EXPERTS IN ANALYSiS



aqua 40.00

AQUA 40.00 Vario/Vario PLUS

Application

Water determination in oils and pasty substances

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Application

Water determination in oils, solids, and pasty substances by using the device AQUA 40.00 Vario of ECH.
Different kind of oil samples with different viscosities, additives, water concentration ranges - Diesel, Biodiesel, hydraulic fluids, insulating fluid, lubricant additives, engine lubricants, In-service lubricants turbine oils, white mineral oil, gear grease can be analyzed with one method in one analyzer (figure1).



Fig. 1: Different kind of oil samples - waiting for measurement of water content

Introduction

Today, the Karl Fischer titration is one of the most important methods of water determination. Most of the commercial or routine laboratories as well as modern industry standards cannot be thought without it. At universities and technical colleges, the principle of the Karl Fischer titration is still included in the curriculum, and often forms the object of dissertations and practical training.

What is the secret of this titration method that was first introduced under the title ”New Method for Volumetric Determination of the Water Content in Liquid and Solid Materials” by Karl Fischer 1935. It was a brilliant idea to convert water, iodine and sulphur dioxide according to the Bunsen reaction:

$$2\ H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2\ HI$$

A look at the early publications on the Karl Fischer titration, however, is rather disillusioning. None of the basic demands on volumetric titration /1/ were met sufficiently:

Firstly, the chemical reaction, on which the titration is based, was neither fast nor precise.

Secondly, the stoichiometry of the reaction equation had not been known by this time. It was said to vary between 1:1 and 1:2 and was adapted by the daily titer adjustment with a water standard.

Thirdly, because of the slow reaction and (at that time) visual indication, the end point of titration could not be determined exactly.

Step by step, these problems were solved. The works of Smith, Bryant and Mitchell /2/, Cedergren /3/ and Verhoef and Barendrecht /4/ offered first explications for the reaction mechanism. An essential contribution was made by Scholz /5/ who successfully modified the Karl Fischer reagent in order to guarantee an accurate, fast and quantitative titration.

At the same time, the development of titration instruments made fast progress. The electrochemical indication allows a reliable recognition of the end point of the Karl Fischer titration.

Finally, the rapid development of instruments controlled by microprocessors brought the real breakthrough.

Two methods of titrator dosing proved to be useful:

1. The volumetric dosing of a methanolic iodine solution into the Karl Fischer reagent

2. The coulometric generation of iodine by electrochemical means directly in the Karl Fischer reagent

Principle of the coulometric titration

The coulometric titration /6/ is based on the electrochemical generation of the iodine needed for the determination. The following reactions are performed at the electrodes:

generator electrode anode: $2\ I^- \rightarrow I_2 + 2\ e^-$
auxiliary electrode cathode: $2\ H^+ + 2\ e^- \rightarrow H_2$

According to the Faraday Law: $Q = I \cdot t = m/M \cdot z \cdot F$

Q	- charge
I	- titration current
T	- time
M	- mass of converted water
M	- molar mass of water
z	- stoichiometric valence
F	- Faraday constant

The amount of electrochemically produced iodine can be calculated from the electrical charge input. According to the Karl Fischer reaction equation, the amount of converted water can then be determined. There is no need for any titer adjustment.

Important is the use of 100 % of the electric current. Therefore the electrodes are of specific shape and position, for example the anode has a large surface whereas the cathode consists of a thin platinum wire only.

Indication of the titration end point is performed electrochemically by means of two thin platinum electrodes.

Even smallest charges can be precisely “dosed” by coulometric titration. Therefore, the coulometric method of the Karl Fischer applications is especially suitable for trace analysis. The handling of the Karl Fischer reagent is much simpler, too.

Practical performance of the coulometric analysis

1. Direct dosing into the measuring cell

Through a septum, liquids are injected into the measuring cell. This method is only to be applied if all disturbing side reactions can be excluded. In order to obtain reliable trace analysis results, an intact septum is needed to prevent the penetration of humidity. Overall glass cells are recommended. As experiences have shown plastic tops are not completely impermeable to humidity /7/.

