METROHM Ltd. CH-9100 Herisau (Switzerland)

KF Coulometer

684

Series 13 ...

8.684.1013

684 /c
90.04 Ti/mm

684 KF Coulometer

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1. Introduction

The coulometric Karl Fischer titration is a variant of the classical Karl Fischer method for the determination of water. In the conventional method methanolic solutions of iodine, sulphur dioxide and an organic base are used, the organic base serving as a buffer. During the titration of a water-containing sample several reactions occur which are summarised in the following equation:

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2\ RN \rightarrow [RNH]SO_4CH_3 + 2\ [RNH]I$$

The quantitative determination of the water content of a sample is based on the fact – illustrated by the above equation – that a given amount of substance I_2 leads to the conversion of an equivalent amount of substance H_2O.

Since its invention in 1935, the classical Karl Fischer method has undergone continuous development involving the improvement of endpoint detection and of reagents used as well as the refining and automation of reagent addition. In spite of these advances the classical Karl Fischer method suffers from the fact that the one-component reagent generally used is not completely stable and therefore requires periodic recalibration.

In the coulometric Karl Fischer titration the iodine needed is generated electrochemically within the titration vessel itself. The quantitative relationship existing between the electric charge passed and the amount of iodine produced is used for the precise dosing of iodine. As the coulometric Karl Fischer titration is an absolute method it does not require any calibration.

The voltametric* method is used for the detection of the endpoint: An alternating current is applied to a pair of indicator electrodes. The voltage difference thus generated decreases drastically if traces of iodine are present. This fact is used to detect the endpoint of the titration.

A good summary on Karl Fischer titration is given in the following books:
- E. Scholz, Karl Fischer Titration, Springer-Verlag, Berlin-New York, 1984.
- G. Wieland, Water Determination by Karl Fischer Titration, GIT Verlag, Darmstadt, 1987

The 684 KF Coulometer is an automated instrument for the exact determination of small amounts of water in the range 10 µg ... 10 mg. Normally, no parameters have to be adjusted. In special cases some straightforward parameters have to be set.

* The term recommended by IUPAC for this technique is: "Controlled-current potentiometry with two indicator electrodes".

2. Preparations

2.1 Setup of 684 KF Coulometer with Stirrer or 703 Ti Stand

Before the instrument is switched on for the first time, the values of mains voltage and frequency should be checked at the rear of the instrument. If required, the mains voltage can be changed after the rear plate and the mains cable have been removed. After this the fuse rating must be checked and the fuse exchanged if necessary. To convert the instrument to a mains frequency of 60 Hz insert bridge no. 1 on print 3.540.2140.

Fuses:

0.2 A (slow) for 220 and 240 V

0.4 A (slow) for 100 and 117 V

Mains connections:

The mains cable supplied to order

6.2122.010 with SEV type 12 plug (Switzerland...)

6.2122.030 with CEE(7), VII plug (Germany...)

6.2122.060 with NEMA/ASA plug (USA)

is three-cored and fitted with a plug carrying an earthing pin. If another type of plug has to be fitted, the yellow/green lead (IEC Standard) must be connected to a protective earth.

If no wall-socket with an earth connection is available, the instrument should be connected to a good earth connection (via the earthing socket ⏚).

Connection of Stirrer or 703 Ti Stand:

Mount the stand rod onto the 684 KF Coulometer and fix Stirrer or Ti Stand on it. The Stirrer should be fastened in the lowest possible position (see Instructions for Use of Magnetic Stirrer, page 40). Connect Stirrer or Ti Stand to the 684 KF Coulometer, plug ⏚, by means of the 6.2108.110 cable, see Fig. 1.

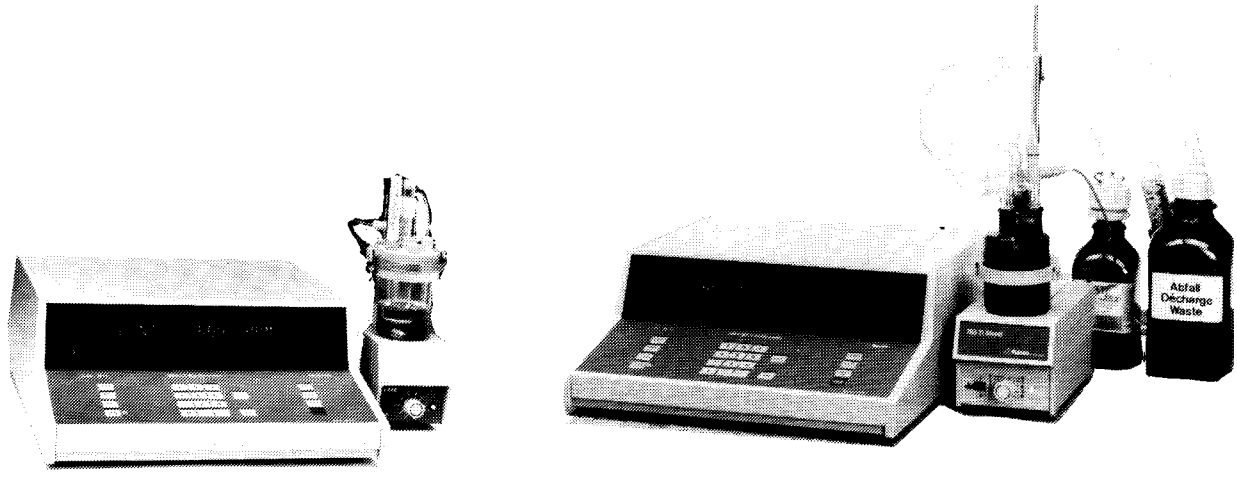

Fig. 1: Setup of 684 KF Coulometer with Stirrer and 703 Ti Stand

2.2 Connection of printer

For the connection of a printer the 3.540.2441 data transfer interface is necessary. Set the switches for RS data transfer on the interface (see page 30) according to the requirements of your printer. The correspondingly prepared interface is inserted in slot F of the 684 KF Coulometer and the printer connected according to Fig. 2:

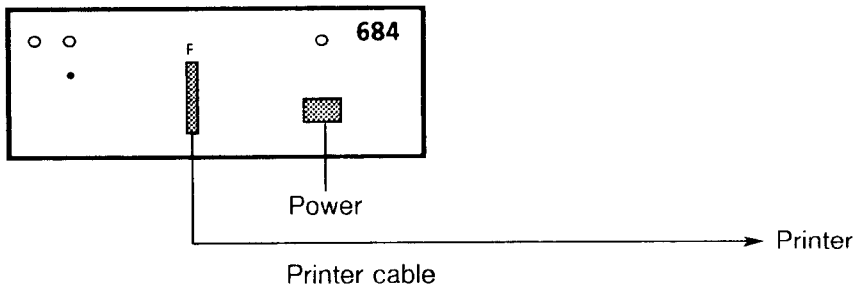

Fig. 2: Connection of a Printer

Printer cable:	
Citizen Printer iDP-560 RS	3.980.3550
EPSON Printer with #8148 serial interface	3.980.3550
EPSON Printer P40/P80	3.980.3401

DIP switch settings of printers and for the connection of other printers see page 31ff.

Results are printed out at the end of a titration if "send" is on (corresponding LED is on).

2.3 Connection of an external data system

An external data system can be connected via 3.540.2441 data transfer interface. The parameters for RS data transfer can be set on the interface, see page 30. The interface is inserted in slot F of the 684 KF Coulometer.

Interconnecting cables:	
IBM® PC/XT/PS-2 or compatible	3.980.3480
IBM® AT	3.980.3480 + 6.2125.010
HP calculator with 82939A serial interface	3.980.2810
EPSON HX 20	3.980.2890

An example for a PC program is given on page 32.

3. Measuring cell

3.1 Preparation and connection

The components of the measuring cell have to be clean and as dry as possible before being assembled. The drying of the cleaned components can be done by putting them into a desiccator or a drying oven (not above 70 °C = 158 °F) or by treating them with a hot-air blower immediately before use. Incompletely dried cells require long waiting times during the initial phase (display shows /WAIT).

3.1.1 Measuring cell with diaphragm

When assembling the cell all the parts screwed into the lid have to be tightened firmly without using too much force, however. The measuring cell is designed such that it does not require any grease or other sealing agent.

