

## Sample Preparation & Processing

### Automated Karl Fischer titration - reliable water determination with no ifs and buts

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The determination of water content in the trace range, e.g. in insulating oils, mineral oils or gases, requires measuring methods that are capable of accurately and reproducibly determining moisture contents of less than 0.001%. Karl Fischer titration is an established method for determining the water content in liquid, solid and gaseous samples. The challenge is to minimise the permanent risk of excessive measured values due to humidity in the laboratory. The handling of the samples is often decisive for correct analysis results. If the results are not reproducible, fundamental questions quickly arise:

Was there perhaps still a moist sample residue on the dosing tip? How long did the weighing process take for this sample? Were the transfer lines and vessels absolutely leak proof? The automation of the analysis process offers a high degree of reliability here.

The Karl Fischer titrators developed by ECH Elektrochemie Halle GmbH are working efficiently and are high precise analysers for water content in a measuring range from 1 ppm to 100%. A high degree of automation ensures that even complex measurement procedures are clear and structured and easy to use. Through their modular design, the devices nevertheless remain flexible and are highly adaptable to a wide range of individual tasks. ECH devices are very easy to operate thanks to the clearly structured standardised device control software.

Measurements can be carried out stably and cost-effectively in the laboratory, on site or online, even under difficult conditions, directly without external gases, without sample preparation and without blank value determinations.

The coulometric variant of Karl Fischer titration offers essential advantages, as this absolute method requires practically no titre determination, which highly simplifies the analysis procedure. A coulometric method means that the iodine required for Karl Fischer titration is generated by electrolysis on platinum electrodes directly during the analysis. The continuous adjustment of the electrolysis current to the amount of water to be titrated means that the measuring range is very wide: The smallest amounts of water are detected with very high precision. Large quantities of water can also be titrated in a very short time.

ECH has now provided the coulometric Karl Fischer titration with various extensions, so that an automated solution is available for practically every application.

By combining coulometric titration with intelligent heating technology, it is possible to selectively separate the water from liquid, solid and viscous samples and transfer it to the titration cell with the internal carrier gas flow. The closed-loop principle of the extraction gas in the titrators of ECH Elektrochemie Halle GmbH realised for this purpose is unique (see Figure 1). The coupling of coulometric titration with this heating technique and with the circulated extraction gas results in a very robust process, as there is no need for an additional carrier gas, which is expensive to dry. At the same time, this prevents the release of toxic methanol, which increases work safety in the laboratory. As there is no evaporation of the methanol, the Karl Fischer reagent can be used to practically its full capacity. This saves costs for consumables and minimises operating costs.

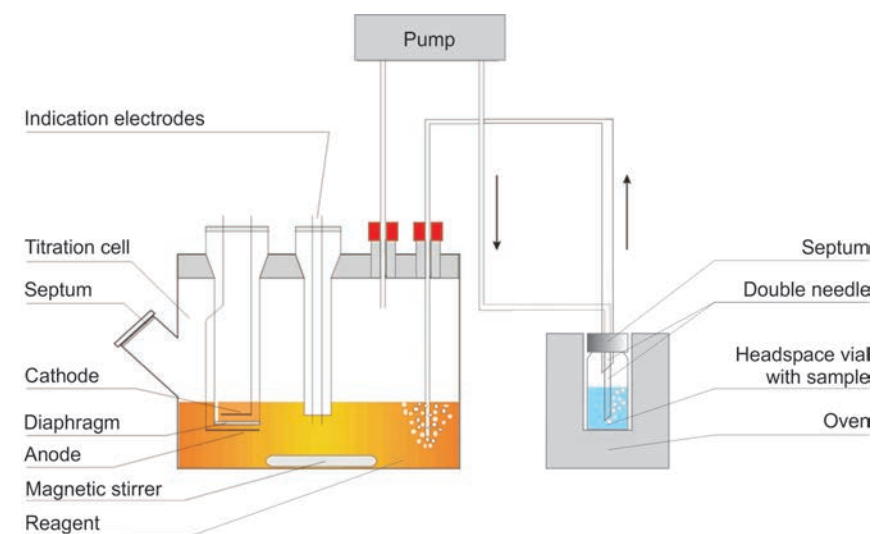


Figure 1: Principle of Karl Fischer titration in ECH measuring devices with unique closed-loop gas extraction.

