

# Karl-Fischer-Titration

## in solids, pastuous substances and oils

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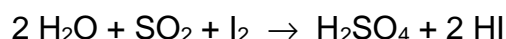
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### **1. Introduction**

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 can not 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:



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.

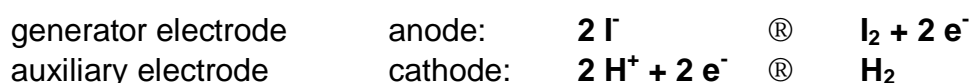
Finally, the rapid development of instruments controlled by micro processors brought the real breakthrough.

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

## **2. 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:



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-reagents is much simpler, too.

## **3. Practical Performance of the Coulometric Analysis**

### **3.1. 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. homogenisation 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.

### 3.2. Sample Heating at High Temperatures

The heating technique is an elegant and universal tool for selective water determination in solids, pastuous 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].

A carrier gas circulation, as realised 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 led back to the measuring cell.

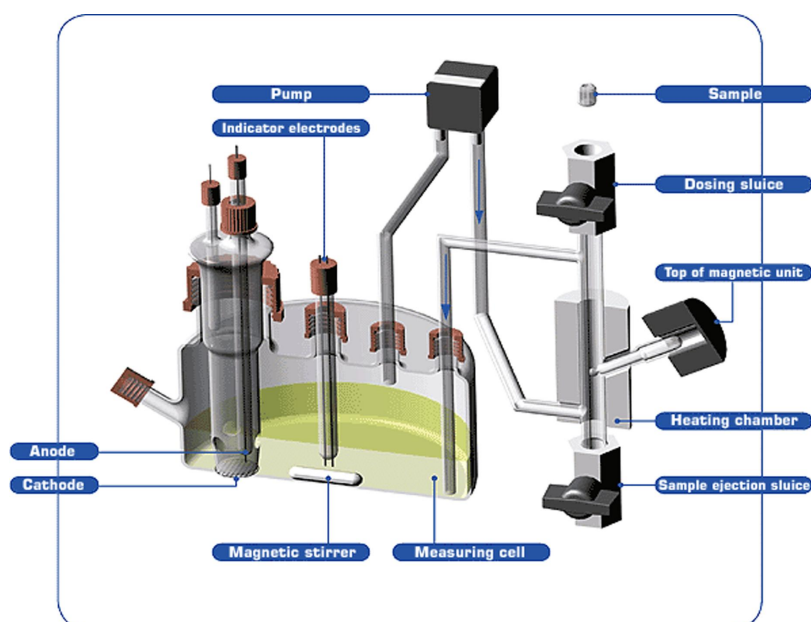


Fig.1: Principle of the coulometric Karl-Fischer-titration with gas circulation for solid and pastuous materials

The circulation system makes a separate gas drying redundant. The system has also the advantage that no methanol from the Karl-Fischer-reagent evaporates.

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 0,01 to 10 °C/min. The computer controlled 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 also be used to answer additional questions, such as bonding strength and origin of the water.

## 4. Analysis Examples

### 4.1. Water Determination in Inorganic Salts

The adsorptively bonded surface water can be regarded as important criterion for the flowability of inorganic salts.

At heating temperatures of > 120 °C, the water is fully desorbed (Fig. 2). The analysis times range between 3 and 6 minutes. The result list shows the high precision of the analysis (Fig. 3).