A practical sequence of assembling the cell is given in the following:

1. Mount gasket into groove in lower part of titration vessel lid and fix lid onto rod by means of clamping ring.

2. Put stirring bar into titration vessel supplied with holding ring and fasten titration vessel to lid by means of the latter's locking lever. Move locking lever downward such that titration vessel and lid are pushed together firmly.

3. Slip gland onto generator electrode so that its thread is looking towards the lower part of the generator electrode. Carefully roll O-ring over the outer platinum mesh and move O-ring upwards until the gland is pushed against the connecting piece of the cable. If still available, the cardboard tube which protects the generator electrode during transport can be used to mount the O-ring. Check whether the outer platinum mesh has a separation of 1 ... 2 mm from the ceramic diaphragm.
   Caution: Adjust the outer platinum mesh only if necessary and proceed very carefully when doing this, as otherwise the platinum mesh may break off.

4. Screw generator electrode into titration vessel lid by means of gland. Make sure that the fastened generator electrode reaches as far as possible downwards into the titration vessel and that the connecting cable is pointing outwards.

5. Insert indicator electrode into the outer right hand one of the remaining three openings (seen from the front) after checking whether the O-ring is inserted and whether the two platinum electrodes are not bent and are roughly parallel to each other.

6. Seal the right hand one of the remaining two openings (seen from the front) of the titration vessel lid with a screw nipple after making sure that the screw nipple contains a septum.

7. Fill anolyte*) solution through the remaining opening of the lid into the anode compartment, using the plastic funnel supplied, up to the lower margin of the number marked on the titration vessel.

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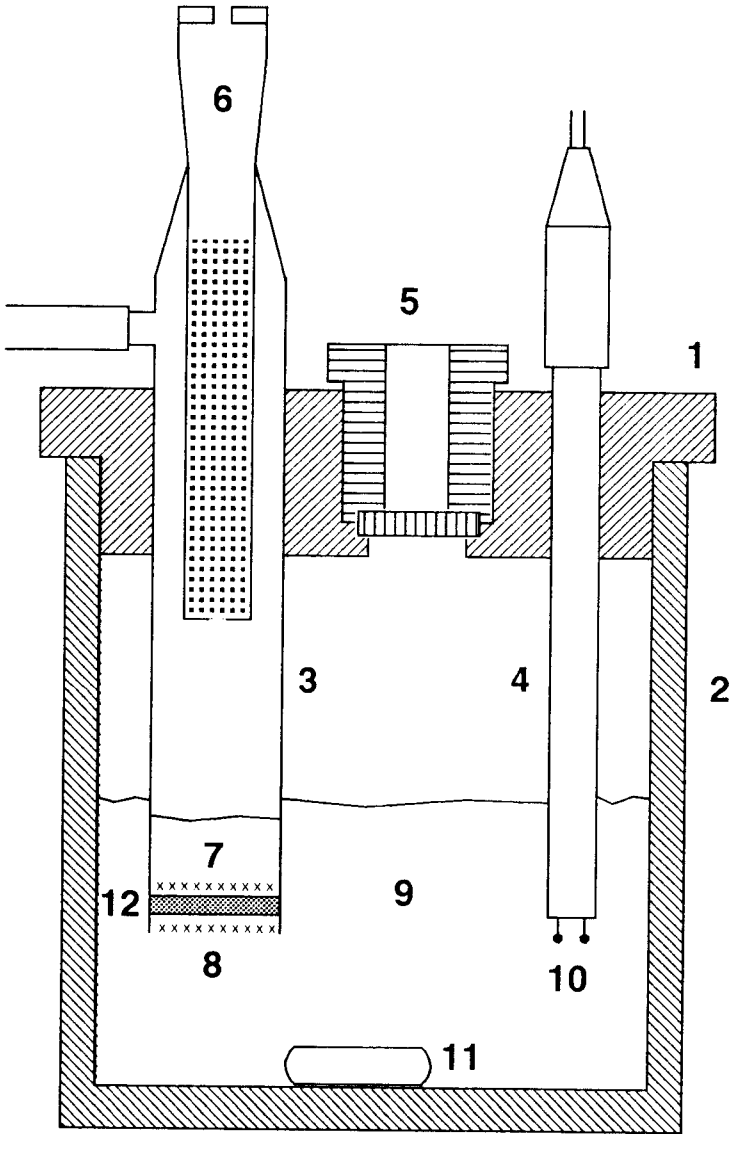
*) Reagents for coulometric Karl Fischer water determination using a cell with diaphragm consist of an anode solution (anolyte), which is filled into the anode compartment, and a cathode solution (catholyte), which is filled into the cathode compartment (see also Fig. 3).

8. Seal the remaining opening of the lid with a screw nipple (with septum) or fasten gas inlet tube by means of a screw nipple in that opening (if the drying oven is to be used). Check whether the gas inlet tube is supplied with an O-ring. If the gas inlet tube is not used for some time, it has to be sealed with screw cap 6.1446.040.

9. Fill catholyte*) solution into generator electrode, using the funnel, until the level of the liquid inside the generator electrode is 2 ... 3 mm below that outside. Remove any excess catholyte solution, e.g. by means of a pipette.

10. Insert drying tube filled with Molecular Sieve 3 Å (0.3 nm) into generator electrode, applying slight pressure. Make sure that the Teflon sleeve is sitting on the ground joint cone of the drying tube and that the plastic plug with hole is inserted into the top of the drying tube.

11. Plug in generator electrode (larger plug) and indicator electrode (smaller plug) at the rear of the instrument. Please note that both of these plugs are engaged and can be pulled out only if held at their metal sleeves. Any attempt to remove these plugs by pulling at their cables may lead to their destruction.
Also make sure that the generator and the indicator electrode are never connected to each other with an electrical conductor.



1 Titration vessel lid
2 Titration vessel
3 Generator electrode
4 Indicator electrode
5 Screw nipple with septum (second screw nipple not shown)
6 Drying tube with Molecular Sieve 3 Å (0,3 nm)
7 Cathode compartment with catholyte and cathode
8 Anode of generator electrode
9 Anode compartment with anolyte
10 Pt wires of indicator electrode
11 PTFE stirring bar
12 Diaphragm

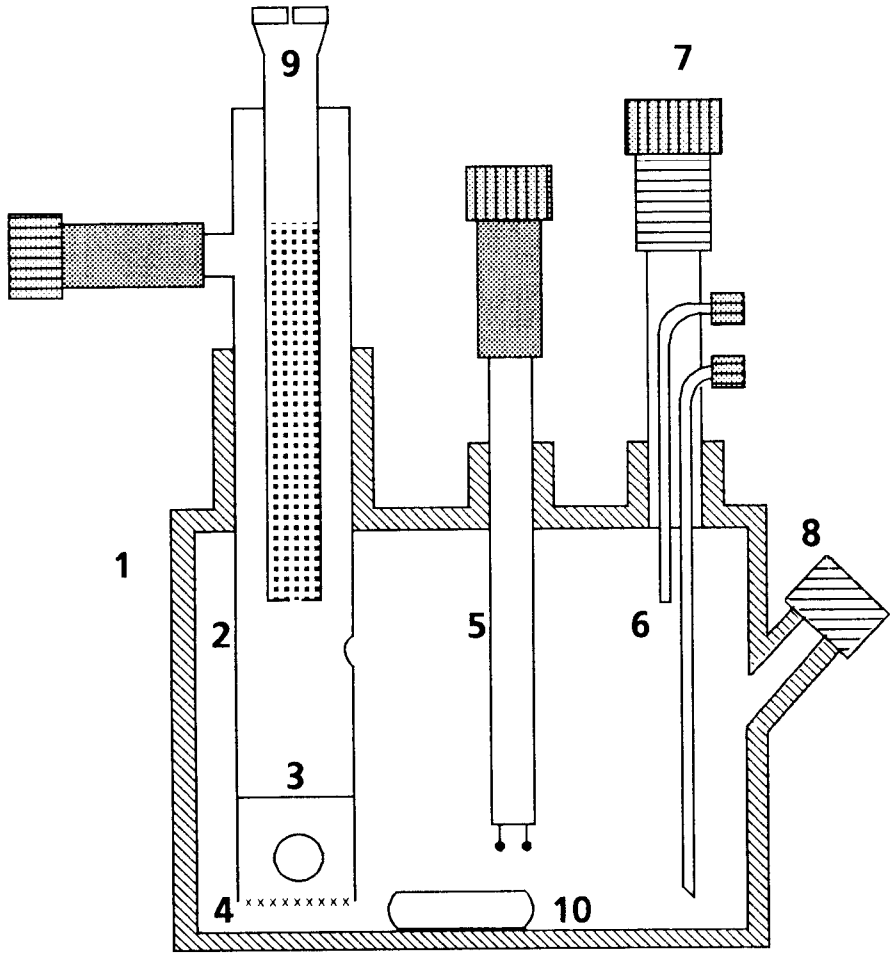
Fig. 3: Assembly of measuring cell with diaphragm

3.1.2 Measuring cell without diaphragm

1. Mount titration vessel in the titration vessel holder and fix it onto rod by means of clamping ring.
2. Put stirring bar into the titration vessel.
3. Cut ground joint sleeves into right length and provide all ground joints with them.
4. Put indicator electrode (**5**) into titration vessel.
5. Take the electrode cable with the smaller plug (plug F), screw it onto indicator electrode and connect it on the rear side of the 684 KF Coulometer on the socket "Ind.El.".
6. Put generator electrode (**2**) into titration vessel.
7. Fill drying tube (**9**) with molecular sieve and put it into the generator electrode.
8. Screw the electrode cable with the bigger plug (plug H) onto generator electrode and connect it on the rear side of the 684 KF Coulometer on the socket "Gen.El.".

