

Application Bulletin 280/3 e

Automated water content determination with the 874 Oven Sample Processor

Branch

All branches

Keywords

Titration; Karl Fischer titration; coulometric; gas extraction; oven technique; automation; 874 Oven Sample Processor; water standard; sodium tartrate

Summary

In principle the gas extraction or oven technique can be used with all types of samples which release the contained water when the samples are heated. The oven technique is essential whenever direct Karl Fischer titration is impossible because the sample contains interfering components or, due to its consistency, is difficult to place in the titration vessel.

This Application Bulletin shows examples from food, pharmaceutical, plastics and petrochemical industry to describe automated water content determination using the oven technique in combination with coulometric KF titration.

Instruments

874 Oven Sample Processor

KF Titrator (coulometric)

Electrodes

Double Pt wire electrode (for coulometry)

Generator electrode with or without diaphragm (for coulometry)*

* For measurements of samples with absolute water contents < 100 µg, the generator electrode with diaphragm is recommended.

Reagents

For the coulometric technique, special reagents suitable for the oven technique are available.

Due to the constant gas flow during measurements, methanol contained in the reagents evaporates. With the generator electrode without diaphragm a decreasing methanol content can lead to false high results, with recoveries of up to 110%.

The methanol loss should therefore be compensated regularly to avoid too high results.

Coulometric reagents have a limited water capacity. The capacity is equivalent to the amount of sulfur dioxide. Decreasing sulfur dioxide concentrations (lower than half of the initial concentration) lead to longer determination times. The reagent should be completely replaced. The monitoring of the reagent capacity and the exchange of the reagent can be done by the titration system and the software.

Standards

Standards (with different water contents) suitable for the oven technique are commercially available.

Carrier gas

The carrier gas transports the released water into the titration vessel. In principle it is not important what gas is used. However, due to oxidation reactions with oxygen, the thermal stability of organic substances at higher temperatures is often poor, when using dry air as carrier gas. Inert gases, usually nitrogen, offer more flexibility and reliability.

For solids with a water content below 1% we recommend a gas flow rate of 50 mL/min. Gas flow rates of up to 100 mL/min can be used for solids with higher water contents. Higher flow rates do usually not lead to shorter determination times.

Measurements in liquid samples (oil, fuel, solvents,...) should be carried out using gas flow rates of 80 mL/min or higher. Furthermore it is recommended that the inlet needle is immersed in the sample and the gas is allowed to flow through the sample.

General

The combination of the oven technique with coulometric Karl Fischer titration is ideal for samples with low water content. Foodstuff, pharmaceutical products, plastics or mineral oil products can be analyzed fully automated and accurately.

In accordance with the gas extraction principle the water is driven out of the heated sample by a stream of dry carrier gas and transferred to the titration vessel, where the water content is determined.

Preparation

Sample

The sample is thoroughly mixed. Make sure the sample does not change its water content during the mixing. The optimal sample size depends on the water content of the sample. Unfortunately there is no equation describing the relation between water content and sample size. But there is a rule of thumb: the higher the water content, the smaller the sample size and vice versa. Sample weights that are too low have a negative effect on the measuring accuracy (balance error). The upper limit for the sample size is defined by the volume of the sample vial. Theoretically the maximum sample weight is also limited by the water capacity of the reagent. Usually the capacity is approximately 1000 mg H₂O per 100 mL reagent (please contact reagent manufacturer for more information). In other words, with one sample this capacity is never used.

The absolute amount of water transferred to the titration vessel is recommended to be in the range of 300 to 5000 µg. If the absolute amount of water for a sample cannot be reduced (e.g. smaller sample size ...) also larger amounts of water (> 5000 µg) can be determined using the oven technique. Please be aware that in such cases the determination times will increase.

The appropriate amounts of sample are weighed into the sample vials and the vials are sealed with a septum cap. Previous to usage, the vials and caps should be conditioned for at least 24 hours at ambient air.

Table 2 on pages 5 and 6 shows recommended sample weights for a choice of samples.

Instrument and software

The 874 Oven Sample Processor and the KF Titrator are connected to a PC. The *tiamo*TM software is started. After the instruments are recognized and therefore visible in the device list, the work position for the conditioning vial, the tower (sample positions) and the shift position are defined. The *tiamo*TM software includes several preprogrammed methods which can be loaded and used with an 874 system. Depending on the KF Titrator, the methods need to be adapted with the right instruments. For the analysis of sample series, the following sequence of methods is recommended:

- systemprep
- blank value
- water content

The method "systemprep" is run once before a sample series. This makes sure that the system of tubes is purged and ready for the sample determinations. Afterwards the blank values of

empty sample vials are determined. Three replicas of the blank value determination are recommended. Finally the analysis of the water content of the sample takes place.