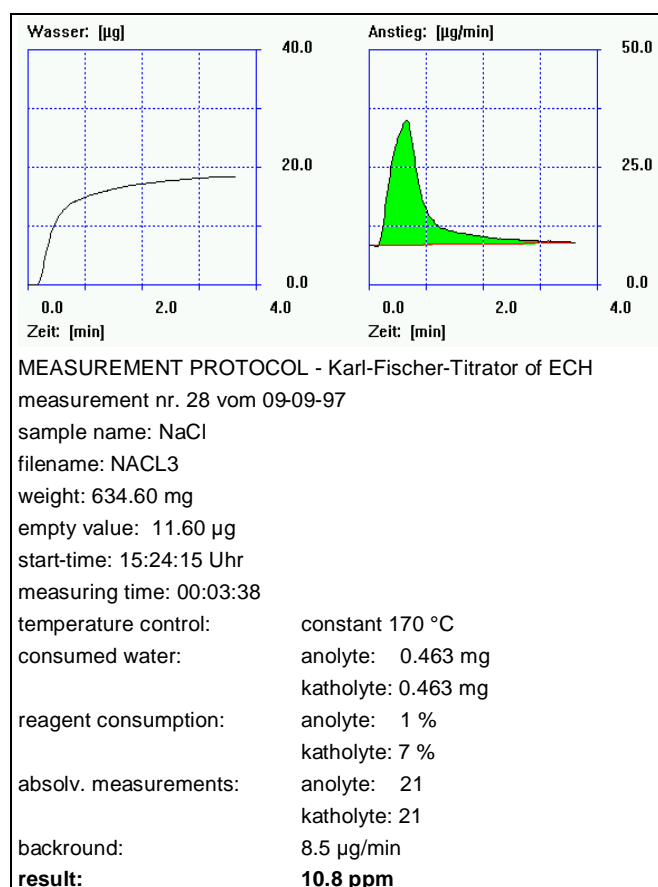


Fig. 2: protocol of the water determination in NaCl

Result list - Karl-Fischer-Titrator AQUA 30.00 of ECH							
Measurement	nr.	26	from	09.09.97,	time:	15:14	Uhr
sample name:	NaCl						
	<b>result: 9.5 ppm</b>						
Measurement	nr.	27	from	09.09.97,	time:	15:19	Uhr
sample name:	NaCl						
	<b>result: 10.3 ppm</b>						
Measurement	nr.	28	from	09.09.97,	time:	15:24	Uhr
sample name:	NaCl						
	<b>result: 10.8 ppm</b>						
Measurement	nr.	29	from	09.09.97,	time:	15:33	Uhr
sample name:	NaCl						
	<b>result: 12.7 ppm</b>						
Measurement	nr.	30	from	09.09.97,	time:	15:37	Uhr
sample name:	NaCl						
	<b>result: 9.4 ppm</b>						
Measurement	nr.	31	from	09.09.97,	time:	15:51	Uhr
sample name:	NaCl						
	<b>result: 10.2 ppm</b>						
-----							
Measurement	nr.	32	from	09.09.97,	time:	16:10	Uhr
sample name:	KBr						
	<b>result: 150.7 ppm</b>						
Measurement	nr.	33	from	09.09.97,	time:	16:21	Uhr
sample name:	KBr						
	<b>result: 147.3 ppm</b>						
Measurement	nr.	34	from	09.09.97,	time:	16:33	Uhr
sample name:	KBr						
	<b>result: 151.6 ppm</b>						
Measurement	nr.	35	from	09.09.97,	time:	16:44	Uhr
sample name:	KBr						
	<b>result: 146.5 ppm</b>						

Fig. 3: Result list of water determination in inorganic salts

## 4.2. Water Determination in Tar-containing Sludges

Experience has shown that determination of the water content in tar-containing sludges by the traditional Karl-Fischer-method 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.

Fig. 4 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.

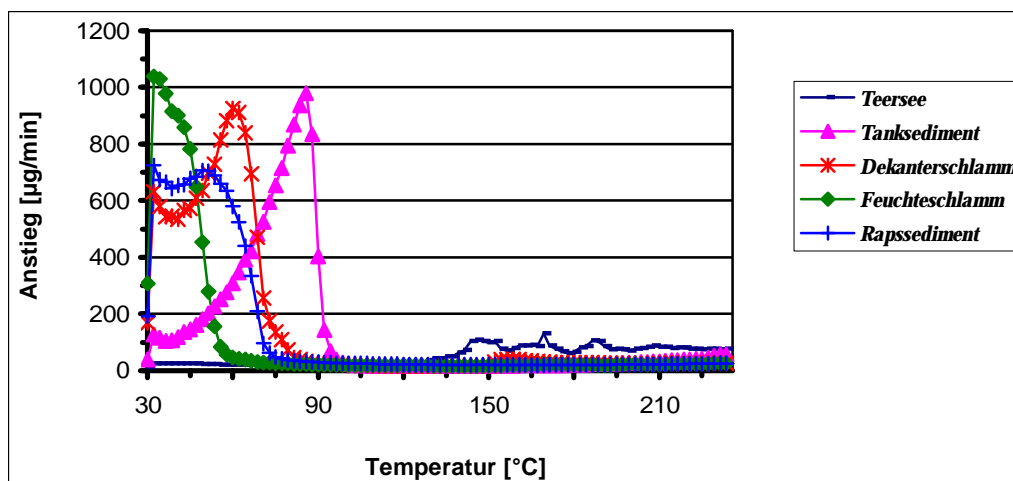


Fig. 4: Temperature-controlled heating of different tar-containing sludges

### 4.3 Water Determination in 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 heating techniques. Short determination times at high selectivity are obtained. Table 1 shows some analysis examples:

sample	dosing volume [ml]	water content [ppm]	measurement time [min]	heating temperature [°C]
transformer oil 1	2 - 5	9,5 +/- 0,4	3 - 4	120
transformer oil 2		12,2 +/- 0,5		
compressor oil	2 - 5	34,4 +/- 0,7	3 - 4	120
lubricating oil 1	2 - 5	23,9 +/- 0,5	3 - 4	120
lubricating oil 2		52,1 +/- 1,0		
silicone oil 1	1 - 2	204 +/- 4	4 - 8	70
silicone oil 2		308 +/- 2		
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

Tab.1: Water determination in different oils

For determination of the water content in suspensions, the temperature-controlled heating opens up interesting possibilities. The temperature-controlled heating graph of an silicone oil suspension (Fig. 5) shows that free water is desorbed at lower temperatures than bonded water. The measurement graph illustrates the gradual water desorption.

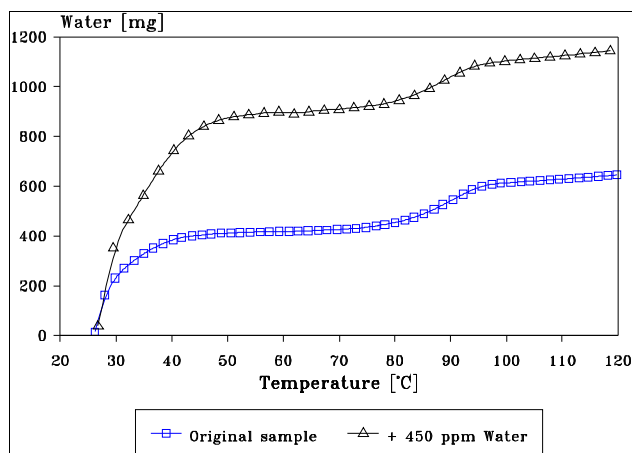


Fig. 5: Water determination in silicone oil suspension, temperature-controlled heating: 3°/min, dosing quantity: 900 mg

The Karl-Fischer-titration is also suitable for characterisation 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. (Fig. 6)

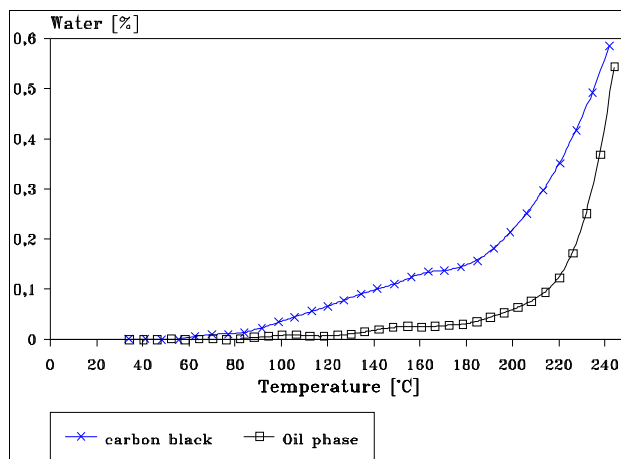


Fig. 6: Water determination in switch oils containing carbon black, temperature-controlled heating: 2°/min

#### 4.4. Bond Strength of Water of Crystallisation

By means of the temperature-controlled heating not only the total water content, but also the different types of water of crystallisation can be determined.

$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  is a typical example (Fig. 7). Water desorption occurs gradually: First, two water molecules are desorbed at temperatures up to 80° C. Between 100 and 120° C another two water molecules are desorbed. The last molecules are split off above 180° C.