Note: Avoid mixing up the two electrode cables! In order not to confound them, mark one of the cables and the corresponding electrode socket accordingly.

9. Introduce a septum into the screw cap (**8**) and screw it onto the glass connection piece.
10. Fill the cell with reagent up to the lower margin of the article number (app. 80–90 ml). Use only reagents which are especially designated for applications with cells without diaphragm.
11. Close the last ground joint aperture with stopper (**7**) .



1 Titration vessel
2 Generator electrode
3 Cathode
4 Anode
5 Indicator electrode
6 Inlet/outlet tube
7 Stopper
8 Screw cap with septum
9 Drying tube with molecular sieve
10 PTFE stirring bar

Dry all parts well,
see page 4.

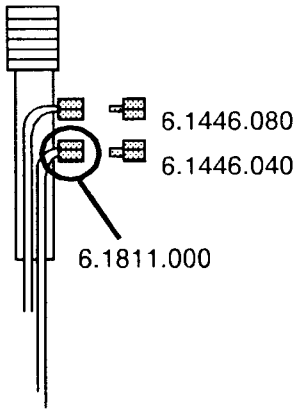
Fig. 4: Assembly of measuring cell without diaphragm

Alternatively, you may use the inlet/outlet tube (**6**) instead of stopper (**7**) for the connection of a pump, to add fresh solvent and aspirate used solution. That means:

12. Put stopper (**7**) onto inlet/outlet tube (**6**) and place it in titration vessel.
13. Screw on outlet/inlet tubing (the outlet is the longer tube)
14. If the pump is not connected during a certain period, the stoppers with thread M8 (6.1446.080) are used to close the tubing connection of the inlet/outlet tube.

If you see a drop hanging on the inlet tube after the addition of electrolyte, remove it by quickly pressing the "add" key of the pump several times.

For work with the KF Oven the inlet/outlet tube (**6**) is transformed as follows:



1. Remove the screw connector for tubing with thread M8 on the inlet tube (longer tube) and replace it by screw connector for tubing with thread M6 (6.1811.000).
2. Screw tubing from KF Oven onto inlet tube.
3. If the KF Oven is not connected for a certain period, the tube is closed with a stopper with thread M6 (6.1446.040) and M8 (6.1446.080) each.

Fig. 5: Changing the inlet/outlet tube to become the gas inlet tube for work with the KF Oven.

3.2 Cleaning and drying

Under favourable conditions the measuring cell can be used for a large number of analyses without requiring replacement of the electrolyte. During this time the cell does not need any special maintenance. Even if the electrolyte is replaced the cell usually does not have to be cleaned. However, if the cell is strongly contamined or if it is not to be used for a long time, the cell has to be cleaned thoroughly. For this purpose the cell is taken apart and the components are cleaned according to the nature and degree of their contamination. During these operations the platinum mesh of the generator electrode must be handled very carefully, as otherwise it may break off. Contaminations by oil-like substances have to be removed by means of suitable solvents (chloroform, hexane, etc.). If salt-like deposits are present, cleaning has to be done with water which is subsequently removed by rinsing with methanol or ethanol.

With measuring cell with diaphragm, special care should be devoted to the cleaning of the diaphragm which may contain deposits of salt-like substances which are not visible from the outside. Accordingly, the diaphragm should always be rinsed with water. This is done by holding the generator electrode upright, filling it with water and leaving it standing for 10 ... 30 min such that the water can leave the diaphragm. After that the same is done using methanol or ethanol to remove the water from the inside of the diaphragm.
If the ceramic diaphragm cannot be cleaned with water, other cleaning agents generally used for glassware can be applied (please note that the plastic parts of the cell are not resistant to some of these chemicals). However, in these cases, the diaphragm has to be rinsed very carefully. Be aware that the pores of the diaphragm are very small and rinsing therefore takes time.

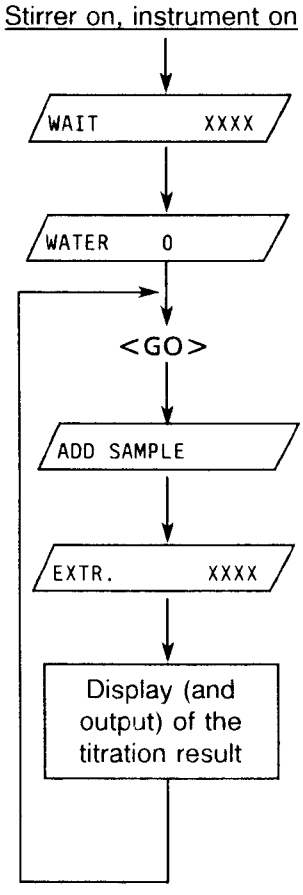
After being cleaned and rinsed with methanol or ethanol the cell components can be thoroughly dried by storing them in a desiccator. They can also be left as they are. In this case, however, they have to be dried by means of a hot-air blower before being assembled.

If an oven is used for drying the components its temperature must by no means exceed 70 °C (158 °F) to avoid damage to the plastic parts, especially to the cables.

4. Operation

4.1 Operation sequence

An overview of the operation sequence is given in the following scheme:



The measuring cell is dried automatically, i.e. conditioned.

The measuring cell is dry ...
Parameters may be introduced. Prepare sample.

Start titration.

Add sample, display remains during 6 s, afterwards titration starts automatically.

With an extraction time ≠ 0, the remaining waiting time is displayed.

According to the calculation the following displays are possible:

WATER XXXX: Mass of titrated water in µg, $m(H_2O)$ (b = 0, s = 0)

WATER-B XXXX: Mass of titrated water minus blank in µg $m(H_2O)$, (b ≠ 0, s = 0)

CONT. XXXX P.C.: Water content of sample in P.C. (%) or ppm, $w(H_2O)$, (b = 0, s ≠ 0)

CONT.-B XXXX PPM: Water content of sample minus blank in P.C. (%) or ppm, $w(H_2O)$, (b ≠ 0, s ≠ 0)

During this display the measuring cell is dried continuously, i.e. conditioned. Parameters may be introduced, calculations repeated and the drift displayed.

