Determination of water in food by automated Karl Fischer titration

A. Felgner[1], R. Schlink[2], P. Kirschenbühler[2], B. Faas[3], H.-D. Isengard[1]

Metrohm
ion analysis

Karl Fischer

Summary

Karl Fischer titration (KFT) is a method for determining the water content in different matrices, based on a selective reaction between water and the Karl Fischer reagent. In comparison to other water detection methods, Karl Fischer titration is less time-consuming and often more accurate.

Low water contents from approx. 0.001% to 1% can be detected by coulometric Karl Fischer titration, where the required iodine is generated electrochemically in the titration vessel. Higher water contents from approx. 1% up to 100% can be determined by volumetric Karl Fischer titration, where an iodine solution serves as titrant.

Automated Karl Fischer titration allows to increase sample throughput; automated sequences can include different methods for the determination of titers and blank values and for different types of samples.

In this work, current Karl Fischer methods using commercially available water standards and solvents were developed with an automated Karl Fischer titration system, both volumetric and coulometric, and applied to different edible oils such as soy bean, sun flower, olive, rapeseed, sesame and pumpkin seed oil.

The determined water contents of the vegetable oils varied between 79 and 690 µg/g. At 79.2 µg/g soy bean oil had the lowest water content and automated KFT yielded higher results than manual KFT. The other oils had higher water contents and showed good agreement between manual and automated KFT.

Introduction

Several methods exist for the determination of water in vegetable oils: loss on drying, reaction with calcium hydride, Karl Fischer titration (KFT), Fourier Transform Infrared (FTIR) and Raman spectroscopy as well as dielectric measurements. Among these, KFT is certainly the method of choice when trace amounts of free, emulsified or dissolved water have to be accurately determined in a reasonable time.

KFT is based on the stoichiometric reaction of water with iodine and sulfur dioxide in the presence of a short-chain alcohol (R` = CH_3, C_2H_5) and an organic base (RN), according to the following equations:

$$R`OH + SO_2 + RN \rightarrow R`OSO_2^- + RNH^+$$

$$R`OSO_2^- + I_2 + H_2O + 2\,RN \rightarrow 2\,RNH^+ + R`OSO_3^- + 2\,I^-$$

$$R`OH + SO_2 + 3\,RN + I_2 + H_2O \rightarrow 3\,RNH^+ + R`OSO_3^- + 2\,I^-$$

Whereas volumetric KFT is applied to samples containing higher water contents from approximately 1% up to 100%, the coulometric technique is ideally suited for smaller water contents in the range of a few µg/g. In the volumetric KF technique a titrating agent containing iodine is added directly to the sample via a buret. In contrast, in coulometric KFT iodine is generated electrochemically from iodide in the titration cell. In both cases iodine reacts with the water in the sample. Once all the available water has reacted (equivalence point), the indicator electrode detects the first excess of iodine and the KFT stops. The amount of water is calculated by measuring the titrant consumption (volumetric KFT) or the electric charge needed for the oxidation of iodide to iodine (coulometric KFT).

Due to its selectivity and absolute nature of the method, KFT is ideally suited for automation. Especially automated KF sequences, including different determination methods for different types of samples, enhance sample throughput and improve accuracy.

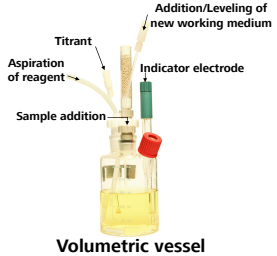
Materials and methods

Volumetric KFT

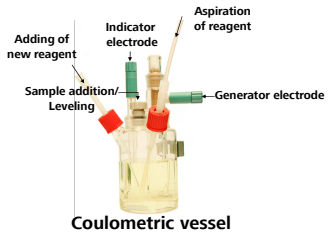
- 841 Titrando
- 801 Magnetic Stirrer
- 815 Robotic USB Sample Processor
- 800 Dosino
- 807 Dosing Unit

Coulometric KFT

- 756 KF Coulometer
- 801 Magnetic Stirrer
- 815 Robotic USB Sample Processor
- 800 Dosino
- 807 Dosing Unit



Volumetric vessel

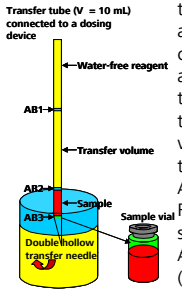


Coulometric vessel

	Volumetric KFT	Coulometric KFT	
	Water standards	Water standards	Edible oils
Titrating agent	HYDRANAL®-Composite 2*	–	–
Working medium	HYDRANAL®-Methanol dry*	HYDRANAL®-Coulomat AD*	HYDRANAL®-Coulomat AG-H*
Generator electrode	–	without diaphragm	
Generator current	–	400 mA	
Endpoint detection	bivoltametric	bivoltametric	
Polarization current	50 µA	10 µA	
Stop voltage	250 mV	50 mV	
Drift rate	10 µl/min	10 µg/min	
Extraction time	120 s	120 s	660 s

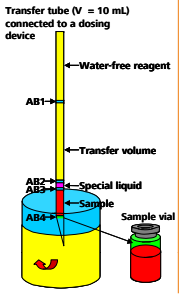
*All chemical products were kindly provided by Sigma-Aldrich Laborchemikalien, Seelze, Germany.

The elaborated methods involve the aspiration and transfer of different combinations of so-called transfer volumes, air bubbles, special liquids and sample volumes.



