Water determination in oils with low water content (with oven)

Description

This application describes the determination of water in oils that contain very little water. This method is also suitable for oils that cannot be titrated directly due to the additives they contain.
The carrier gas can be either air or an inert gas (e.g. nitrogen). For oxygen - sensitive samples an inert gas should be used.
The background drift of the complete system is determined with the 0-Vial.
The blank value, the water content of an empty vial, must be determined for accurate results. Depending on the humidity, the blank value of the 5ml - vials is approx. 40µg to over 100µg!
For oils with very low water contents, the volume of the sample must also be taken into account: The amount of water in the air in the vial is sometimes higher than the amount of water contained in the same volume of oil! If the blank value of the empty vial is subtracted from the amount of water found during sample titration, one would obtain a negative water content.
Assuming that all the water found in the blank titration is contained in the air in the vial and is not adsorbed on the vessel wall, the blank value can be corrected for the volume displaced by the sample. For this purpose, the density of the sample must be known or the sample quantity must be measured by volume. For samples that have a small volume with a high water content, the volume of the sample can be neglected.

Devices

Titrator	TL 7500 KF trace M6
Oven	TO 7280
Generator elektrode	TZ 1752 (without diaphragm)
Elektrode	KF 1150
Vials	TZ 3988
Titration cell	TZ 1754

Reagents

1	Reagent for generator without diaphragm, suitable for use with oven
2	Molecular sieve, dried

Titration procedure

Reagents

Karl Fischer reagents are available as ready-to-use solutions.
The molecular sieve must be replaced regularly, at least every 4 weeks.

Cleaning and handling the KF 1100 electrode

The KF 1100 electrode does not require any special treatment.
The two platinum pins must not touch each other. For cleaning, Isopropanol or other solvents that do not attack glass and platinum are suitable.

Cleaning and handling the generator electrode

The TZ 1752 electrode does not require any special treatment.
The platinum sieve must not be mechanically stressed or bent. For cleaning, Isopropanol or other solvents that do not attack glass and platinum are suitable.

Preparation of the titration cell

The titration cell is filled with approx. 140 ml KF reagent and the titrator is switched on. A method with headspace oven is selected or the oven control is activated. The cell is automatically titrated dry and is ready when the drift is constantly below 15µg/min.

Preparation of the vials

The vials and crimp caps should be in equilibrium with the laboratory air. Especially different temperatures between vial and laboratory air lead to wrong or strongly fluctuating blank values. Previous drying in a drying oven or breathing air in the vial also lead to strongly fluctuating blank values! It is best to place vials and crimp caps a few hours before starting work where the sample will be weighed into the vial (i.e. next to the balance).
The vials for the blank value must be treated exactly in the same way as the vials for the sample and also closed at the same time if possible.
Another empty vial is closed and used as a 0-vial.
To correct the blank value, the total volume of the vials used is required. This can be determined, for example, by weighing with water. The volume of the 5 ml vials is approx. 7.8 ml.

The correct temperature

The correct oven temperature depends strongly on the sample. The temperature must be high enough to quickly release all the water from the sample. However, it must not be too high that the sample decomposes. For most oils, a temperature of about 100 - 120°C is suitable.