These innovations from ECH Elektrochemie Halle GmbH provide the Karl Fischer titrators with unique advantages:

- significantly longer operating life for the Karl Fischer reagent
- avoidance of evaporation of methanol into the laboratory atmosphere
- traces of water measurable down to 1 ppm
- no costs and equipment required for carrier gases
- high robustness of the method even for complex applications
- fast operational readiness after measurement breaks

Taking automated sample feeds into account, the analysis of solids, oils and gases can be fully automated, which increases the sample throughput, and also enables fully automated online processes.

The following examples will demonstrate it.

#### 1. Automation of the analysis of solids and highly viscous samples

**AQUA 40.00 Vario** is combining coulometric Karl Fischer titration with headspace technique. For this purpose, the samples are weighed into vials (size 2 R to 50 R) and sealed airtight (see Figure 2). The vials are positioned in the headspace oven and heated. This vaporises the water from the samples. No additional sample preparation is required. The dry carrier gas flows over the sample and transports the extracted water to the titration cell for the subsequent coulometric Karl Fischer titration.

With the **AQUA 40.00 Vario PLUS**, the vials are not inserted into the headspace oven manually, but automatically via an autosampler, which significantly increases the efficiency of the measurement series and makes handling much easier (see Figure 3).

The **AQUA 40.00 Vario Plus** has a very compact design, with a small footprint.

The **SWOP Box PRO**, which is integrated into the analysis sequence, can be connected for automatic reagent change. This means that reagents can be changed automatically at any time if required.



Figure 2: AQUA 40.00 Vario PLUS for water determination in solids and highly viscous samples.

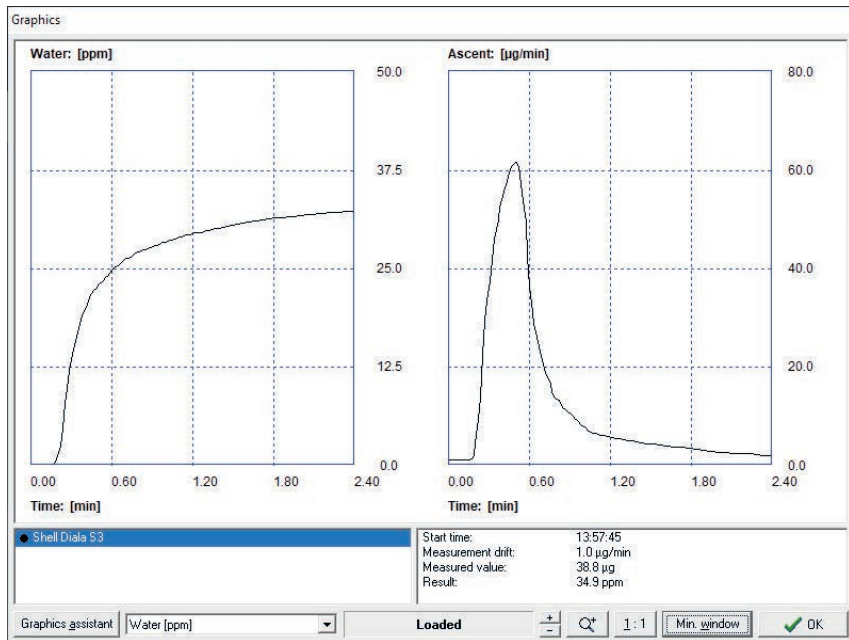


Figure 3: Measurement of a mineral oil sample with heating technique by using an oven.

## 2. Oil analysis with the highest degree of automation for use in the laboratory

The **Aquamax KF PRO Oil** was developed to determine the water content especially of oils and fuels. The **Aquamax KF PRO Oil Automatic** version includes an integrated autosampler that enables the processing of up to 200 samples using disposable dosing syringes. The implemented, miniaturised analytical balance in the device determines the exact sample weight during the analysis. This makes it easy to determine results in mass ppm for widely varying used oil mixtures with unknown density (see Figure 4). Due to its large capacity, this device is the ideal choice for laboratories that deal with a large number of samples. The reagent status in the titration cell is continuously monitored, a replacement is signalled if necessary and integrated into the process (see Figure 5).



Figure 4: Aquamax KF PRO Oil Automatic for automatic water determination in oils.