Like for the volumetric Karl Fischer titration, special reagents have been developed for coulometry, e. g. for water determination in aldehydes and ketones.

For solid and liquid substances non-soluble in the Karl Fischer reagent, the direct dosing method is only partially suitable. The preceding extraction of water by a suitable solvent (e. g., methanol or dioxan) is therefore advisable, but more laborious. In some cases, other methods of sample treatment (e. g., homogenization or titration at low or high temperatures) may lead to an improvement of the titration rate and analysis precision. It should be considered, however, that any additional sample treatment increases the probability of measurement errors, especially within the ppm range.

In figure 2 below, one disadvantage of direct dosing of oils in the measurement cell is shown. Oils are soluble in the solvent of cell particularly, only. In case of use additional solvers, the capacity can be increased in a limited range. The reagent is to exchange very often. Side reactions and precipitations on the electrodes are possible.



Fig. 2: Contamination of the measuring cell by the direct dosing of crude oil

2. Sample heating at high temperatures

The heating technique is an elegant and universal tool for selective water determination in solids, pasty substances and oils.

The sample to be analysed is dosed into a separate oven. At high temperatures, the water is drawn from the sample. A dried carrier gas stream leads the water to the coulometric measuring cell. Reliable analysis results in the ppm range require a carefully dried carrier gas current /7/. Often the labs use nitrogen or dried air for the transfer process. This requires additional equipment and a permanent care.
A carrier gas circulation, as realized in the AQUA 40.00 by the ECH Elektrochemie Halle GmbH, is therefore very convenient. The gas is pumped off from the measuring cell and led through the heating oven. There it is enriched with the water from the sample and finally transfers back to the measuring cell (figure 3).

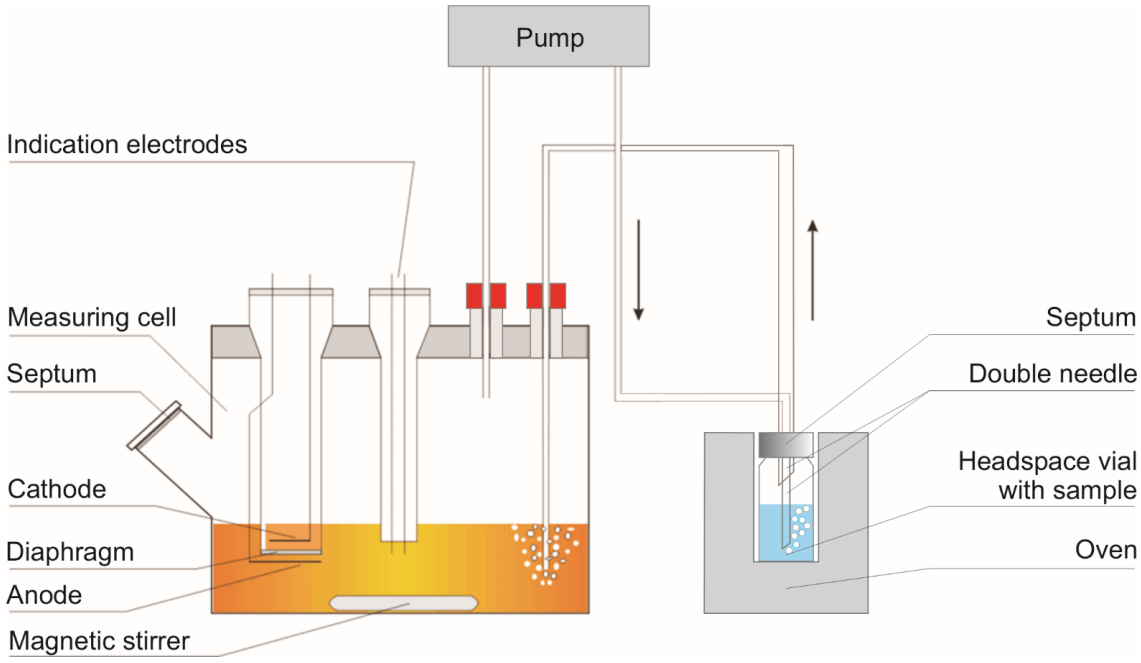


Fig. 3: Principle of the coulometric Karl Fischer titration with gas circulation in a closed loop without external carrier gas

The circulation system makes a separate gas drying redundant. The system has also the advantage that no methanol from the Karl Fischer reagent evaporates in the lab. As the desorbed water is led to the Karl Fischer reagent and undergoes titration immediately, the heating process can be checked at any time.