Titration results are calculated according to the following formula:

$$\text{CONT} - \text{B} = \frac{m(H_2O) - \text{blank}}{\text{sample}} \cdot f$$

$m(H_2O)$	Mass of titrated water of the sample in µg
blank	Mass of water of the blank in µg
sample	Sample size in mg
f	Factor
	$f = 10^3$ for results in ppm
	$f = 10^{-1}$ for results in %

4.2 Operation elements

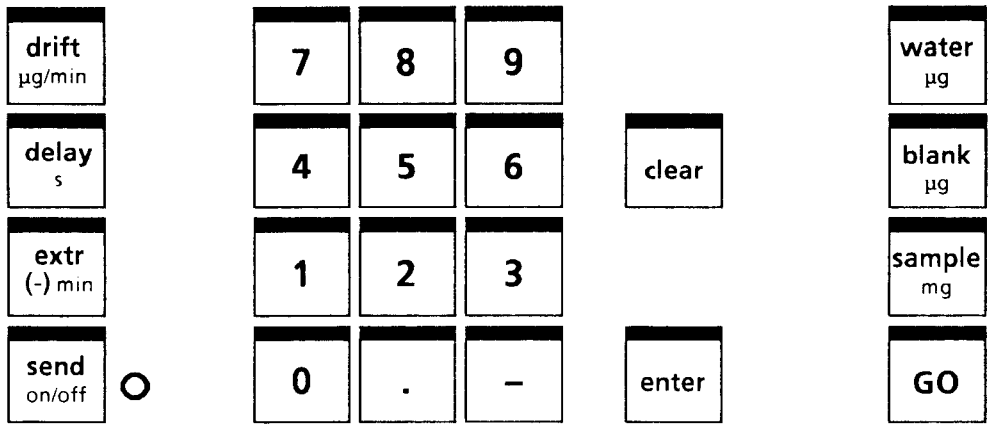


Fig. 6: Keyboard of 684 KF Coulometers

In order to recall a parameter, i.e. to display its stored value, the corresponding key has to be pressed (see Fig. 6). Parameters can be recalled or changed any time (display ADD SAMPLE) except during the initial phase and during sample introduction. If the value of a parameter has to be changed, proceed as follows:

- Press corresponding key, e.g. <blank>; this causes the stored numerical value of the parameter <blank value> in µg to be displayed together with its name :

  BLANK 25

- Key in new value of parameter, e.g.:

  BLANK 35.5

- In case of error press <clear> key to clear the displayed number and start again.

- Press <enter> key to enter the displayed number, i.e. transfer it to the data storage.

Please note: The key <clear> clears the display only; to cancel a stored parameter press <enter> afterwards (entry of 0).

The parameter <sample> is a special case: If one wishes to display the water content (CONT) of the sample immediately at the end of the titration, either the current value of this parameter has to be confirmed, or a new value has to be entered.
The 3.540.2441 RS interface can be adjusted in such a way that the calulation is always carried out whether sample size has been confirmed after <GO> or not, see page 30.

Titration parameters:

drift µg/min

Display of drift in µg/min

This value is based on the residual current needed to maintain endpoint conditions when no titration is running. The residual current is converted to $\Delta m(H_2O)/\Delta t$ and displayed together with the expression DRIFT. The average drift value established before the start of a titration is deducted continously during titration.

After a solvent exchange the cell is well conditioned if its drift is ≤ 12 µg/min. A negative drift at the end of a titration means that the endpoint is overreached or that the sample releases iodine.

delay s

Delay time (0...99 s), initial value 3 s

The titration is concluded if the indicator signal stays below the endpoint voltage during a time interval longer than the delay time. If the drift decreases relatively strongly after titrations, the delay time should be increased. However, too long delay times should be avoided as they can have a detrimental influence on the error of determination.

extr (–)min

Extraction time (0 ... 999.99 min und 0 ... – 999.99 min), initial value 0 min

With positive extraction times the titration is started immediately after the introduction of the sample. The mass of the titrated water is displayed continuously together with the count-down of the extraction time. Thus, e.g. the display.

EXTR 5.25 256

means that the remaining extraction time is 5 min 25 s and that the mass of the water titrated so far is 256 µg. After the positive extraction time has passed the titration is concluded taking into account the delay time.

Positive extraction times are used for samples which release their water content too slowly for normal titrations. Keep positive extraction times as low as possible, because very long titration times may increase the titration error.

If a negative extraction time is entered, the titration will not be started before the extraction time has elapsed. The count-down of the extraction time is displayed, e.g.

EXTR-3.50 0

means that the titration will be started in 3 min 50 s and that no water has been titrated so far.

Negative extraction times are used for samples which release their water content slowly and on top of that react with iodine.

Changes of running extraction times are possible; the elapsed portion of the running extraction time is taken into account, as shown by the following example:

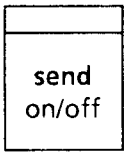
Display:	EXTR-7.35 0	count-down of previously entered extraction time
press <extr>		
Display:	EXTRACT-10.00	previously entered extraction time
Key in new value:	-6.00 <enter>	
Display:	EXTR-3.25 0	count-down of newly entered extraction time assuming that 10 s have passed since the display EXTR-7.35 0 appeared

When entering extraction times one has to be aware that the figures after the decimal point indicate the seconds. Entered values which do not conform to this format are converted accordingly. If e.g. a value of -3.80 is entered, this results in a negative extraction time of 4 min 20 s. If the stored value is recalled by pressing the <extr> key, however, the initially entered value of -3.80 will be displayed.

EP Voltage setting (high ... low); at the rear of the instrument

By means of this screw-driver potentiometer the endpoint voltage can be adjusted between the positions "high" (high endpoint voltage, i.e. steep section of the titration curve) and "low" (low endpoint voltage, i.e. flatter section of the titration curve). An endpoint voltage which is too high can cause the error message /SAMPLE UNFIT/ which appears if the indicator voltage drops too far below the endpoint voltage (overshoot). This may happen if a fast reagent is used and if the stirring intensity is too low. After being used for some time, the indicator electrode becomes more sensitive to changes in the concentration of excess iodine. An endpoint voltage which is set too high can then lead to large periodic oscillations of the drift value. In this case the endpoint voltage is changed towards "low", but only as far as necessary to stabilize the drift value. Too low endpoint voltages will prolong the titrations and thus have a detrimental influence on the error of the water determinations.

Parameters for result output



Switch on/off of data transfer

Titration results are transferred to a connected printer or an external data system. The following data are transferred: a current number #, the mass of the titrated water m(H_2O) and the mass fraction of the water w(H_2O), possibly corrected with a blank value -B.

Data transfer occurs automatically at the end of the titration. Additionally, if the following keys are pressed (possibility of recalculation):