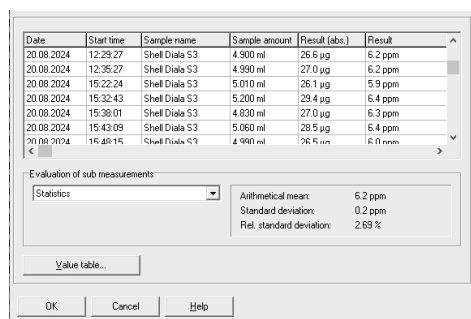


Figure 5: Example of multiple measurement with statistical evaluation of a transformer oil 'Shell Diala S3'.

## 3. Online application for oil analysis

The **Aquamax KF Online** was developed for the continuous online monitoring of water content in oil samples. The integrated pump module enables automated sampling directly from the pipeline in the production process. The sample is dosed into the integrated heating chamber of oils (see Figure 6). At a suitable temperature, the water is separated from the oil sample and transferred to the titration cell with the circulated carrier gas. The closed-loop gas circulation minimises reagent consumption considerably and ensures precise and reproducible results.

The Aquamax KF Online is a very robust and easy-to-use monitoring instrument in the petrochemical industry (see Figure 7).

## 4. Automated determination of water in gases

Special equipment is required for the determination of water content in pressurised gases and liquefied gases in order to transfer the gases to the titration cell in an unpressurised state without contamination. The combination of coulometric titration with gas dosing via switching valves can be used for the automated analysis of gases and liquefied gases (LPG - Liquefied Petroleum Gas, LNG - Liquefied Natural Gas) and is described as a procedure in the **ASTM D 7995-19** standard.

Based on the software-controlled gas dosing, the complex process, consisting of purging steps and multiple dosing steps of the sample, is fully automated. In addition, an integrated sulphur trap prevents side reactions caused by sulphides or hydrogen sulphide.



Figure 6: Aquamax KF Online for continuous online monitoring of water content in oil samples.

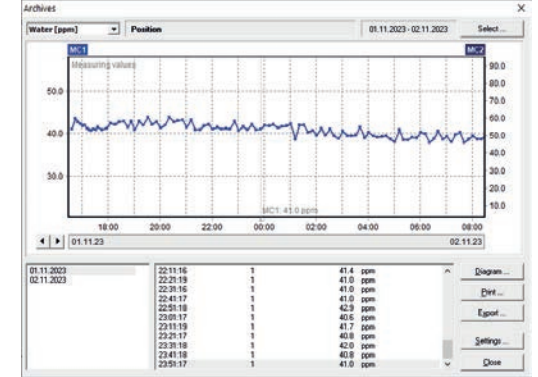


Figure 7: Overview of a continuous online measurement of the water content of a diesel pipeline (display in mass ppm - Measurement interval: 10 min, heating temperature 120 °C).

The **LPG Selection Box** module of the Karl Fischer Aquamax KF PRO LPG titrator fully automates the sample feed from several sample cylinders in the process (see Figure 8). 16 sample cylinders can be analysed in a continuous measurement series. The unique sample loop dosing principle allows up to 125 fully automated measurements per day and makes the device to a robust and safe system for laboratories in the chemical and petrochemical industries (see Figure 9).

## Diversity of application in practice

Automated Karl Fischer titrators from ECH are used in a wide range of industries.

As part of pharmaceutical analyses, they are used to analyse hygroscopic substances and freeze-dried products automatically.

In the petrochemical industry, they are used to determine the water content of oils, lubricants and fuels such as diesel, petrol or paraffin, where online measurements are often carried out to monitor the processes.

Karl Fischer titrators are used in the food industry and plastics production to determine the water content of powdery and viscous samples.

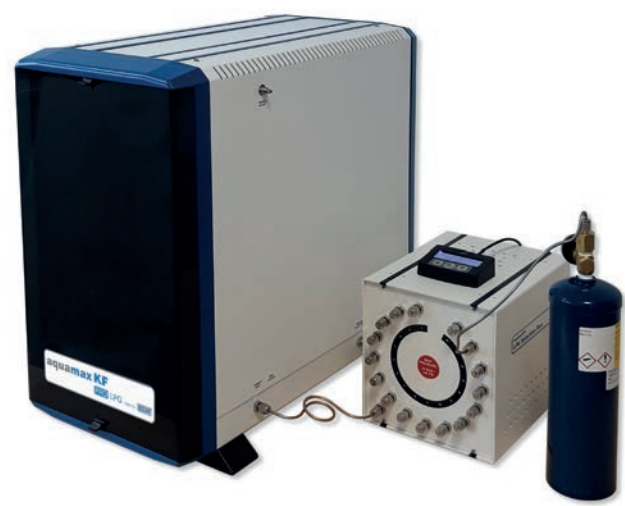


Figure 8: Aquamax KF PRO LPG with connected LPG Selection Box for the automated analysis of gases and liquefied gases (LPG, LNG).

