

Application Bulletin 280/2 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 applied to all types of samples that release their water when heated. However, the oven technique is essential whenever direct volumetric or coulometric 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 describes the automated determination of the water content using the oven technique and coulometric KF titration. Examples stem from food, pharmaceutical, plastics, and petrochemical industry.

Instruments

874 Oven Sample Processor

KF Titrator (coulometric)

Electrodes

Double Pt wire electrode (for coulometry)

Generator electrode (for coulometry)

Reagents

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

Standards

Solid water standard for oven

Standards with different water contents are commercially available.

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. On the other hand, volumetric Karl Fischer titration is to be preferred for samples with high water contents (> 50%).

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.

For temperature-sensitive samples, e.g. foodstuff, the water can be released at lower temperatures by simultaneous extraction with methanol (see chapter "water extraction". In this way it is possible to prevent the release of water by decomposition.

Preparation

Sample

The sample is thoroughly mixed under conditions which are as dry as possible. The optimal sample size depends on the water content of the sample. Sample weights that are too low have a negative effect on the measuring accuracy (balance error). The maximum sample weight is 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). The absolute amount of water transferred to the titration vessel should be in the range of 300 to 1000 µg.

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 h at ambient air.

Table 2 on page 5 shows recommended sample weights for some 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*[™] 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 rinsed 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.

The flow rate of the carrier gas (air, nitrogen or a different inert gas) should lie in the range of 40 to 60 mL/min. On the one hand the gas flow must be high enough to transfer the released water as fast as possible into the titration vessel, on the other hand the gas flow has to be low enough to ensure complete absorption of the water in the working medium.

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 (for volumetric KF titration with 30 to 40 mL of working medium) 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*[™] software. The heating rate should be selected in such a way that it can be guaranteed that the temperature is actually achieved in the sample vial. A heating rate of 2 °C/min has proven to be suitable for all types of samples. Figure 1 shows a temperature gradient where the sample is heated from 50 to 250 °C in 100 min.

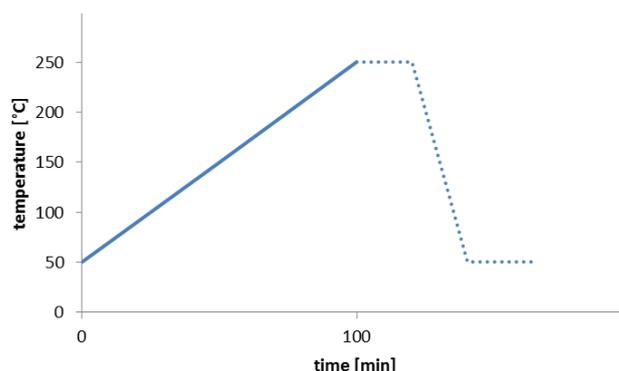


Fig. 1: Diagram showing a theoretical temperature gradient.

While a temperature gradient is being recorded it is possible to record both, the amount of water released and the drift as a function of time (see Fig. 2). By using the heating rate and the elapsed time, it is possible to calculate the associated temperature curve (see figure 2). This allows statements about the kinetics of the water release as a function of the temperature. Additionally thermally unstable samples decomposition reactions can be recognized.

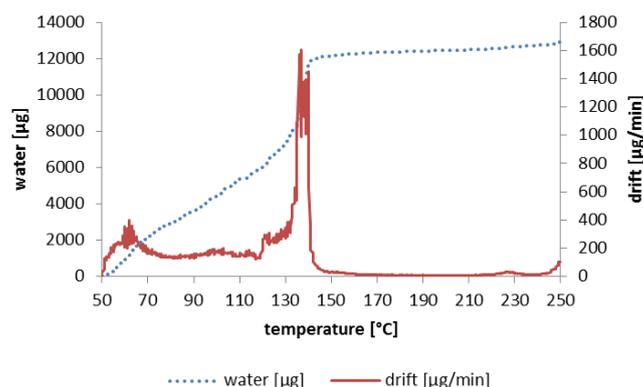


Fig. 2: Temperature gradient of sodium tartrate dihydrate showing the amount of released water and the associated drift value as a function of the temperature

The temperature gradient of the sodium tartrate (Fig. 2) shows that the surface water is 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 water of crystallization is released. This is visible in Fig. 2 by the occurrence of a “drift peak”. 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).