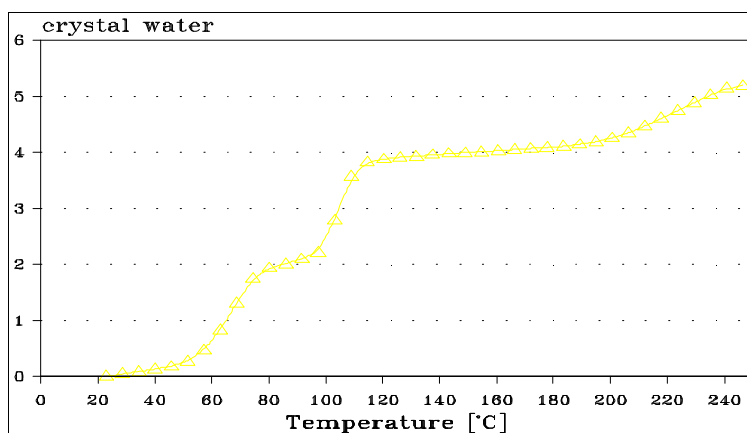


Fig. 7: Temperature-controlled heating of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$

Water release can be defined as follows:

temperature	water release		
30 - 90° C	$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	→	$\text{CuSO}_4 \cdot 3 \text{H}_2\text{O} + 2 \text{H}_2\text{O}$
90 - 140° C	$\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$	→	$\text{CuSO}_4 \cdot \text{H}_2\text{O} + 2 \text{H}_2\text{O}$
200 - 250° C	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	→	$\text{CuSO}_4$

#### 4.5. Different Types of Bonded Water

The analysis of lactose-monohydrate (Fig. 8) demonstrates that by means of the temperature-controlled heating it can be distinguished between surface water, water of crystallisation, and water produced by decomposition reactions. At temperatures ranging between 100 and 180° C, the water of crystallisation is split off from the lactose monohydrate. If the lactose is brought in contact with water, for instance by steaming the sample, this surficially adsorbed water will be let off at 60°C. With longer retention times of the sample in humid environment, only the step height but not its position to the heating temperature will change.

Similar experiments with glucose (Fig. 9) have shown that for long retention times in humid environment, the water is first adsorbed at the surface and gradually chemisorbed as water of crystallisation within the substance. This process is indicated by two clearly divided steps which occur with increasing water content (longer contact times).

The combination of the Karl-Fischer-titration and heating technique allows therefore also conclusions about kinetic processes.

Technical processes can be described by means of the temperature-controlled heating. This is demonstrated by the processing of two cellulose materials. During the process, the starting materials were brought to a temperature of 200°C for a short time, and then moulded to the final product.

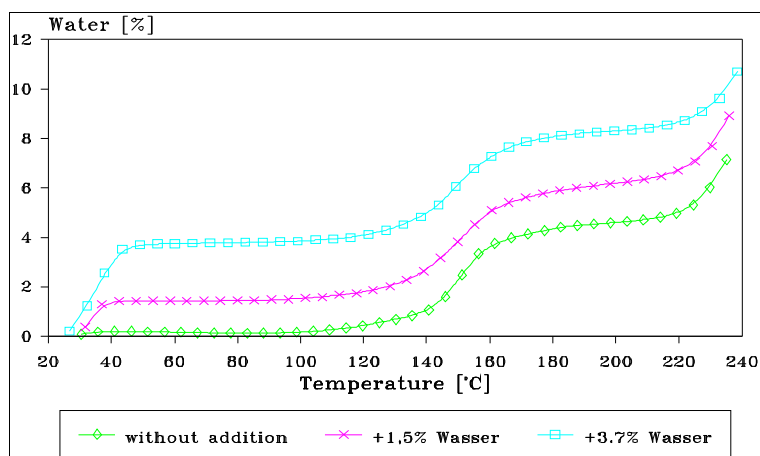


Fig. 8: Water determination in lactose-monohydrate after water addition, temperature-controlled heating 2°/min