Meas. no.	File name	Sample name	Dosing parameter	Sample amount	Measurement date	Measurement time	Result [abs.]	Result
1	2024070408	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	2602.679 ml	2.1 µg/min	00:05:26	147.89 µg	68.573 midppm
2.1	2024070409	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1714.177 ml	2.1 µg/min	00:05:12	71.67 µg (Mean), 0.04 µg (S)	55.762 midppm (Mean), 0.692 midppm (STD)
2.2	2024070409	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1717.347 ml	2.3 µg/min	00:05:13	71.48 µg	55.570 midppm
2.3	2024070409	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1717.007 ml	1.9 µg/min	00:05:13	71.35 µg	55.680 midppm
2.4	2024070409	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1715.458 ml	1.9 µg/min	00:05:12	70.27 µg	55.236 midppm
3	2024070410	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 4 POS: 4	2203.783 ml	1.5 µg/min	00:06:47	126.18 µg	74.283 midppm
3.1	2024070410	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 4 POS: 4	2202.462 ml	2.2 µg/min	00:06:48	54.50 µg	55.540 midppm
3.2	2024070410	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 4 POS: 4	2201.814 ml	2.3 µg/min	00:06:41	50.90 µg	53.233 midppm
3.3	2024070410	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 4 POS: 4	2202.240 ml	2.2 µg/min	00:06:42	89.65 µg	52.491 midppm
3.4	2024070410	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 4 POS: 4	2202.240 ml	2.2 µg/min	00:06:42	89.65 µg	52.491 midppm
4	2024070411	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1710.284 ml	2.1 µg/min	00:05:12	67.19 µg	52.400 midppm
4.1	2024070411	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1709.191 ml	1.7 µg/min	00:05:14	69.11 µg	53.964 midppm
4.2	2024070411	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1710.282 ml	1.9 µg/min	00:05:15	68.02 µg	53.967 midppm
4.3	2024070411	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1710.282 ml	1.9 µg/min	00:05:15	68.02 µg	53.967 midppm
4.4	2024070411	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1710.299 ml	1.9 µg/min	00:05:12	67.17 µg	52.434 midppm
4.5	2024070411	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1709.629 ml	1.9 µg/min	00:05:12	66.93 µg	52.208 midppm (Mean), 1.189 midppm (STD)
5	2024070412	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1711.851 ml	1.6 µg/min	00:05:12	67.90 µg	53.959 midppm
5.1	2024070412	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1712.652 ml	1.7 µg/min	00:05:22	68.24 µg	53.195 midppm
5.2	2024070412	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1712.643 ml	1.7 µg/min	00:05:12	67.26 µg	52.526 midppm
5.3	2024070412	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1712.643 ml	1.7 µg/min	00:05:12	67.26 µg	52.526 midppm
5.4	2024070412	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1711.514 ml	2.1 µg/min	00:05:13	65.50 µg	51.094 midppm
5.5	2024070412	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1709.691 ml	2.0 µg/min	00:05:11	64.04 µg	50.673 midppm
6	2024070413	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1713.214 ml	1.4 µg/min	00:05:16	66.27 µg (Mean), 1.33 µg (S)	51.660 midppm (Mean), 1.050 midppm (STD)
6.1	2024070413	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1711.118 ml	1.7 µg/min	00:05:12	67.03 µg	52.300 midppm
6.2	2024070413	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1712.320 ml	1.8 µg/min	00:05:12	65.29 µg	50.962 midppm
6.3	2024070413	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1711.451 ml	1.6 µg/min	00:05:11	66.74 µg	52.363 midppm
6.4	2024070413	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1714.207 ml	1.9 µg/min	00:05:12	64.48 µg	50.185 midppm
6.5	2024070413	49.96 ml ppm water in Nitrogen	LPG module QR - RI: 0:005; 3 POS: 4	1713.214 ml	1.4 µg/min	00:05:16	67.24 µg	52.760 midppm
7	2024070501	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1840.102 ml	1.6 µg/min	00:06:04	36.60 µg (Mean), 4.64 µg (S)	27.847 midppm (Mean), 3.267 midppm (STD)
8	2024070501	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1832.916 ml	1.2 µg/min	00:06:04	40.34 µg	26.902 midppm
8.1	2024070501	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1830.759 ml	1.1 µg/min	00:06:05	37.43 µg	26.888 midppm
8.2	2024070501	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1831.226 ml	1.0 µg/min	00:06:07	35.24 µg	25.264 midppm
8.3	2024070501	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1831.417 ml	1.1 µg/min	00:06:05	34.09 µg	24.444 midppm
8.4	2024070501	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1830.830 ml	1.0 µg/min	00:06:06	32.49 µg (Mean), 1.24 µg (S)	23.257 midppm (Mean), 0.900 midppm (STD)
8.5	2024070501	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1831.522 ml	0.9 µg/min	00:06:07	33.30 µg	23.916 midppm
9	2024070502	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1835.001 ml	0.9 µg/min	00:06:04	33.13 µg	23.709 midppm
9.1	2024070502	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1835.982 ml	1.0 µg/min	00:06:05	32.27 µg	23.154 midppm
9.2	2024070502	22.4 midppm water in propylene	LPG module QR - RI: 0:005; 4 POS: 2	1834.638 ml	1.1 µg/min	00:06:04	30.37 µg	21.738 midppm