<water>
<blank> <enter>
<sample> <enter>

Example of a result printout:

```
#04 m(H2O) 26.4 ug
#05 m(H2O) 25.3 ug
#06 m(H2O)   91 ug -B
#06 m(H2O)   91 ug -B w(H2O) .3582 %
#07 m(H2O)  102 ug -B w(H2O) .4015 %
#08 m(H2O) 67.4 ug -B
#08 m(H2O) 67.4 ug -B w(H2O) .2653 %
#09 m(H2O)   87 ug -B w(H2O) 826.2 ppm
#10 m(H2O)  117 ug    w(H2O) .1135 %
#11 m(H2O)  113 ug    w(H2O) .1032 %
#12 m(H2O) 94.4 ug    w(H2O) 862.8 ppm
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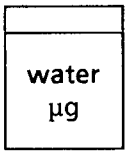
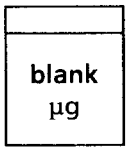


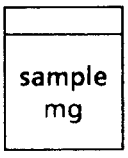
Display of titrated mass of water: 1.0 ... 99.9 µg und 100 ... 65 535 µg

If this key is pressed the mass of the water found during the last titration performed is displayed. If during a titration a parameter value is recalled for control purposes, the mass of the water titrated so far can be displayed again by pressing the <water> key. In any case the expression /WATER / will appear in the display at the end of the titration only.



Blank value (1.0 ... 99.9 und 100 ... 63 999 µg), initial value 0 µg

A stored blank value is automatically subtracted from the result of the titration. The resulting value is displayed together with the expression "WATER - B" or "CONT-B". If the mass of the titrated water is below 100 µg, blank values are calculated with one decimal place. For masses above 100 µg, decimal places are ignored.

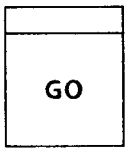


Sample size (1.0 ... 6400.0 und 6400 ... 63999 mg), initial value 0 mg (no calculation of CONT).

This key is used for entering the mass of the sample in mg during or after a titration. Entering a new sample mass or confirming the stored value of this parameter causes the mass fraction to be calculated and displayed as soon as the titration is concluded: Display /CONT 1.23 P.C./ or /CONT 12.35 PPM/.

The 3.540.2441 RS232 interface can be adjusted in such a way, that the calculation of "content" is always carried out, see page 30.

Start of titration



This key has to be pressed if a titration is to be carried out. If the drift meets the starting criteria (drift ≤ 100 µg/min), the expression /ADD SAMPLE / is displayed for six seconds. When this time interval has elapsed, the titration is started.

If the drift does not fulfil the above conditions, /WAIT / is displayed together with the current drift. As soon as the drift meets the conditions /ADD SAMPLE / is displayed and the introduction of the sample has then to be started within six seconds. If longer times are needed for the introduction of the sample, an extraction time can be set.

If no sample is introduced during the time interval consisting of the six seconds mentioned above plus the delay time /WAIT 0/ or with some value near zero will be displayed. After that, another titration can be started immediately.

If, however, the sample is introduced after the interval mentioned (6 seconds + delay time) has elapsed, it will take some time before the instrument has eliminated the added water and is ready for another titration. This process can be monitored by pressing the <drift> key, thus displaying the drift.

Summary of the different parameters:

Parameter		Range	Initial value
delay:	delay time	0 ..... 99 s	3 s
extr:	extraction time	0 ..... 999.99 min 0 ..... – 999.99 min	0 min
blank:	blank value	1.0 ..... 99.9 µg 100 ..... 63 999 µg	0 µg
sample:	sample size	1 ..... 6400.0 µg 6400 ..... 63 999 µg	0 mg

5. Practical hints

5.1 Introduction of samples

General remarks

As each class of samples has its peculiar characteristics, it is not possible to give an exhaustive discussion of all the sampling problems. Here a selection of application notes:

- METROHM Application Bulletins (can be ordered free of cost):
  No. 88: Bibliography concerning Karl Fischer water determinations
  No. 109: Karl Fischer water determinations with the Drying Oven
  No. 137: Karl Fischer water determinations with the KF Coulometer
  No. 142: Karl Fischer moisture determinations in gases
  No. 145: The determination of low water contents in plastics

- Hydranal®, practical course, Water reagents according to Eugen Scholz for Karl Fischer titration, Riedel-de Haën, Seelze, 1987

- Hydranal® Guide PC, Applications for the Karl Fischer titration, Ed. by Eugen Scholz, PC diskette

5.1.1 Liquid samples

Care should be taken that no organic solvents get in contact with the keyboard. The foil covering the keyboard is made of specially coated polycarbonate and may be damaged by organic solvents.

Syringes are used for the introduction of liquid samples into the measuring cell. The needles used should be as thin as possible to make the septa last longer.
The volume of the sample introduced should be as small as possible to allow the titration of a larger number of samples with the same batch of reagent. Another advantage resulting from small sample volumes is the shorter duration of the analysis. Fig. 7 informs the user about the sample size needed to bring the result of the titration into the desired range.

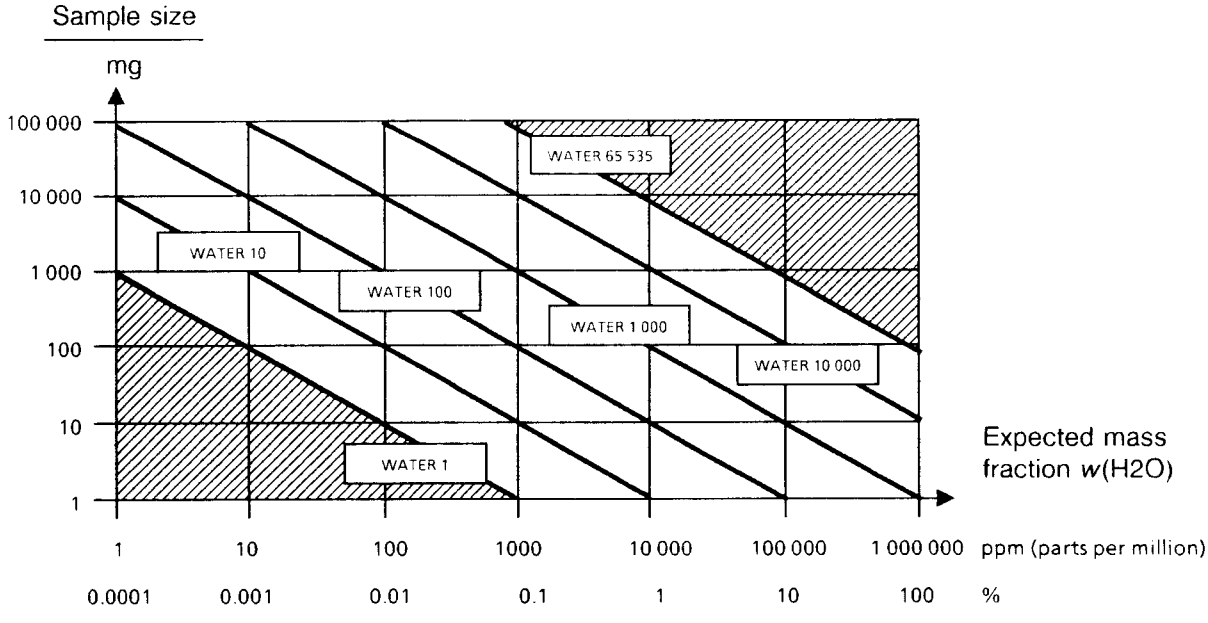


Fig. 7: Recommended sample sizes in relation to their water content

Example:
The mass fraction $w(H_2O)$ of the sample to be analysed is known to be about 1%. In order to obtain a result in the region of 1000 µg, corresponding to the display /WATER 1000/, the injected sample should have a mass of approximately 100 mg. Assuming the density of the sample to be roughly 1 g/cm³, the sample volume to be injected would be chosen as 100 µl.

Volatile and low viscous samples have to be cooled to avoid losses during sampling. However, the syringe itself should not be cooled as this may result in the formation of condensed water. For the same reason air should not be aspirated into a syringe cooled by the handling of cooled samples.

Highly viscous samples can be made less viscous by heating. In this case the syringe has to be warmed as well. The same effect can be obtained by diluting the sample with a suitable solvent. The water content of the solvent has to be determined beforehand and subtracted as a blank value, taking into account the proportion of the solvent in the sample.

If the sample has a high water content, the needle should not be introduced through the septum before the <GO> key has been pressed, as otherwise the drift will be affected and the measuring error increased accordingly.

Before handling samples which contain only traces of water, the syringe has to be dried thoroughly by putting it into a desiccator or by treating it with a hot-air blower. If possible the syringe should be rinsed by aspirating and rejecting sample solution several times.

5.1.2 Solid samples

If possible solid samples are either extracted or dissolved by means of a suitable solvent. The resulting solution is injected and the water content of the solvent entered as a blank value.

If no suitable solvent can be found or if the sample reacts with the Karl Fischer reagent, the Drying Oven has to be used according to the following procedure:

- **Measuring cell with diaphragm**: The screw nipple situated nearest to the KF Coulometer is unscrewed and its septum removed. The gas inlet tube (with O-ring) is inserted by means of the screw nipple. If there are periods during which the gas inlet tube is not used, it has to be sealed with screw cap 6.1446.040.
  Cell without diaphragm, see page 7.

- The Drying Oven is placed on the KF Coulometer such that the oven's outlet (originating inside the oven) is as close as possible to the measuring cell.

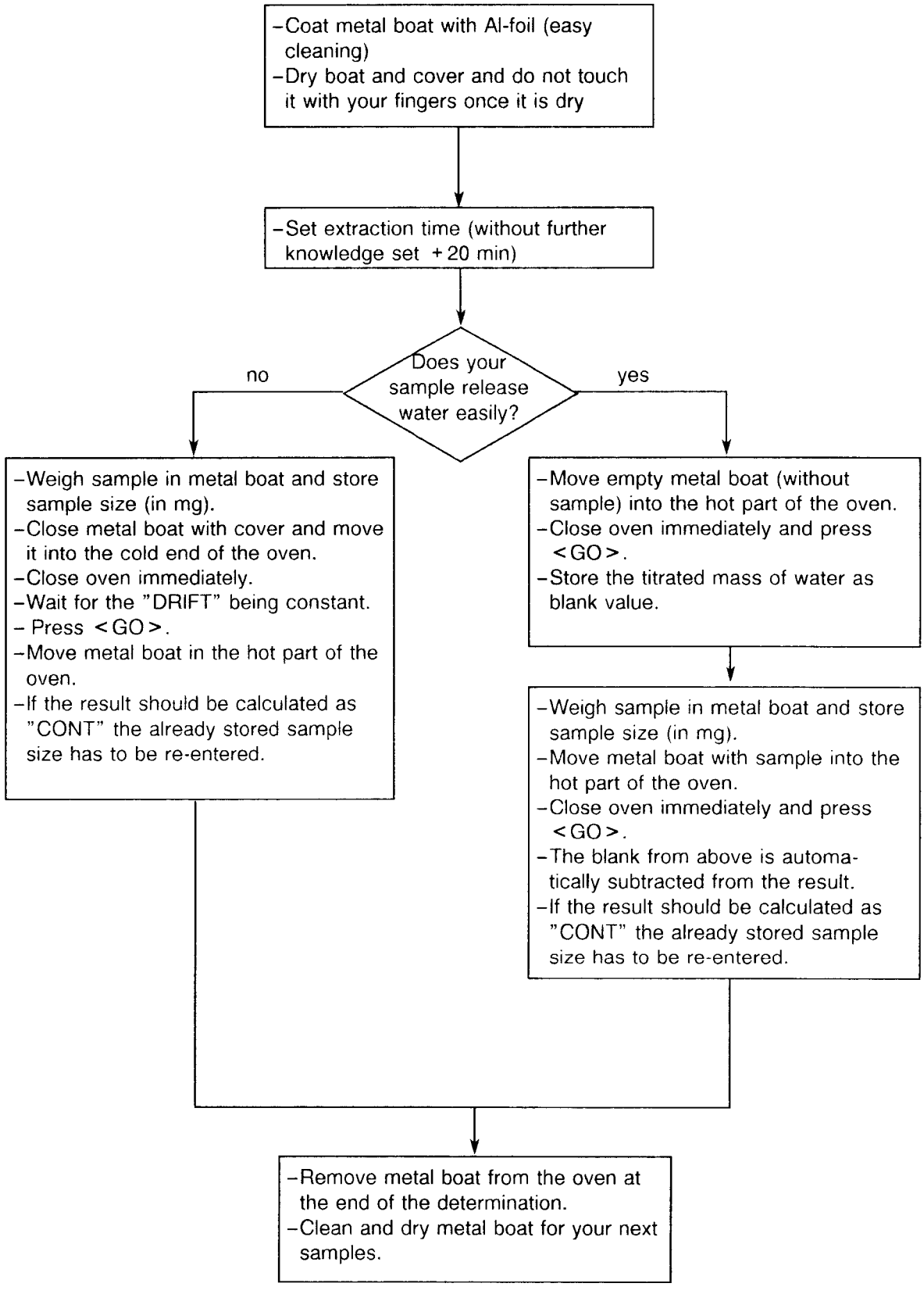
- The outlet of the Drying Oven is connected to the gas inlet tube of the measuring cell by means of connection tube 6.1805.040, whose length is 9 cm (3.5 in). Tighten screw connections firmly.

- The inlet of the Drying Oven is connected to the 661 Pump Unit or to a gas cylinder containing, e.g. air or nitrogen. The gas cylinder has to be equipped with a reducing valve and a device for drying the flowing gas (use Molecular Sieve 3 Å as desiccant). All connections and the screw cap of the heating tube – containing the guide rod – have to be gas-tight.

- Adjusting the gas flow: A rough adjustment is possible by observing the rate of bubble formation at the gas inlet tube. For a more precise adjustment of the gas flow a suitable flow meter has to be used.

- The Drying Oven is set to the desired temperature and switched on. Wait for the oven to reach thermal equilibrium. The drift ("DRIFT") should be as constant as possible before work is continued. Readjust the gas flow if necessary.

- Carry out determinations according to the best technique. It depends on the kind of sample and on the way of working of the operator. It has to be optimised for every kind of deter-mination!



5.2 Optimal working conditions

After being switched on, the instrument – connected to the measuring cell containing the reagents – goes through the initial phase and subsequently enters the conditioning phase. If care was exercised in assembling the cell the instrument will be ready for the first measurement within minutes. If, however, the cell components were not completely dry before being assembled, the corresponding time interval will be up to one hour. In any case, one has to be aware that the residual current is not stationary during that phase but decreases more or less slowly. This can be seen by checking the drift. The time needed for the instrument to be ready for effective measurements is a function of the tolerated measuring error and of the condition of the cell. If one intends, e.g. to carry out exact measurements where the mass of the water to be determined is less than 10 µg, it may be of advantage to leave the instrument switched on overnight before starting the measurements. It may be mentioned that a drift of 8 ... 12 µg/min, which stays reasonably constant, is considered as very good, but lower drift values are attainable.

What has been said above applies not only to freshly started cells but also to cells whose electrolyte has been replaced. Replacement of the electrolyte solutions is necessary if

1) The titration vessel is full.
2) The error message /GEN ELECTRODE / appears (see page 19); for the measuring cell with diaphragm replacing the catholyte may be all that is required.
3) The drift value is too high and cannot be lowered by shaking the cell (see below).
4) There is separation of phases in the titration vessel.

In order to avoid disassembling the cell, the used electrolyte is most conveniently removed by aspiration. When doing this one has to make sure that no solvent gets into the sewage. If the cell is strongly contaminated it can be rinsed with a suitable solvent which is also aspirated before fresh electrolyte is introduced. A pump can be used to remove the electrolyte solutions from the cell. A Pump Unit can be ordered as additional accessory, see page 37.

The drift usually decreases for some time after a titration has been performed. If you wish to minimize the measuring error, check the drift after each measurment by means of key <drift> and wait for it to become constant before starting the next titration. It has to be borne in mind, however, that the drift always has certain fluctuations which are averaged by the instrument.

Consistently high drifts can be caused by water-containing fluid elements located in badly accessible places within the cell. In these cases the drift will be reduced if the measuring cell is shaken. Measuring cells with diaphragm should not be shaken too vigorously to prevent mixing of catholyte and anolyte. If, however, the drift stays unacceptably high for a longer period of time after the cell has been shaken, change the electrolyte solution. For measuring cells with diaphragm, change the catholyte first, then, if the drift is not lower, the anolyte. If the drift is still too high, the cell has to be emptied, taken apart, cleaned and thoroughly dried before being assembled again, see page 8.

If the instrument with the measuring cell containing the reagents is switched off for a longer period of time, some time will pass after the instrument has been switched on again before the cell is ready for use. This waiting time can be shortened by shaking the cell. It is advisable to precondition the cell overnight after it has not been used for a longer time with the reagents filled in. If the instrument is used continuously during working hours it should not be switched off overnight.

A new indicator electrode may require a certain conditioning time, during which unusually high titration times and, possibly, too high results may be observed. These phenomena will disappear after the indicator electrode has been used for some time. In order to promote the conditioning of a new indicator electrode, it can be left immersed in the electrolyte solution with the instrument switched off for some time, e.g. overnight.

6. Error messages and malfunctions

6.1 General malfunctions

Negative drift

Possible causes:
- The measuring cell is in bright light (sun).
- The sample contains oxidizing substances and releases I_2, see also under "SAMPLE UNFIT".

6.2 State and error messages

ADD WATER

The electrolyte is in the range of iodine excess.
Exit: Add water

BLANK ERROR

The blank value is larger than the mass of the titrated water.
Exit: Enter new blank value.

GEN ELECTRODE

The voltage decrease on the generator electrode is too large.
Possible causes:
-Wrong or worked out electrolyte
-Measuring cells with diaphragm: Clogged diaphragm or bubbles between platinum mesh and diaphragm.
-Measuring cells without diaphragm: The electrolyte contains too much solvent. Its conductiviy is therefore too low. → change electrolyte.
-Generator electrode not connected or break in connecting cable.
Exit: Correct error

IND ELECTRODE

The voltage on the indicator electrode is too large.
Possible causes:
-Wrong electrolyte
-Indicator electrode not connected or break in connecting cable.
Exit: Correct error

NO INTERFACE

The function "send" has been activated without the corresponding interface being inserted.
Exit: <clear> and switch off "send"

PROGRAMME

Error in the program.
Remedy: Call METROHM Service

RS 232 ABORTED

Data transfer has been interrupted. The receiver is not ready for data transfer anymore