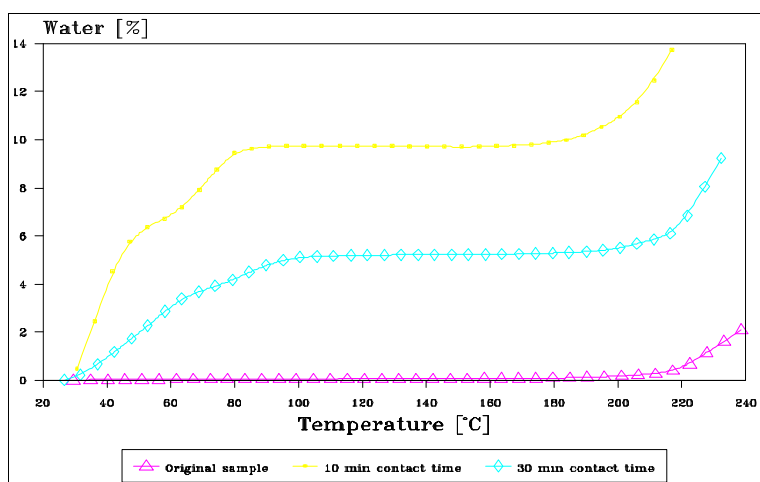


Fig. 9: Water determination in glucose after different contact times in humid environment, temperature-controlled heating 2°/min

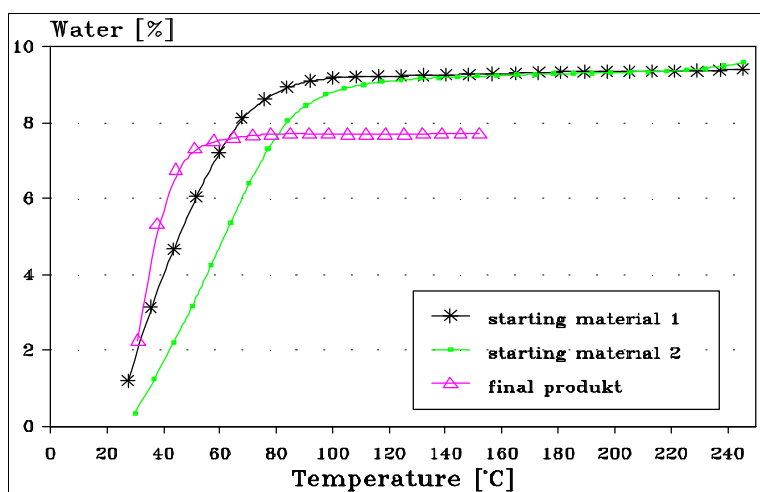


Fig. 10 Water determination in different cellulose substances

It can be seen that the starting materials have a higher water content than the final product (Fig. 10). Additionally it becomes visible that water is described from the final product at lower temperatures than from the starting materials, i.e. the bonding strength of the water is lower in the final product (e.g. due to changes in the cellulose structure).

## 5. Control of Coulometric Titration

All control processes of the coulometric titration (precise adjustment of titration current, end point indication, temperature control and more) are performed by a micro-controller. The comfortable measurement and evaluation programme under Windows offers a wide range of options: graphic representation of all measurement parameters, tools for data management, documentation and archiving as well as tools for plausibility tests. The titration graphs are documented together with all measurement conditions. Various methods of diagnosis (e.g. reagent consumption or titration test) can also be performed. All these helpful tools contribute to ensure the high quality according to the valid standards (e.g. ISO 9000 and others).

Some details of the control and evaluation programme are shown in Fig.11 and Fig.