Normally a flow rate of the carrier gas (air, nitrogen or a different inert gas) of 40 to 60 mL/min is sufficient. The flow rate can be adjusted up to 150 mL/min to make sure that the gas flow is high enough to transfer the released water as fast as possible into the titration vessel. Generally the determination time for liquid samples decreases if the gas flow is increased. Avoid high gas flow rates when analyzing solid samples which could swirl up.

The vials for conditioning, system preparation, determination of the blank and the sample vials are placed on the rack of the 874 Oven Sample Processor. For coulometric KF titrations, the titration cell is filled with 150 mL of reagent and then conditioned.

Temperature gradient

For samples whose temperature behavior is unknown, a so-called temperature gradient is run (available temperature range: 50 to 250 °C). The required method "temp gradient" is a preprogrammed method included in the *tiamo*TM software. This method uses a heating rate of 2 °C/min to heat up samples from 50 to 250 °C. Figure 1 shows a theoretical temperature gradient where the sample is heated from 50 to 250 °C in 100 min.

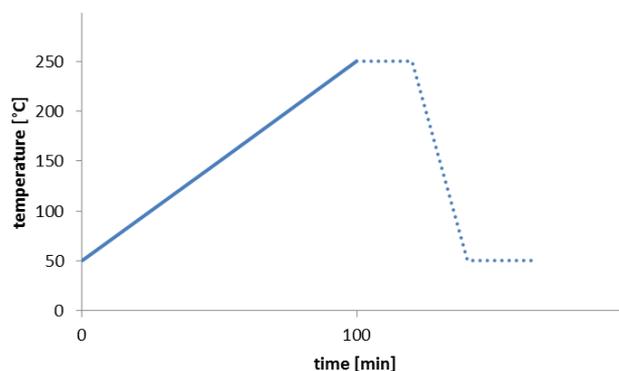


Fig. 1: Diagram showing a theoretical temperature gradient.

While a temperature gradient is being run it is possible to record both, the amount of water released and the drift as a function of time (see Fig. 2). The software *tiamo*TM offers the possibility to correlate the amount of water released and the drift with the oven temperature. This allows statements about the kinetics of the water release as a function of the temperature.

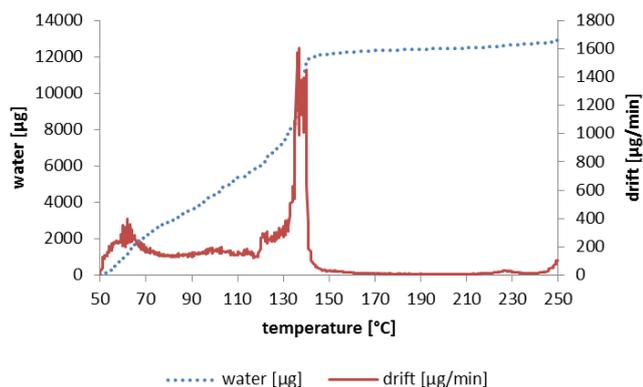


Fig. 2: Temperature gradient (2 °C/min) of sodium tartrate dihydrate showing the amount of released water and the associated drift value as a function of the temperature

The temperature gradient of sodium tartrate (Fig. 2) shows that the surface water and parts of the crystal water are released starting at 50 °C up to approximately 120 °C. At 120 °C both, the amount of water which is released and the drift increase again. Up to 140 °C the remaining water of crystallization is released. After the water of crystallization has been released, the drift decreases to its basic value of approximately 10 µg/min. A sign of decomposition is the drift value, which starts to increase at around 220 °C. Also the color change of the sodium tartrate after running the temperature gradient suggests decomposition (see figure 3).

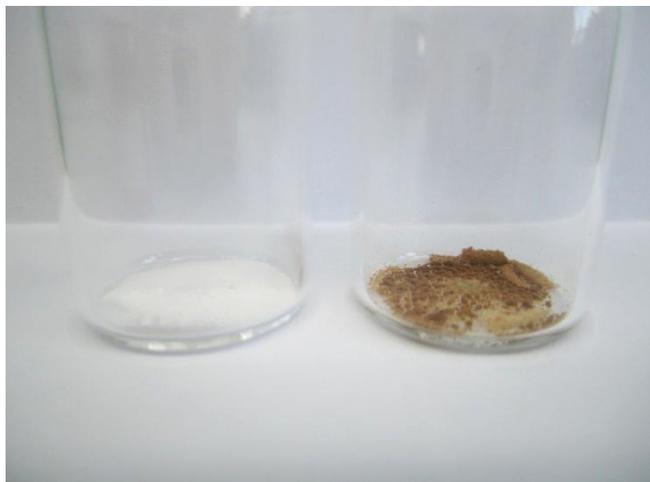


Fig. 3: Sodium tartrate dihydrate before (left) and after (right) running a temperature gradient.

