessel and titrated to dryness (conditioned) with dilute KF reagent (2 mg H₂O/mL). A dry syringe is used to add approx. 5 g sample and its water content is titrated (titrate very quickly).

Wax (e.g. carnauba wax) is titrated as follows:

30 mL of a 1:1 mixture of methanol/1-decanol is placed in the titration vessel, warmed to 50 °C and titrated to dryness (conditioned). Approx. 1 g sample is added and its water content is titrated at the same temperature.

Appendix: Literature

Metrohm Application Bulletins

- No. 069 Titrimetric methods for the chemical analysis of pasta
- No. 109 Karl Fischer water determination with the KF drying oven
- No. 141 Analysis of edible fats and oils
- No. 142 Karl Fischer water determination in gases
- No. 145 Determination of low water contents in plastics using the KF oven method
- No. 193 Fully automatic water determination according to Karl Fischer using a sample changer
- No. 209 Coulometric water determination according to Karl Fischer in insulating oils as well as in hydrocarbons and their derivatives
- No. 255 Validation of Metrohm KF titrators and KF ovens according to GLP/ISO 9001
- No. 273 Validation of Metrohm KF Coulometers using Standard Operating Procedures
- No. 280 Automated Karl Fischer water determination with the 774 Oven Sample Processor
- No. 282 Automated Karl Fischer water determination in pharmaceutical ingredients

Metrohm Application Notes

KF Application Notes K-1 to K-46

Standards

Association of Official Analytical Chemists (AOAC) USA

- AOAC 967.19 Water in dried vegetables. Karl Fischer method
- AOAC 972.01 Water (free) in fertilizers. Alternative extraction method, Karl Fischer method
- AOAC 977.10 Moisture in cacao products. Karl Fischer method
- AOAC 984.20 Moisture in oils and fats. Karl Fischer method

American Society for Testing and Materials

- ASTM D 1364-78 Standard Test Method for Water in Volatile Solvents (Fischer Reagent Titration Method)
- ASTM D 1533-86 Standard Test Method for Water in Insulating Liquids (Karl Fischer Reaction Method)
- ASTM D 1744-92 Standard Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent
- ASTM D 2072-98 Standard Test Method for Water in Fatty Nitrogen Compounds
- ASTM D 3401-97 Standard Test Method for Water in Halogenated Organic Solvents and Their Admixtures
- ASTM D 4017-96a Standard Test Method for Water in Paints and Paint Material by Karl Fischer Method

ASTM D 4017,X1	Test Method for Karl Fischer Water Determination for Latex Paints Using Extraction with Methanol
ASTM D 4017,X2	Test Method for Karl Fischer Determination of Water Content in Paint Using a Homogenizer Accessory
ASTM D 4377-93a	Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration
ASTM D 4928-89	Standard Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration
ASTM D 5460-98	Standard Test Method for Rubber Compounding Materials – Water in Rubber Additives
ASTM E 203-96	Standard Test Method for Water Using Volumetric Karl Fischer Titration
ASTM E 700-79	Standard Test Method for Water in Gases Using Karl Fischer Reagent
ASTM E 1064-92	Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

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BS 6829:1.5:1990	Analysis of surface active agents (raw materials). Part 1. General Methods. section 1.5 Methods for determination of water content
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DIN ISO 10362 Teil 2	Untersuchung von Tabakerzeugnissen. Zigaretten; Wasserbestimmung in Rauchkondensaten. Teil 2: Karl-Fischer-Verfahren
DIN 51777 Teil 1	Prüfung von Mineralöl-Kohlenwasserstoffen und Lösemitteln. Bestimmung des Wassergehaltes nach Karl Fischer. Direktes Verfahren
DIN 51777 Teil 2	Prüfung von Mineralöl-Kohlenwasserstoffen und Lösemitteln. Bestimmung des Wassergehaltes nach Karl Fischer. Indirektes Verfahren

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

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International Electrotechnical Commission, Geneva

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ISO 760: 1978	Determination of water – Karl Fischer method (general method)
ISO 760-1978	Animal and vegetable oils and fats. Determination of water – Karl Fischer method (general method)
ISO 960: 1988	Plastics – Polyamides (PA). Determination of water content
ISO 2097: 1972	Glycerols for industrial use – Determination of water content. Karl Fischer method
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