DSR or/and CTS were set to OFF during data transfer, see page 31.
Exit: <clear> and correct error

RS 232 NOT READY

The receiver and/or the connection to the receiver is not ready for data transfer. CTS and/or DSR are not ON, see page 31.
Exit: <clear> and correct error

SAMPLE UNFIT	Possible causes and remedy: -Stirring intensity is too low: increase stirring intensity -Endpoint voltage is too high for the fast reagent used: Set EP voltage to a lower value by means of the potentiometer at the rear of the instrument -Sample releases iodine: Change solvent; sample may not be suitable for KF titration
SEND RS232	Display remains too long a time. Exit into the specific error message: <clear>
WATER R	The mass of the titrated water exceeds 65 535 µg. (The real mass of titrated water is therefore the sum of the displayed value and 65 535 µg)

6.3 Diagnoseanleitung 684 KF Coulometer

Beinahe alle Störungen am 684 Coulometer entstehen durch Fehlbedienung und -handhabung des Gerätes, der Elektroden, der Lösungen usw. Viele dieser Störungen werden an der Anzeige des KF-Coulometers angezeigt oder sind im Resultat zu erkennen.

Wird aus triftigen Gründen eine Fehlfunktion des 684 Coulometers vermutet, dann hilft die einfach durchzuführende Diagnose mit, die Ursache einzukreisen.

Benötigte Hilfsmittel:

- betriebsbereite Generatorelektrode (oder "Gen. El."-Eingang mit Servicekabel 3.496.5080 [1] kurzschliessen)
- Kabel mit geeignetem Stecker für "Ind. El."-Eingang[2] (z. B. Servicekabel 3.496.5070) [1]
- Widerstandsdekade für Werte 2250 Ω, 3550 Ω, 1300 Ω. Steht keine Dekade zur Verfügung, so können individuelle Widerstände verwendet werden. Siehe Seite 20.
- Bei Geräten mit RS 232-Interface: Datenempfänger (z. B. Drucker)

Vorgehen

- Die Diagnoseschritte sind der Reihe nach auszuführen und mit den Reaktionen des Coulometers (eingerückt) zu vergleichen. Bei Übereinstimmung ist mit der nächsten Anweisung weiterzufahren.

---

[1] Gehört nicht zum Lieferumfang des 684. Kann evtl. aus einer defekten Elektrode angefertigt werden.

[2] Steht kein geeignetes Kabel zur Verfügung: Indikatorelektrode aus der Zelle herausziehen. Dekade oder Widerstandskombination mit Laborkabel und Prüfclips vorsichtig an den Platindrähten der Indikatorelektrode anschliessen. (Achtung: Platindrähte nicht verbiegen!)

Diagnosis Instructions 684 KF Coulometer

Practically all faults occuring with the 684 KF Coulometer are due to false operation or handling of either the instrument, the electrodes, or the solutions etc.. Many of these faults are indicated on the digital display of the KF Coulometer or can be identified from the result.

However, if there is good reason to suspect a fault in the 684 KF Coulometer itself, a short check (Diagnosis) will assist in locating the fault.

Equipment required:

- Generator electrode ready for operation (or short-circuit "Gen. El." input by means of service cable 3.496.5080 [1])
- Cable with suitable plug for "Ind. El." input [2] (e.g. service cable 3.496.5070) [1]
- Resistor switch-box giving values 2250 Ω, 3550 Ω, 1300 Ω. Individual resistors can also be used if no resistor switch-box should be available. See page 20.
- Units with RS 232 interface: data receiver (e.g. printer)

Procedure

- Carry out the test steps one after the other and check the reaction of the Coulometer (indented lines). In case of coincidence carry out the next step.

---

[1] Not included in the scope of delivery of 684. Can possibly be manufactured from a defective electrode.

[2] If no suitable plug is available: Remove the indicator electrode from the cell. Carefully connect the resistor switch-box or the set of 2 resistors to the platinum wires of the indicator electrode with the aid of laboratory cables and test clips. (Please mind: Do not bend the platinum wires!)

- Zeigt das Gerät nicht die erwartete Reaktion, so empfiehlt sich vorerst eine Wiederholung der Diagnose, da auch ein Bedienungsfehler vorliegen könnte (evtl. Gerät aus- und nach einigen Sekunden wieder einschalten). Mehrmalige Falschreaktionen deuten jedoch auf eine Störung hin.

- Sind für genauere Beobachtungen Wiederholungen nötig, so muss bis zum nächsten mit ≫ bezeichneten Wiedereinstiegspunkt zurückgegangen werden. Dabei haben bereits gemachte Eingaben eine entsprechend andere Reaktion des Gerätes zur Folge; bzw. es muss der vor dem Wiederholungspunkt geltende Widerstandswert gewählt werden.

- Bei Rückfragen ist immer die Serienummer des Gerätes sowie evtl. die Nr. des fehlerhaften Diagnoseschrittes anzugeben.

- Eingriffe in das geöffnete Gerät dürfen nur vom METROHM-Service vorgenommen werden!

- If the instrument does not respond as expected repeat the diagnosis to check whether it has been carried out correctly. (Perhaps switch the unit off and some seconds later on again.) If the instrument's response differs repeatedly, the instrument is likely to be defective.

- If repetitions are necessary for more intensive observations, go back to the last re-entry point denoted by the mark ≫. However, consider that new conditions already being keyed-in may give a different reaction to the unit; and / or go back to the resistor value that was selected in the previous steps.

- For inquiries to METROHM always advise the serial number of the unit and possibly also the number of the diagnosis step giving trouble.

- METROHM specialists only are authorized to handle inside the unit!

Vorbereitungen

Die Generatorelektrode bleibt angeschlossen und in die Anolytlösung eingetaucht.

Die Indikatorelektrode wird ausgezogen und an deren Stelle eine Widerstandsdekade mit Hilfe eines Kabels mit geeignetem Stecker [2] (z. B. 3.496.5070 [1]) angeschlossen. Falls keine Dekade zur Verfügung steht, siehe Seite 20.

Ist im Gerät auf Platz F ein RS 232-Interface (3.540.2440) eingesetzt, so muss zu dessen Kontrolle ein Datenempfänger angeschlossen und eingeschaltet sein.

Preparations

The generator electrode remains connected and immersed into the anolyte solution.

Remove the indicator electrode and replace it with a resistor switch-box with the aid of a cable with suitable coaxial plug [2] (e.g. 3.496.5070 [1]). If no decade should be available see page 20.

If the instrument contains an RS 232-interface (3.540.2440) at location F, a data receiver need be connected and switched-on to check the interface.

---

[1] Gehört nicht zum Lieferumfang des 684.
Kann evtl. aus einer defekten Elektrode angefertigt werden.

[2] Steht kein geeignetes Kabel zur Verfügung:
Indikatorelektrode aus der Zelle herausziehen. Dekade oder Widerstandskombination mit Laborkabel und Prüfclips vorsichtig an den Platindrähten der Indikatorelektrode anschliessen.
(Achtung: Platindrähte nicht verbiegen!)

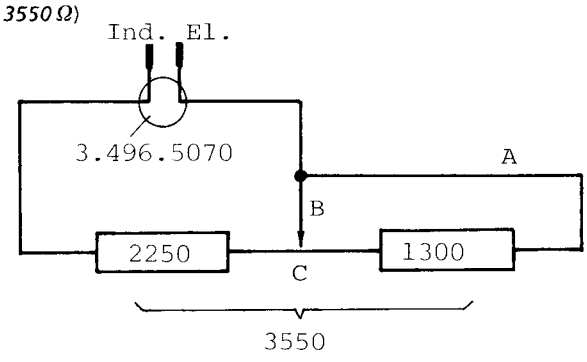
[1] Not included in the scope of delivery of 684.
Can possibly be manufactured from a defective electrode.

[2] If no suitable plug is available:
Remove the indicator electrode from the cell. Carefully connect the resistor switch-box or the set of 2 resistors to the platinum wires of the indicator electrode with the aid of laboratory cables and test clips.
(Please mind: Do not bend the platinum wires!!)