Background drift

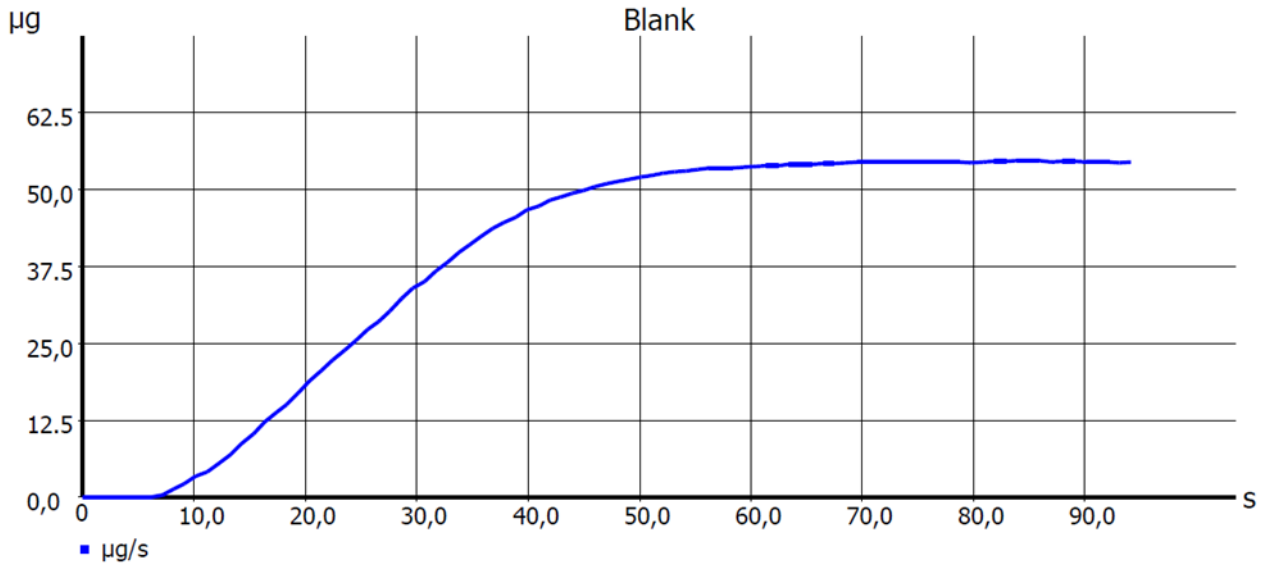
The 0-vial is placed in the oven and the method is started. The gas supply is set to approx. 0.1 L/min on the flowmeter. The background drift is now determined. The sample method can be started as soon as all start criteria (temperature, start drift, Δ) are fulfilled.
It is sufficient to determine the background drift at the beginning of a measurement series using the same method.

Blank value

The blank value should be carried out at least as a 3-fold determination. For the blank value, the same titration parameters must be used as for the sample titration.

The empty vials are closed with the crimp cap. The vials for the blank value must be handled in the same way as the vials for the sample and must also be closed at the same time if possible. It is best to close vials with sample and vials for the blank value alternately.

Titration parameter Blank value



Default method	With Headspace Blank
Method typ	Automatic Titration
Mode	Coulometrie
Start Drift	15
Start Drift Tolerance	0,3 µg/min
Start Drift Tolerance Intervall	20 s
Stop Drift Delta	5
Stop Drift Tolerance	0,02
Min. titration time	90 s
Max. titration time	1200 s
Endpoint delay	5 s
Working point	300 mV
Control faktor	4
Oven	
Oven temperature	110°C*
Oven temperature Delta	0,5 °C
Gas supply	Pump
Automatic fan control	on
0-Vial Interval**	Never
0-Vial on Method change**	yes

*or another suitable temperature **only with TitriSoft

Calculation:

$$B\ [\mu g] = \mu g \quad \rightarrow \text{M01}$$

µg		Absolute Water content in µg

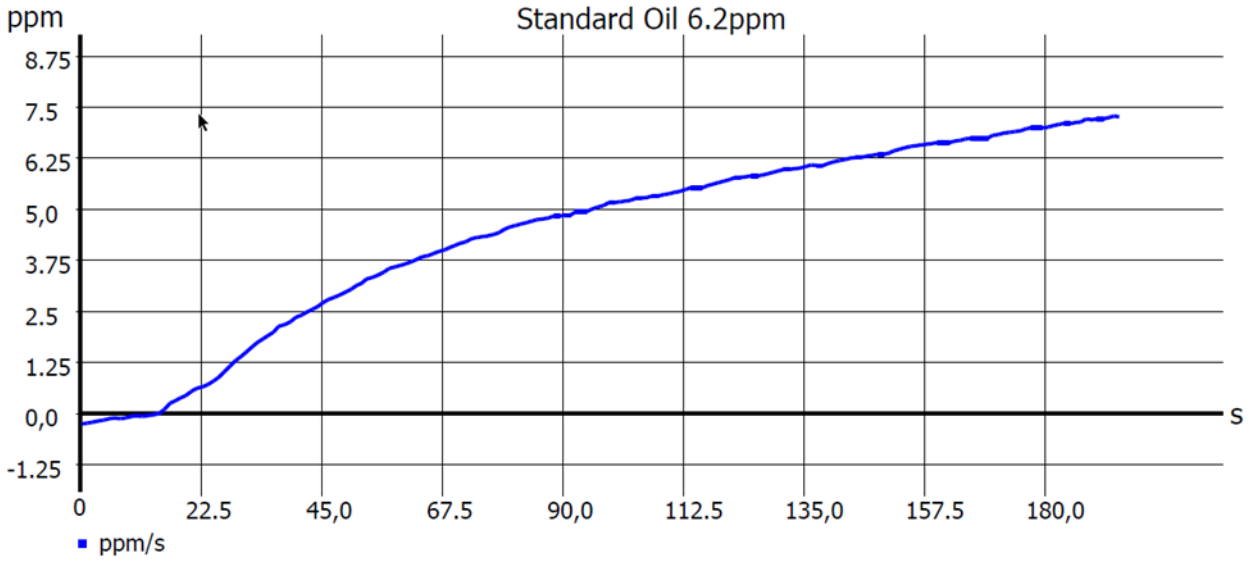
The determination of the blank value should be carried out at least as a 3-fold determination and the mean value calculated. The blank value is stored in a global memory.

Sample preparation

Syringes of the pipettes with which the sample is transferred are rinsed with a small amount of sample directly before use. This prevents the result from being falsified by water adsorbed on the syringe surface and conditions the syringe.

The sample is weighed into a vial and the vial is closed with the crimp cap. The volume of the sample should be approx. 4 - 4.5 ml so that the oven-needle is immersed in the sample - the gas bubbles mix the sample well and the water is expelled quickly.

Titration parameter



Default method	With Headspace Blank
Method typ	Automatic Titration
Mode	Coulometrie
Start Drift	15
Start Drift Tolerance	0,3 µg/min
Start Drift Tolerance Intervall	20 s
Stop Drift Delta	5
Stop Drift Tolerance	0,02
Min. titration time	900 s
Max. titration time	1200 s
Endpoint delay	5 s
Working point	300 mV
Control faktor	4
Oven	
Oven temperature	150°C*
Oven temperature Delta	0,5 °C
Gas supply	Pump
Automatic fan control	on
0-Vial Interval**	Never
0-Vial on Method change**	yes

*or another suitable temperature **only with TitriSoft

The gas flow should be approx. 0.1 L/min.

Calculation:
The blank value corrected by the sample volume can be calculated as follows:

$$corrected\ Blank = \left(F3 - \frac{W}{F4}\right) * \frac{B}{F3}$$

B	M01	Blank value in µg, stored in global memory M01
W	man	Water content in µg
F3		Volume of the vial [cm³]
F4		Density of the sample [g/cm³]

Calculation considering the sample volume, with blank value correction:

$$Wasser\ [ppm] = \frac{\left(\mu g - \left(F3 - \frac{W}{F4}\right) * \frac{B}{F3}\right) * M * F1}{W * F2}$$

B	M01	Blank value in µg, stored in global memory M01
µg		Water content in µg
M	1	Molekular weight
W	man	Sample amount [g]
F1	1	Conversion factor 1
F2	1	Conversion factor 2
F3		Volume of the vial [cm³]
F4		Density of the sample [g/cm³]

The result is calculated as ppm water. If the result should be calculated in other units, F1 must be adjusted.

Hint:
The oven system should be checked regularly by titration of a suitable standard. Suitable standards are e.g. lactose standards with approx. 5% water used at 150 - 160°C. The recovery should be 100 ± 5 % and the standard deviation (RSD) <1.5 %.

Any questions? Please contact the application team:

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