The temperature curve can be used to determine the optimal oven temperature for extracting the water from the sample. This temperature should be high enough for the water to be extracted completely without any decomposition of the sample. The determination time should be kept as short as possible. Therefore the oven temperature should be chosen as high as possible, but approximately 20 °C below the start of decomposition. This procedure works for many different samples and can be used for a fast assessment of the oven temperature.

However, for sodium tartrate dihydrate the manufacturer recommends an oven temperature of 160 °C. According to the temperature gradient in figure 2, an oven temperature of 200 °C could be used. The reason for this discrepancy is the fact that for some samples a heating rate of 2 °C is too high. In such cases the heating rate may be reduced to find the optimal oven temperature for the sample analysis. Figure 4 shows the temperature gradient of sodium tartrate dihydrate using a low heating rate of 0.07 °C/min.

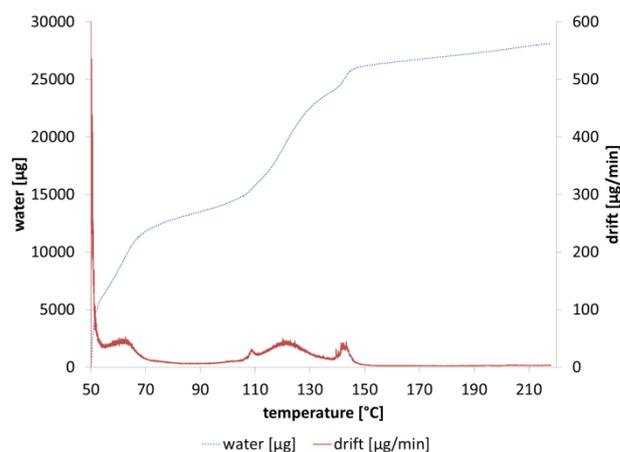


Fig. 4: Temperature gradient (0.07 °C/min) of sodium tartrate dihydrate.

A closer look at the drift values between 170 and 220 °C shows that the drift starts to increase already around 190 °C (see figure 5). Therefore an oven temperature of 160 °C is used for the analysis of sodium tartrate dihydrate.

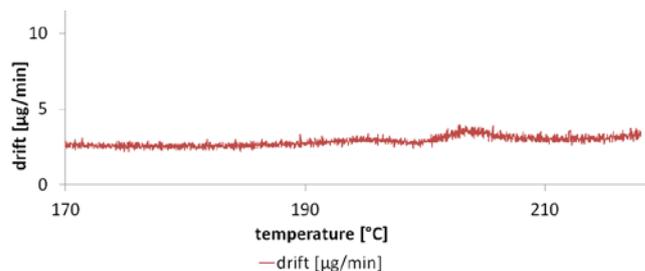


Fig. 5: Temperature gradient (0.07 °C/min) of sodium tartrate dihydrate between 170 and 220 °C.

Please note that the time to record a temperature gradient increases if the heating rate is reduced. The temperature gradient in figure 4 took more than 24 hours to finish.

Analysis

Each analysis consists of the following steps:

- Conditioning of the complete titration system (titration cell and tubing)

- Extraction of the water from the sample
- Transport of the water into the titration cell
- Karl Fischer titration
- Calculation of the result

Conditioning

Conditioning or titrating the titration cell to dryness is carried out under stirring in the so-called conditioning position. This conditioning step must be carried out before every determination. The oven is heated up to the defined temperature. After the temperature is reached and the titration system is conditioned, the first measurement can start.

Carrier gas dried with molecular sieve is used to transport the released water into the titration cell, where the determination of the water content takes place. By means of a double hollow needle (figure 6), the gas is led through the sample vial. The length of the needle can be adjusted depending on the sample which is analyzed. Generally it is recommended to use a short immersion depth of the needle for solid samples (needle holder 6.2049.050). This prevents the needle from being blocked by the sample. In addition swirling of powdery samples can be avoided. For liquid samples the needle can be immersed in the sample (needle holder 6.2049.040). In this way the gas flows through the sample, which mixes the sample and leads to faster extraction of the water.