Figure 9: Overview of various measurements of the water content in pressurised gases using the automated Aquamax KF PRO LPG with connected LPG Selection Box

## Sample Preparation & Processing

As part of trace analysis, they are used for the various materials of batteries of EV or in the finished products itself.

Automated measurements are very helpful when monitoring gases and liquefied gases such as LPG and LNG as well as corrosive gases such as hydrogen chloride (HCl) or ammonia (NH<sub>3</sub>).

In the field of research and development, ECH's Karl Fischer titrators with various temperature programmes enable the differentiation of adsorbed and chemically bound water.

### The benefits of ECH's automated Karl Fischer titrators

#### 1. Optimisation of the workflow and increase in efficiency

Automating Karl Fischer titration optimises the workflow in laboratories and industrial environments and have a lasting effect.

Automated systems significantly reduce the workload. The preparation of a large number of samples and the subsequent analysis can be carried out in a continuous process. The subsequent automated water content determination of the samples in series can be carried out without constant supervision, which increases efficiency and significantly reduces the time required.

#### 2. Precision and reproducibility

The reduction of human error sources, which can occur with manual methods, is a significant advantage of automated titration systems. ECH devices are automated throughout the entire process, resulting in a very high quality of analysis.

Even the water content of oils and gases down in the trace range to 1 ppm can be determined with the highest precision. The device software of the ECH titrators enables multiple measurements, which guarantees high reproducibility.

#### 3. Sustainability and cost control

The consumption of Karl Fischer reagents is significantly minimised through the closed gas circulation principle used in ECH-titrators. This can reduce reagent consumption and minimise operating costs, which is sustainable because less chemical waste is generated. In addition, working without external carrier gases saves further operating costs.

The condition of the reagent in the titration cell is continuously monitored and is always shown in the software.

Various criteria can be used to determine when the reagent needs to be replaced:

- capacity,
- period of use,
- number of measurements.

Statistical data on reagent consumption are also saved, such as the number of measurements performed, the time period in days and the total amount of titrated water.

With the additional **SWOP Box PRO** module (see *Figure 10*), the Karl Fischer reagent can be replaced automatically so that laboratory staff do not come into contact with toxic chemicals.

#### 4. Flexibility and safety

A wide variety of samples can be analysed with the ECH titrators. The automated analysis process is carrying out a quickly titration with maximum of precision. When analysing high-pressurised samples from industrial plants, automation guarantees an additional level of safety.

In sum, the automation of Karl Fischer titration represents a significant further development that raises both the efficiency and precision of water content determination in a wide variety of sample matrices to a new level. The combination of state-of-the-art technology, versatile application possibilities and sustainable solutions makes ECH devices such as the AQUA 40.00 Vario, the Aquamax KF Online, the Aquamax KF PRO LPG and the Aquamax KF PRO Oil indispensable equipment for laboratories and industrial users.

The Karl Fischer titrators from ECH Elektrochemie Halle GmbH offer a high degree of flexibility and versatility in terms of possible applications. Based on the modular extensions and the possibility of varying measurement methods, the devices can be easily adapted to different sample types and requirements.



Figure 10: Universal reagent change module SWOP Box.