Additionally to operation at constant temperature, the sample can also be heated by a temperature ramp. The heating rate can be programmed in a range from 0.1 to 10 °K/min. The automatic heating by temperature gradient offers new ways for interpretation and evaluation of the measurement results. The Karl Fischer titration can therefore be used as a tool for determination of substance specific properties /8-11/.

The following examples will demonstrate that modern heating techniques, combined with fast and reliable coulometric titration, can be used for technical oil products as one of the most popular application. The oils are easy measurable with the AQUA 40.00 Vario with oven technique in a convenient and accurate way.

Examples of analysis

1. Water determination in crude oil

The determination of water in natural crude oil is one of the important parameters in the subsequent process of petroleum production.
The dosing of the viscous oils is able by a syringe without needle. The dosing in the hermetic closed titration cell requires needles for piercing a septum. This is not the best way. The dosing in a glass vial and weighing the amount is an easy procedure. The vial is to close by a septum cap immediately. By this, the ambient humidity cannot influence the water content of the sample in this closed glass vial.
The titrator is equipped with the compact oven unit and the titration coulometer (figure 4). It is expandable with an autosampler for 50 sample vials, when the sample numbers increase meanwhile.



Fig. 4: Heating oven (manual version with sample vial and the gas circulation)

The titration time is insignificantly larger, the advantage of clean and correct titration is more important by using the oven technique. The measurement duration is 1 – 5 min (figure 5).
One titration cell filling (100 ml) can be used for > 200 samples. Using direct doing, the reagent is to exchange after 5-10 measurements for such complex mixtures.

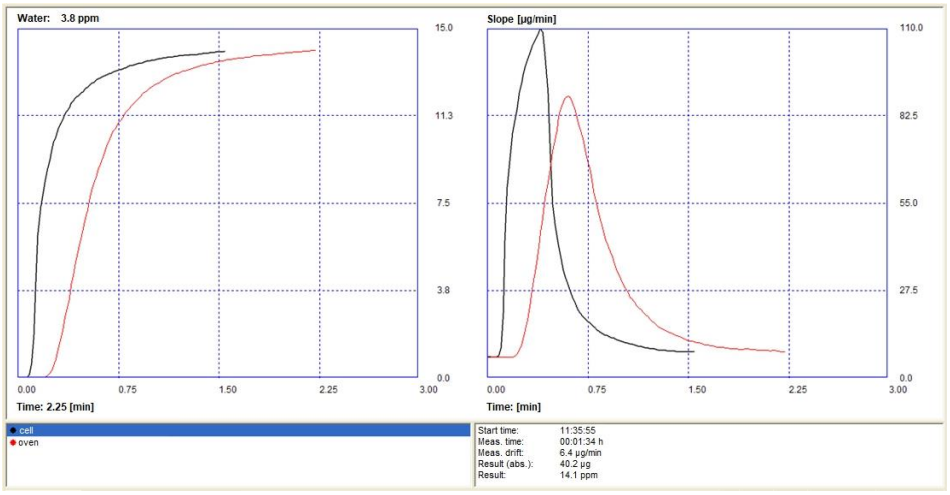


Fig. 5: titration curves of water determination of oil sample: black line: Injected directly into measuring cell, red line: heating procedure

Some results of a big measurement series of different determination methods for water in the crude oil are presented in table 1.
The comparison with classical standard methods shows strong correlation.
Some differences are to see, especially the distillation method is more inaccurate.