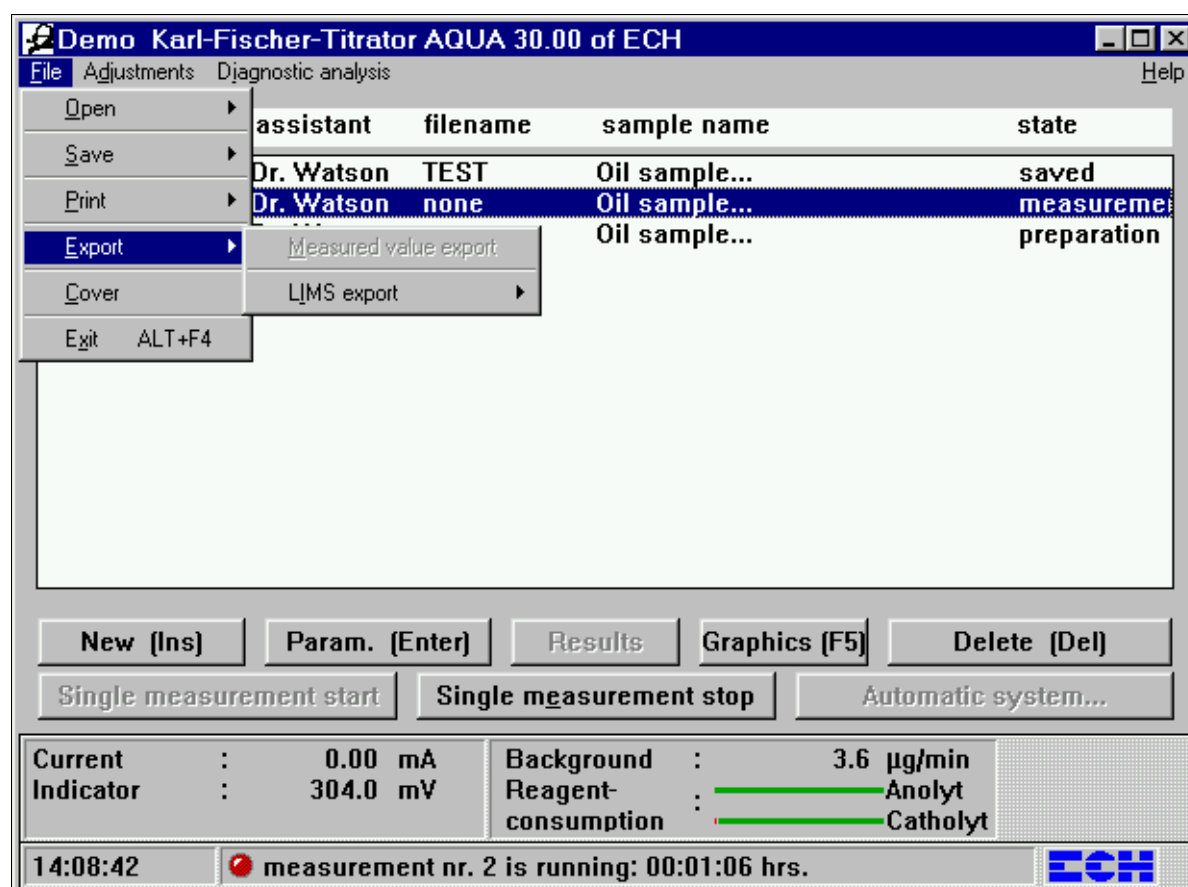


Fig.11: Measurement list of the control and evaluation programme

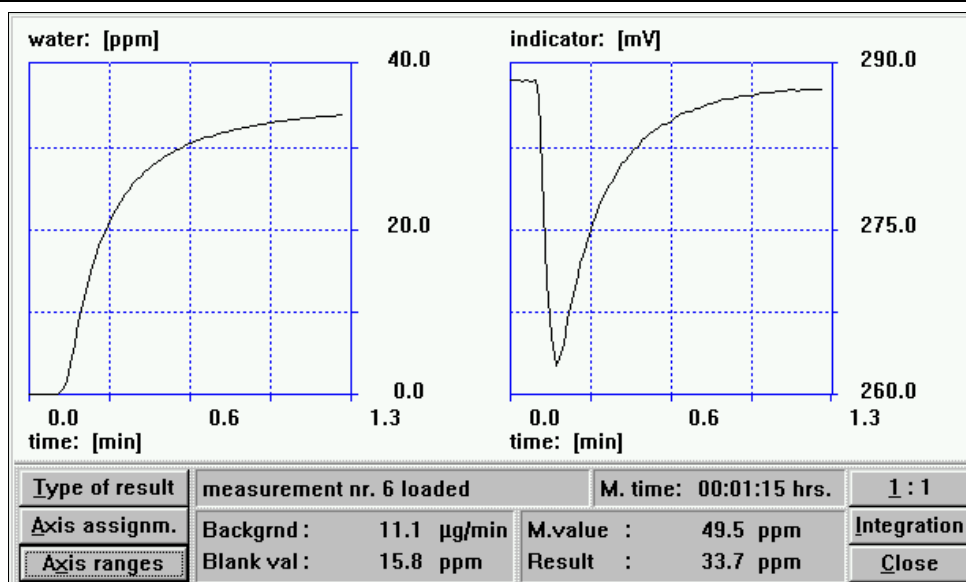


Fig.12: Graphic representation of the measurement:  
sample: compressor oil

## 6. Conclusion

The combination of computer-controlled Karl-Fischer-titration and heating technique offers an efficient method for water determination in solids, pastuous substances and highly viscous liquids.

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

Heating with temperature ramp allows differentiation between surface water, chemically bonded water and water produced during decomposition reactions.

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