Volumetric vessel

First the transfer tube is completely filled with water-free reagent from the titration vessel. Subsequently an air bubble (AB1), then a defined so-called transfer volume followed by another air bubble (AB2) is aspirated through the needle into the transfer tube. Afterwards a defined sample volume and another air bubble out of the sample headspace (volumetric: AB3, coulometric: AB4) is aspirated. For coulometric measurements, a special liquid, embedded between AB2 and an additional air bubble (AB3), is aspirated before the sample. After discharging the sample and parts of the transfer volume into the vessel, the titration starts.



Coulometric vessel

Method optimization

Method parameters such as number and size of the air bubbles between the different fluids as well as the speed of aspiration and transfer of fluids are crucial for the present water determination in oils and have to be determined in preliminary tests.

Technique	Volumetric KFT	Coulometric KFT	
Sample	Water standards	Water standards	Edible oils
Aspiration sequence	AB1 (0.05 mL) Transfer volume AB2 (0.02 mL) – – Sample Volume AB3	AB1 (0.05 mL) Transfer volume AB2 (0.05 mL) Special liquid AB3 (0.05 mL) Sample volume AB4 (0.05 mL)	AB1 (0.05 mL) Transfer volume AB2 (0.05 mL) Special liquid AB3 (0.05 mL) Sample volume AB4 (0.05 mL)
Aspiration and transfer speed	5 mL/min	2 mL/min	1 mL/min
Transfer volume	3 × sample volume	3 × sample volume	10 mL (complete tube volume)
Sample volume	0.5 mL	1 or 2 mL*	0.5…4 mL
Special liquid	–	0.05 mL methanol	0.1 mL hexane

*1 mL for Hydranal water standard 1.00 and 2 mL for Hydranal water standard 0.1, respectively.

- The edible oils have small water contents (79…690 µg/g) and are therefore analyzed by the coulometric technique.
- Only coulometric KFT requires the aspiration of a special liquid. The latter helps to rinse the complete sample amount into the titration vessel.
- The higher the viscosity (and the lower the water content) of the sample, the lower the aspiration and the transfer speed should be.

Recovery rates

Recovery rates for volumetric and coulometric KFT were determined by means of water standards. They refer to the manually determined water content.

Recovery rates [%][1]	Measurement		
	1	2	3
Volumetric KFT Water Std 5.00[2]	100.2 ± 0.5	99.4 ± 0.4	99.7 ± 0.6
Coulometric KFT Water Std 1.00[3]	99.0 ± 0.2	98.7 ± 0.3	99.7 ± 0.2
Coulometric KFT Water Std 0.10[4]	98.6 ± 1.0	98.7 ± 1.2	99.0 ± 1.6

[1]mean of six determinations, [2]5.0 mg/mL, [3]1.0 mg/g, [4]0.1 mg/g

Water content in edible oils

For every oil two sequences of measurements (n = 6) were carried out using different sample volumes.

Sample		Manual KFT (= KFT_{Manual})	Automated KFT (= $KFT_{Automated}$)	$\frac{KFT_{Automated}}{KFT_{Manual}} \times 100$
Edible oil	Volume [mL]	Water content [µg/g]	Water content [µg/g]	[%]
Soy bean oil	3.0	79.2 ± 1.5	102.5 ± 1.5	129.5 ± 1.8
Soy bean oil	4.0	79.2 ± 1.5	97.5 ± 2.9	123.2 ± 3.7
Sun flower oil	3.0	194.0 ± 8.2	202.1 ± 3.5	104.2 ± 1.8
Sun flower oil	4.0	194.0 ± 8.2	200.7 ± 6.1	103.5 ± 3.1
Olive oil	2.0	207.3 ± 3.2	210.2 ± 1.1	101.4 ± 0.6
Olive oil	3.0	207.3 ± 3.2	211.7 ± 4.9	102.1 ± 2.4
Rapeseed oil	1.0	435.0 ± 1.7	425.6 ± 6.7	97.8 ± 1.5
Rapeseed oil	2.0	435.0 ± 1.7	430.6 ± 6.3	99.0 ± 1.4
Sesame oil	1.0	534.7 ± 3.8	538.2 ± 6.1	100.6 ± 1.1
Sesame oil	2.0	534.7 ± 3.8	537.2 ± 1.5	100.5 ± 0.3
Pumpkin seed oil	0.5	684.3 ± 2.1	689.0 ± 32.1	100.7 ± 4.7
Pumpkin seed oil	1.0	684.3 ± 2.1	681.8 ± 11.0	99.6 ± 1.6

The ratio (100 × $KFT_{Automated}/KFT_{Manual}$) found for sun flower, olive, rapeseed, sesame and pumpkin seed oil was between 97 and 105%. For soy bean oil the automated KFT yielded higher results than the manual KFT (123…130%). These differences can be attributed to the very low water content in the soy bean oil (79.2 µg/g), which in this application corresponds to the detection limit.

Download a copy of this poster from http://www.metrohm.com/com/Applications (search for 8.000.6079EN).

[1] University of Hohenheim, Inst. for Food Science and Biotechnology, D-70593 Stuttgart/Germany
[2] Metrohm AG, CH-9101 Herisau/Switzerland, res@metrohm.com, phone +41 71 353 86 64
[3] Deutsche Metrohm GmbH & Co. KG, D-70794 Filderstadt/Germany