Tab.1: Water determination in crude oil with different methods

Crude oil sample ID	ASTM 4006 / ISO 3733 (Xylol distillation)	ASTM D6403 / DIN 51777 KF Headspace oven (indirect method)	ASTM D6403 / ASTM D4928 / DIN 51777 Cell measurement (direct method)
	Vol.-%	mg/kg	mg/kg
111711	0.15	901	937.1
111753	0.05	787	844.1
111803	0.1	739	766.0
111831	<0.1	885	932.0
111848	0.1	1011	1043.0
111956	<0.1	2071	2006.0
111977	0.1	2043	1932.0
112127	0.1	1538	1516.0
112153	0.1	2538	2487.0
112211	0.1	2345	2286.0
112312	0.1	2460	2421.0
112448	0.15	2231	2174.0
112596	0.1	1785	1754.0
112648	0.1	2040	2038.0
112657	0.1	2178	1938.0
112684	0.1	680	684.0
112701	0.1	1599	1471.0
112780	<0.1	2327	2177.0
112811	<0.1	2176	1975.0
112116	0.15	3954	3678.0

The diagram in figure 6 clarifies the high comparability.

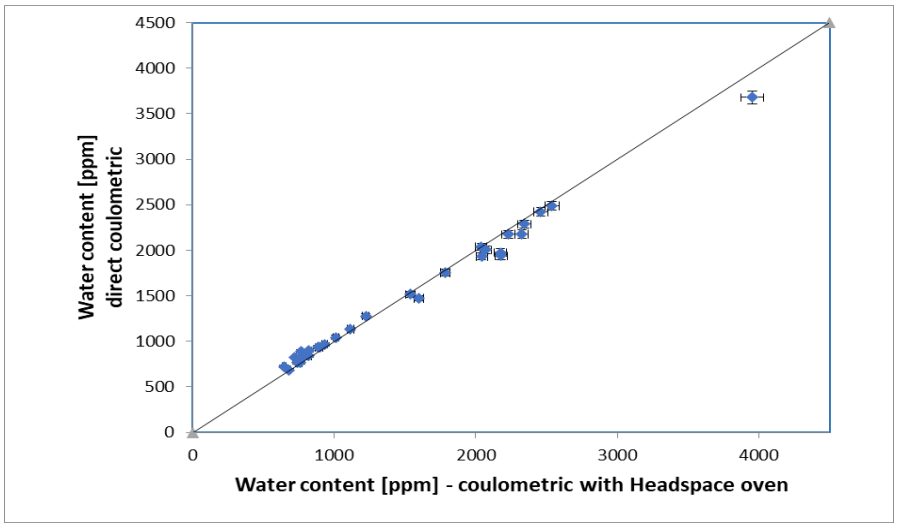




Fig. 6: Diagram of the correlation of water determination in crude oil by oven method and direct dosing

The homogeneity of the oil sample is important for right results. In crude oil samples, this aspect is so much more relevant because of the higher water content, which is not complete soluble in the oil. In table 2 the effect of storage with partially separation of the water is illustrated.
The gas tight sample bottles are very helpful for a good storage.

Tab 2.: Water determination in crude oil samples after longer storage times

Crude oil sample	Measurement after storage days	Water content (ppm)
110272	2	1116
	27	1133
	46	1100
	123	1125
112312	2	2460
	123	without shaking 1567
	123	with shaking 2421

2. Water determination in different oils

The water content in highly viscous liquids such as transformer oils, switch oils or hydraulic fluids can be conveniently determined by the coulometric Karl Fischer titration in combination with headspace techniques. Short determination times at high selectivity are obtained. Table 3 shows some analysis examples:

Tab.3: Water determination in different oils (reproducibility, sample amount, recommended temperatures)

Sample [ml]	Dosing volume [ml]	Water content [ppm]	Measurement time [min]	Heating temperature [°C]
Transformer oil 1 Transformer oil 2	2 - 5	9.5 ± 0.4 12.2 ± 0.5	3 - 4	120
Compressor oil	2 – 5	34.4 ± 0.7	3 - 4	120
Lubricating oil 1 Lubricating oil 2	2 - 5	23.9 ± 0.5 52.1 ± 1.0	3 - 4	120
Silicone oil 1 Silicone oil 2	1 - 2	204 ± 4 308 ± 2	4 - 8	70
Used oil	0.5 - 1	641 ± 10	8 - 10	120
Hydraulic oil	0.5 - 1	1415 ± 9	6 - 8	100
Engine oil (used)	0.5 - 1	1826 ± 9	8 - 12	120
Linseed oil	1 - 2	856 ± 3	7 - 10	60

For determination of the water content in suspensions, the temperature-controlled heating opens up interesting possibilities. The temperature-controlled heating graph of a silicone oil suspension (figure. 7) shows that free water is desorbed at lower temperatures than bonded water. The measurement graph illustrates the gradual water desorption.