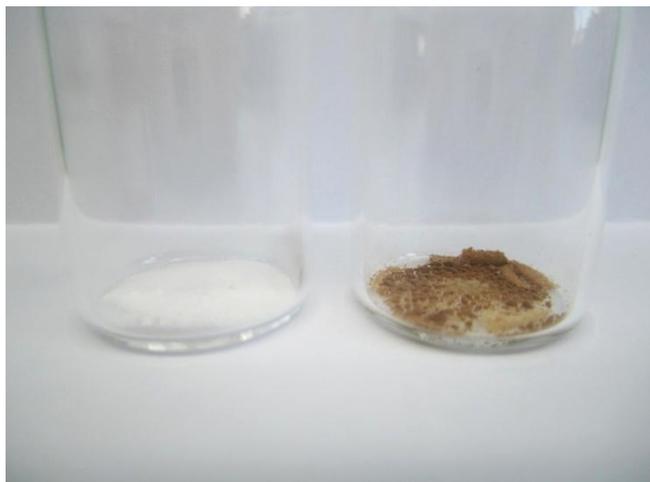


Fig. 3: Sodium tartrate dihydrate before (left) and after (right) running a temperature gradient.

The temperature curve is 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. For sodium tartrate dihydrate an oven temperature of 160 °C is recommended by the manufacturer.

Analysis

Each analysis consists of the following steps:

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

Conditioning

Conditioning or titrating the titration cell to dryness is carried out under stirring without increasing the oven temperature (oven temperature = initial temperature), with the 874 Oven Sample Processor 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 cell 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 4), 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 6.2049.040). This prevents the needle from being blocked by the sample. In addition the needle cannot be bent if it comes in contact with voluminous solid samples, such as granulated plastics. For liquid samples the needle can be immersed in the sample (needle holder 6.2049.050). In this way the gas flows through the sample, which mixes the sample and leads to faster extraction of the water.

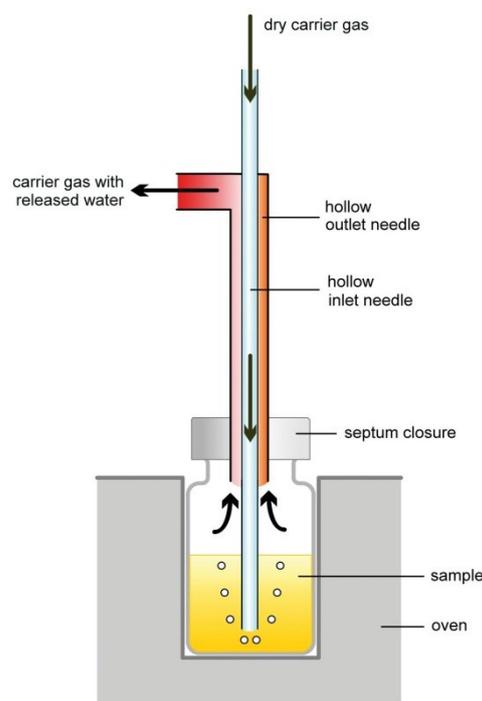


Fig. 4: Principle of the oven technique

Water extraction

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

Temperature sensitive samples can be analyzed at lower temperatures by using dry methanol as extraction agent. The methanol is placed in the sample vial together with the sample. Methanol supports the release of water, particularly during the boiling process in the oven. It is transferred to the titration vessel with the water but does not interfere with the titration as the KF reagent also contains methanol.

It is generally advisable to set an extraction time that depends on the water content of the sample. This ensures that the driven off water is completely transferred to the titration cell. We recommend a time of 3 to 5 min. For high water contents this time must be extended accordingly or the sample should first be diluted in order to avoid extremely

long extraction times (> 30 min). If methanol is used as additional extraction agent, it is important that a sufficiently long extraction time is chosen in order to prevent a premature termination of the determination. In this case we recommend an extraction time of at least 15 min.

Karl Fischer titration

To determine the water content, both, the volumetric and the coulometric technique can be combined with an oven.

For a coulometric Karl Fischer titration a modified 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. As in volumetric Karl Fischer titration, 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; this indicates the endpoint of the titration.

In volumetric Karl Fischer titration, the titer of the titrant must first be determined by using a certified water standard. In combination with the 874 Oven Sample Processor, this is done by driving off the water from a water standard suitable for the oven technique (e.g. potassium citrate monohydrate or sodium tartrate dihydrate ...)

Titration sequence

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

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

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 10 to 20 µg/min is achieved. If the automatic drift correction is activated, 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.