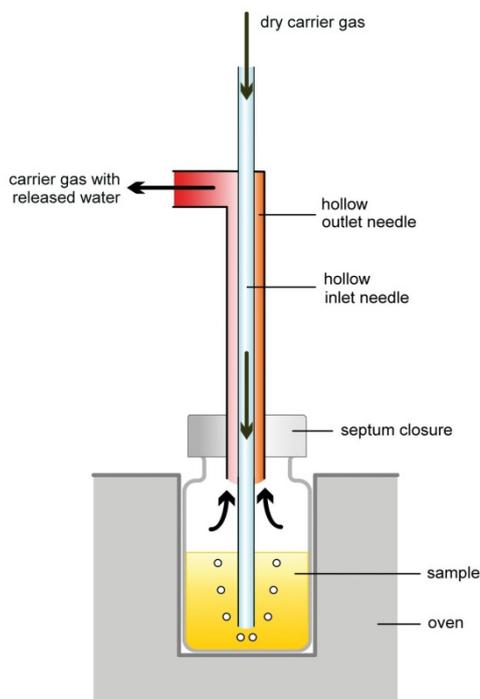


Fig. 6: Principle of the oven technique in liquid samples

Water extraction

The dried carrier gas is passed through the sample vial and transfers the released water into the titration cell. The temperature of the oven can be varied according to the temperature stability of the sample.

It is generally advisable to set an extraction time. During the extraction time no endpoint is accepted, even if the endpoint criteria are fulfilled. In this way, there is enough time for the sample to heat up to the defined temperature. We recommend a time of 2 to 5 min.

Karl Fischer titration

For a coulometric Karl Fischer titration a KF reagent which contains iodide is used. During the determination the iodide is oxidized to iodine at the anode of the generator electrode. The iodine is used for the KF reaction. The coulometric technique is an absolute method and there is no titer determination required. The endpoint indication is bi-voltametric using a double Pt-wire electrode (indicator electrode) to which a constant alternating current is applied. This creates a potential difference (voltage) between the two platinum wires. If even very small amounts of free iodine are present, the voltage drops suddenly; which indicates the endpoint of the titration.

Titration sequence

The water content determined by the gas extraction with subsequent KF titration is made up as follows:

$$\text{water content}_{\text{absolute}} = \text{water content}_{\text{sample}} + \text{blank value} + \text{drift} \times \text{determination time}$$

During “conditioning” the needle is located in the conditioning vial, water contained in the system, is removed until a constant low drift in the range of 1 to 10 µg/min is achieved. If the automatic drift correction is activated the drift value must be stable. A stabilizing time can be defined to ensure a stable drift value. For drift correction, the drift value measured at the start of the determination is multiplied with the determination time and subtracted from the found water content at the end of the determination.

Alternatively the value for drift correction can be determined using a separate method, which is carried out prior to every sample series. In a first step, the system is conditioned until a stable drift is achieved. Depending on the reagent this can take between approximately 15 min and 2 hours. Then the consumption of iodine is recorded during 10 min. The determined mean value is stored and can be used for drift correction and as stop criterion. It is essential that during the sample series the system drift does not change (e.g. interfering additives in sample).

System preparation means that the whole system is adjusted to the selected conditions. An empty sample vial is treated in exactly the same way as the following samples, but the value is not taken into account. We recommend that this step – which is at the same time used for checking that the analysis system is working properly – is carried out before every new sample series.

Apart from the water in the sample, the sample vial also contains atmospheric humidity; this makes a blank value determination necessary. A three-fold determination of the blank value is normally sufficient. The mean value is stored as a Common Variable and taken into account in the calculation of the water content (subtracted). If large sample sizes are used, it might be necessary to correct the blank value (see KF Application note AN-K-048).

The system preparation and the blank value determination must be carried out using the same method parameters as for the analysis of the samples. In order to do this, an empty system preparation vial and three empty blank value vials are placed on the rack of the 874 Oven Sample Processor and analyzed before the samples.

End of titration

The titration and the gas extraction of the sample is stopped as soon as the drift value (amount of water per time) falls below a predefined value. Usually the parameter “relative drift” is used to stop a determination. The stop drift is calculated by adding the drift at the start of the determination and the value entered for the “relative drift”. The endpoint is reached if the actual drift is smaller than the sum of the two mentioned values. The higher the chosen value for the “relative drift” the sooner the determination is stopped and the more water remains in the sample. The “relative drift” value should not be higher than 5 µg/min. If high accuracy is required and for small water contents the “relative drift” should be reduced (e.g. to 2 µg/min).

Parameters

Table 1: Recommended parameters for the oven technique in combination with coulometry.