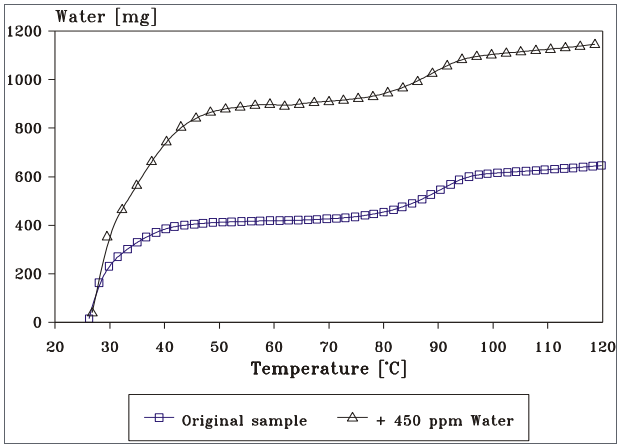


Fig. 7: Water determination in silicone oil suspension: temperature-controlled heating: 3 K/min, dosing quantity: 900 mg

The Karl Fischer titration is also suitable for characterization of switch oils. Switch processes in oils are accompanied by electric spark discharge. This leads to decomposition of the switch oil and finally produces carbon black. This substance adsorbs degradation products like water, thereby increasing conductivity. By using the temperature-controlled heating it can be distinguished between water in the oil phase and water adsorbed by carbon black. (figure 8)

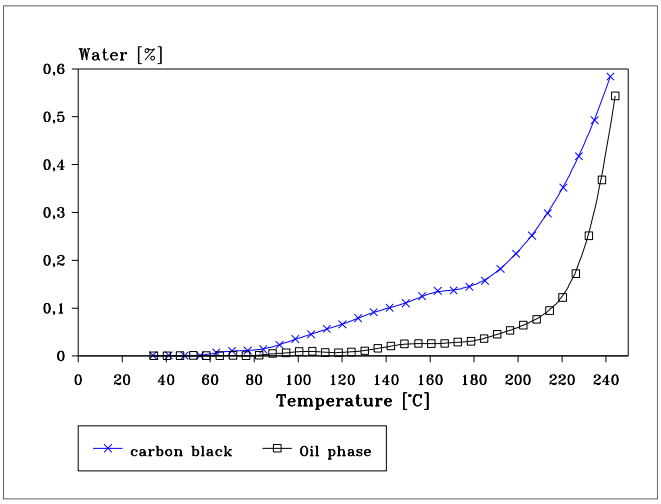


Fig. 8: Water determination in switch oils containing carbon black, temperature-controlled heating: 2 K/min

3. Water determination in tar-containing sludges

Experience has shown that determination of the water content in tar-containing sludges by the traditional Karl Fischermethod is rather problematic. Determination by direct sample dosing into the reagent does not produce reproducible results. This is due to scales on the electrodes and in the measuring cell, further to side reactions under either iodine production or consumption. Another great problem is the precise dosing of highly viscous sludges into the measuring cell (e.g., handling of injectors etc.) During the dosing process humidity can enter the measuring cell leading to wrong results.

Therefore, an indirect method by heating proves to be more convenient.

Figure 9 shows the heating graphs for different sludges. Up to a temperature of 120 °C free water is desorbed at different desorption rates, indicating different bond strengths in the sludges. Above 140 °C the thermal elimination of water from the organic matrix starts to set in. Using controlled heating technique, the temperature optimum for water determination can be easily worked out. For the examined sludges, it is at approx. 120 °C.