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. If methanol is used as an additional extraction agent then its water content must also be determined and included in the blank value. 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).

The system preparation and the blank value determination must be carried out under exactly the same conditions as the analysis of the samples. In order to do this, an empty system preparation vial and three empty (or filled with solvent) blank value vials are placed on the rack of the 874 Oven Sample Processor and analyzed before the samples.

Parameters

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

	Parameter	Setting
Control parameters coulometry	EP at	50 mV
	Dynamics	70 mV
	Max. rate	Maximum µg/min
	Min. rate	15 µg/min
	Stop criterion	rel. drift
General parameters coulometry	Relative stop drift	10 µg/min
	Start drift	10 µg/min
	I(pol)	10 µA
Control parameters volumetry	Generator current	400 mA
	EP at	250 mV
	Dynamics	100 mV
	Max. rate	Maximum mL/min
	Min. volume increment	minimum µL
General parameters volumetry	Stop criterion	Drift
	Stop drift	20 µL/min
	Titration direction	- (minus)
Oven settings	I(pol)	50 µA
	Initial temperature	normally 50 °C
	Gas flow	Flow rate 40–60 mL/min
	Gas type	Air or N ₂

Troubleshooting

Procedure for poor precision (reproducibility):

- Optimize the titration and control parameters.
- Check whether the sample vials are tightly sealed.
- Drift too high: check titration cell, septum and/or seals leak, molecular sieve exhausted, poorly conditioned reagent, ensure thorough mixing
- Clean electrodes according to the electrode leaflet
- KF reagent contaminated/exhausted: change the solution, use a different batch number if necessary.
- Check electrical contacts.
- Check oven temperature
- Balance: too inexact, drafts, temperature influences, 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 [ppm]
<i>Foodstuff</i>			
Lyophilizate	120	0.06	14000
Aromas ¹	100	0.03–0.08	25000–54000
Maltodextrin	100	0.03–0.08	47000–88000
Lactose monohydrate	155	0.06	52000
Skimmed milk powder ²	90	0.06	44000
Whole milk powder ²	90	0.06	39000
Sweet whey powder ²	90	0.06	49000
Glucose monohydrate ²	90	0.06	89000
Maltose monohydrate ³	120	0.06	59000
Coffee, ground	145	0.06	48200
Garlic powder	110	0.2	35000

Mineral mixtures	110	0.3	60000–70000
<i>Plastics</i>			
Polypropylene	170	3.0	380
Polyethylene ⁴	115	3.0	40
Olefins	180	3.0	100
Polyamide	180	0.3	7800
Polyoxy-methylene (POM)	170	0.3	1400
Polystyrene ⁵	120	0.05...0.2	200–500
<i>Refinery products</i>			
Transformer oil	150	3.0	80
Mineral oil	120	1–3	10–100
Insulating oil	140	3	5
Crude oil	140	2	500–1200
Additive	120	0.01...0.03	44000
Antimony dialkyl-thiocarbamate in crude oil	50–130	3.0	700
<i>Pharmaceutical products</i>			
Collagens	160	0.07–0.4	106000–919000
Denture cleaner, effervescent tablets ⁶	70	0.2–1.5	38000
Drugs	140	0.04	67000
Lyophilizate	150	0.01	50000
<i>Others</i>			
Sodium tartrate dihydrate	160	0.02–0.08	155000
Potassium citrate monohydrate	220	0.03	55500
Methanol	110	0.5	230
Polyammonium compounds	220	0.03–0.3	10000–850000
Emulsified fat compound	220	0.03–0.08	850000
Formamidulosulfonic acid	220	0.2–0.3	< 10000
Pigment	100	0.03–0.3	79000
Polyol ether	150	0.6–1.3	1500
Dibutene	100–140	0.03	250
Inorganic salt	100	0.01–0.03	580

Lithium cobaltite	100	0.45–1.0	64
Building rubble			
Surface water	50–60	0.3	6000
Bound water	85–140	0.3	10000

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.

³ With the addition of 4 mL 1,5-pentandiol, extraction time 600 s.

⁴ 20 ppm water could be determined as the detection limit.

⁵ With self-expanding plastics, only the surface water can be determined with the oven technique. The plastics also contain trapped water. This can only be calculated as the difference between the total water and the surface water. The total water is determined by completely dissolving the sample and subsequent direct volumetric KF titration.

⁶ Above 70 °C the contained carbonate decomposes.

Reference

- Metrohm Monograph 8.026.5013 - Water Determination by Karl Fischer Titration

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