	Parameter	Setting
General parameters	I(pol)	10 µA
	Generator current	400 mA or auto*
Control parameters	EP at	50 mV
	Dynamics	70 mV
	Max. rate	Maximum µg/min
	Min. rate	15 µg/min

	Stop criterion	rel. drift
	Relative stop drift	5 µg/min
Conditioning parameters	Start drift	10 µg/min
	Stabilizing time	60 s

* 400 mA are used with the generator electrode without diaphragm. The setting auto is chosen for the generator electrode with diaphragm.

Troubleshooting

Procedure for poor precision (reproducibility):

- Optimize the titration and control parameters.
- Check whether the sample vials are tightly sealed.
- Drift too high: Switch off the gas flow.
If drift value decreases: Check the needle system, transfer tube.
If drift value does not change: check titration cell, septum and/or seals leak, molecular sieve exhausted, poorly conditioned reagent, ensure thorough mixing.
- Clean electrodes according to the electrode leaflet.
- Check the needle system and possibly clean it with water and methanol. Dry the components afterwards.
- Check the transfer tube and clean it with water and methanol to remove condensates and dirt.
- KF reagent contaminated/exhausted: change the solution, possibly use a different batch.
- Check electrical contacts; defective contacts can lead to an unstable measuring signal.
- Check if chosen oven temperature is suitable for sample analysis.
- Balance: too inexact, drafts, temperature equilibrium not reached, sample weight not optimal/too low.
- Possibly carry out a qualification of the analysis system. Please contact Metrohm Service for further information.

Example applications

The following table 2 provides an overview of samples analyzed by the oven technique. In each case the Karl Fischer water determination was carried out in combination with a Coulometer using N₂ as a carrier gas (flow rate 40 mL/min).

Table 2: Selection of samples which can be analyzed using the oven technique

Sample	Temp. [°C]	Sample weight [g]	Water content
Foodstuff			
Lyophilizate	120	0.06	1.4%
Aromas ¹	100	0.03–0.08	2.5-5.4%
Maltodextrin	100	0.03–0.08	4.7-8.8%
Lactose monohydrate	155	0.06	5.2%
Skimmed milk powder ²	90	0.06	4.4%
Whole milk powder ²	90	0.06	3.9%
Sweet whey powder ²	90	0.06	4.9%
Glucose monohydrate ²	90	0.06	8.9%
Maltose monohydrate ³	120	0.06	5.9%
Garlic powder	110	0.2	3.5%
Mineral mixtures	110	0.3	6.0-7.0%
Plastics			
Polypropylene	170	3.0	380 µg/g
Polyethylene	115	3.0	40 µg/g
Olefins	180	3.0	100 µg/g
Polyamide	180	0.3	0.8%
Polyoxymethylene (POM)	170	0.3	0.1%
Polystyrene	120	0.05...0.2	200–500 µg/g
Refinery products			
Transformer oil	150	3.0	80 µg/g
Mineral oil	120	1–3	10–100 µg/g
Insulating oil	140	3	5 µg/g
Crude oil	140	2	500-1200 µg/g
Additive	120	0.01...0.03	4.4%
Antimony dialkylthiocarbamate in crude oil	50–130	3.0	700 µg/g
Pharmaceutical products			
Collagens	160	0.07–0.4	10.6-9.2%

Denture cleaner, effervescent tablets ⁴	70	0.2–1.5	3.8%
Drugs	140	0.04	6.7%
Lyophilizate	150	0.01	5.0%
Others			
Sodium tartrate dihydrate	160	0.02–0.08	15.5%
Potassium citrate monohydrate	220	0.03	5.6%
Polyammonium compounds	220	0.03–0.3	1.0-85.0%
Emulsified fat compound	220	0.03–0.08	85.0%
Formamidulosulfonic acid	220	0.2–0.3	< 1.0%
Pigment	100	0.03–0.3	7.9%
Polyol ether	150	0.6–1.3	0.2%
Dibutene	100–140	0.03	250 µg/g
Lithium cobaltite	100	0.45–1.0	64 µg/g
Building rubble			
Surface water	50–60	0.3	0.6%
Bound water	85–140	0.3	1.0%

¹ With the 874 Oven Sample Processor the dissolution of the sample in KF reagent, which is required in a direct Karl Fischer titration and which frequently cannot be carried out completely, is no longer necessary

² With the addition of 4 mL methanol as extraction agent (the water content of the methanol must be determined and included in the blank value).

³ With the addition of 4 mL 1,5-pentandiol, extraction time 600 s (the water content of the 1,5-pentandiol must also be determined and included in the blank value).

⁴ Above 70 °C the contained carbonate decomposes.

Reference

- Metrohm Monograph 8.026.5013 - Water Determination by Karl Fischer Titration
- AN-K-048 – Sample preparation with the oven technique – relative blank (available on www.metrohm.com)

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