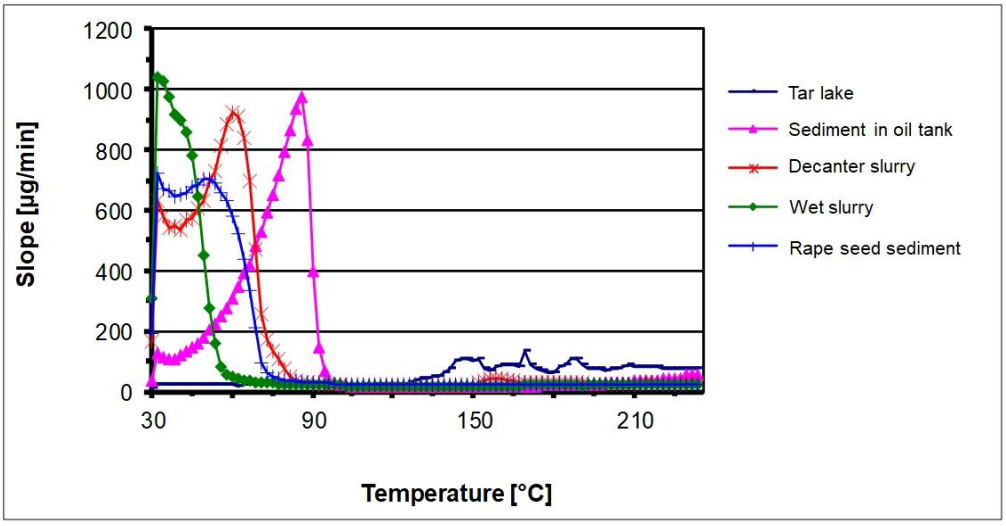


Fig. 9: Temperature-controlled heating of different tar-containing sludges

The headspace module of the AQUA40.00 Vario is equipped with a change mechanism for different vial sizes. By interchanging of the oven and sample plate of the autosampler, the system can quickly and comfortably be adapted to different sizes of sample vials (figure 10). Sample vials in a range of 2 ml up to 50 ml are available.



Fig. 10: For different vial sizes: sample rack and oven unit easy interchangeably

Technical specifications

Unit	Basic module	Headspace oven with autosampler
Dimensions:	Width: 111 mm Height: 446 mm Depth: 187 mm	Width: 400 mm Height: 446 mm Depth: 920 mm
Weight:	8 kg	16.5 kg
Mains voltage:	Mains voltage: 110 - 240 V Frequency: 50 - 60 Hz Power consumption: 100 W Fuse: 1.6 A	Mains voltage: 24 V DC Power consumption: 280 W Incl. External power supply Input Mains voltage: 110 - 240 V Current: 2.5 – 1.3 A Frequency: 50 - 60 Hz Output Mains voltage: 24 V DC Current: 9.2 A Power consumption: 221 W max.
Sample dosing:	0.1-5 ml	Headspace vials (size 2 R – 50 R)
Measuring range:	1 µg - 100 mg, absolute	10 µg - 100 mg, absolute
Reproducibility:	± 3 µg for 10 … 1000 µg, 3 % for > 1 mg	± 5 µg for 10 … 1000 µg, 3 % for > 1 mg
Temperature range:	35 °C ... 300 °C (isothermal or temperature programmed)	35 °C ... 300 °C (isothermal or temperature programmed)
Resolution	0.1 µg	0.1 µg

Conclusion

The combination of computer-controlled Karl Fischer titration and heating technique offers an efficient method for water determination in grease, engine oils, crude oil, used oils, other highly viscous liquids. The headspace technique is the universal method for water determination in a wide range of kinds of samples. The isotherm heating process transfers the water vapor of the sample into the titration cell without contamination of the titration system. The unique closed gas circulation is easier, cheaper and healthier than the supply of external dry carrier gas.
Heating with temperature ramp allows differentiation between surface water, chemically bonded water and water produced during decomposition reactions.

By use of coulometric titration, reproducible and selective results are obtained. There is no need for calibration of the measurement system.

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