Nur beachten, wenn keine Widerstandsdekade vorhanden:

Alle benötigten Widerstandswerte können mit 2 Einzelwiderständen von 2250 Ω und 1300 Ω (Genauigkeitsklasse 1 %) und entsprechenden Verbindungskabeln (Laborkabel und Anschlussklemmen) erstellt werden. Allerdings darf beim Umstellen auf andere Werte am Elektrodeneingang ***kein Unterbruch*** *(R ≠ ∞) entstehen, was durch Vorgehen nach Anordnungen 1 und 2 möglich ist.*

Anordnung 1 *(Werte 2250 Ωund 3550 Ω)*

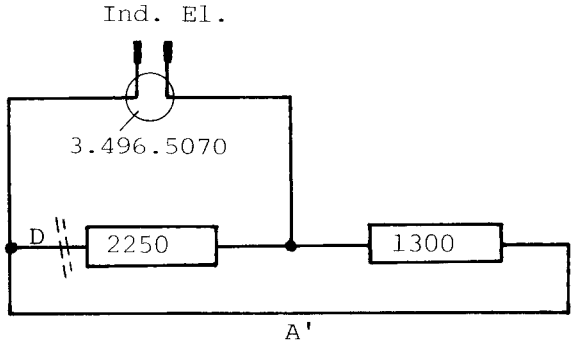


A = Laborkabel
laboratory cable

B – C verbunden = 2250 Ω
B – C unterbrochen = 3550 Ω (Ersatzwert für 3250 Ω)

Der in der Anleitung genannte Wert 3250 Ω muss nicht unbedingt genau stimmen. Es kann daher der Wert 3550 Ω verwendet werden, der sich aus den obigen Widerständen herstellen lässt.

Anordnung 2 *(Wert 1300 Ω)*



Verbindung A (Anordnung 1) auf A' (Anordnung 2) ändern. Dann Verbindung D zum Widerstand 2250 Ω unterbrechen: ergibt 1300 Ω.

To be observed if no resistor switch-box available:

All required resistor values may be obtained with 2 single resistors of 2250 Ω and 1300 Ω (1 % accuracy) and the appropriate connecting cables (laboratory cables and clamps). However, changing the values must be perfomred ***without interruption*** *(R ≠ ∞) at the electrode input. This is possible by observing the arrangements 1 and 2.*

Arrangement 1 *(values 2250 Ω and 3550 Ω)*

B – C connected = 2250 Ω
B – C disconnected = 3550 Ω (replacement value for 3250 Ω)

The value 3250 Ω, mentioned in the following instructions does not have to be absolutely true. The value 3550 Ω can therefore be used instead, which can be made with the above 2 resistors.

Arrangement 2 *(value 1300 Ω)*

Modify connection A (arrangement 1) to A' (arrangement 2). Then disconnect between D and resistor 2250 Ω: giving 1300 Ω.

Diagnoseschritte

1) Dekade auf 2250 Ω

2) Stellung des Potentiometers 'EP Voltage' markieren, dann auf 'High' (Rechtsanschlag) stellen

» 3) Gerät einschalten

Anzeige: 888... / XXX... / I.I... / ADD WATER } 16-stellig } Falls in der Anzeige 'PROGRAMME' erscheint,Service anfordern

Überprüfen, ob alle Stellen der Anzeige richtig angezeigt werden (nötigenfalls aus- und einschalten wiederholen).

4) Dekade auf ≥ 3250 Ω

Anzeige: WAIT XXXXX [3] (Zahl positiv, d.h. ohne negatives Vorzeichen)

5) Dekade auf 2250 Ω

Anzeige: WATER 0 [4]
'piep'

6) Nur wenn RS 232-Interface vorhanden, ausführen; sonst weiter mit Schritt 7!

Tastatur: **send** drücken

LED send leuchtet

» 7) Tastatur: **GO** drücken

Anzeige: ADD SAMPLE

sofort (d. h. innerhalb 6 s) Dekade auf 3250 Ω umschalten

Anzeige: XXXXX [3] (zählt fortlaufend)
Die Grösse der Inkremente ist ungefähr 6 ÷ 12

[3] Die Anzahl Stellen und die Position des Dezimalpunktes ändern mit fortschreitender Titration laufend. Diese Anzeige wird daher generell mit XXXXX angegeben.

[4] Falls 'WATER 0' nicht erscheint, kann die Dekade um ± 50 Ω variiert werden.

Diagnosis steps

1) Resistor switch-box to 2250 Ω

2) Mark the position of Potentiometer 'EP Voltage', then set to 'High' (right stop)

» 3) Switch on unit

display: 888... / XXX... / I.I... / ADD WATER } 16 figures } If 'PROGRAMME' appears in the display, request for service

Check if all the figures of the display are displayed correctly (switch off and on if necessary).

4) Resistor switch-box to ≥ 3250 Ω

display: WAIT XXXXX [3] (positive number, i.e. without negative sign)

5) Resistor switch-box to 2250 Ω

display: WATER 0 [4]
'beep'

6) Carry out if RS 232-interface fitted only otherwise go on with step 7!

key board: depress **send**

send lamp comes on

» 7) Key board: depress **GO**

display: ADD SAMPLE

change immediately (i.e. within 6 s) the resistor switch-box to 3250 Ω

display: XXXXX [3] (counts continuously)
The size of the increments is about 6 ÷ 12

[3] The number of figures and the position of the decimal point change continuously with the progress of the titration. This reading is therefore generally indicated with XXXXX.

[4] Vary the value on the resistor switch-box for ± 50 Ω if 'WATER 0' does not appear.

8) Dekade auf 2250 Ω

'piep'
Anzeige: WATER XXXXX[3)]

Drucker schreibt: `#01 m(H2O) XXXX 3) ug`

Immer wenn ein Resultat gedruckt wird, muss der Wert auf dem Papier mit demjenigen in der Anzeige übereinstimmen.

» 9) Tastatur: **smpl** drücken

Anzeige: SAMPLE 00000

10) Tastatur: **1, 2, 3, 4, 5, enter**

Wert aus Pkt. 8
↓
Drucker: `#01 m(H2O) XXXX ug`
`w(H2O) XXXX ppm oder %`

Anzeige: CONT. XXXX PPM oder P.C.

» 11) Tastatur: **drift** drücken

Anzeige: DRIFT XXXXX (Wert zwischen 00000 und ca. 00100)

» 12) Tastatur: **delay** drücken

Anzeige: DELAY 0003

13) Tastatur: **0, 1, enter** drücken

Anzeige: DRIFT XXXXX

» 14) Tastatur: **delay** drücken

Anzeige: DELAY 01

» 15) Tastatur: **water** drücken

Drucker: `#01 m(H2O) XXXX ug`

Anzeige: WATER XXXXX

» 16) Tastatur: **blank** drücken

Anzeige: BLANK 00000

[3)] Die Anzahl Stellen und die Position des Dezimalpunktes ändern mit fortschreitender Titration laufend. Diese Anzeige wird daher generell mit XXXXX angegeben.

8) Resistor switch-box to 2250 Ω

'beep'
display: WATER XXXXX[3)]

printer: `#01 m(H2O) XXXX 3) ug`

Each time a result is printed out, both the printed value and the displayed value must be identical.

» 9) Key board: depress **smpl**

display: SAMPLE 00000

10) Key board: depress **1, 2, 3, 4, 5, enter**

value from item 8
↓
printer: `#01 m(H2O) XXXX ug`
`w(H2O) XXXX ppm or %`

display: CONT. XXXX PPM or P.C.

» 11) Key board: depress **drift**

display: DRIFT XXXXX (value between 00000 and approx. 00100)

» 12) Key board: depress **delay**

display: DELAY 0003

13) Key board: depress **0, 1, enter**

display: DRIFT XXXXX

» 14) Key board: depress **delay**

display: DELAY 01

» 15) Key board: depress **water**

printer: `#01 m(H2O) XXXX ug`

display: WATER XXXXX

» 16) Key board: depress **blank**

display: BLANK 00000

[3)] The number of figures and the position of the decimal point change continuously with the progress of the titration. This reading is therefore generally indicated with XXXXX.

17) Tastatur: **1, enter** drücken

Drucker: `#01 m(H20) XXXX ug -B`

Anzeige: WATER-B XXXXX

» 18) Tastatur: **smpl** drücken

Anzeige: SAMPLE 12345

19) Tastatur: **enter** drücken

Wert aus Pkt. 17 ↓

Drucker: `#01 m(H20) XXXX ug -B`
`w(H20) XXXX ppm oder %`

Anzeige: CONT.-B XXXX PPM oder P.C.

» 20) Tastatur: **extr** drücken

Anzeige: EXTRACT 0

21) Tastatur: **clear, ·, 1, 2, enter** drücken

Anzeige: CONT.-B XXXX PPM oder P.C.

22) Tastatur: **extr** drücken

Anzeige: EXTRACT 0.12

» 23) Tastatur: **GO** drücken

Anzeige: ADD SAMPLE und sofort Dekade auf 3250 Ω umschalten

Anzeige: EXTRACT . | XXXXX ↓

. 0.06[5] .

. 0.00

zählt im Sekundentakt gegen 0 | Wert ändert laufend, auch wenn EXTRACT-Zeit abgelaufen

24) Dekade auf 2250 Ω

'piep'

Drucker: `#02 m(H20) XXXX ug -B`

Anzeige: WATER-B XXXXX

---

[5] Die Zeit läuft auch während 'ADD SAMPLE'

17) Key board: depress **1, enter**

printer: `#01 m(H20) XXXX ug -B`

display: WATER-B XXXXX

» 18) Key board: depress **smpl**

display: SAMPLE 12345

19) Key board: depress **enter**

value from item 17 ↓

printer: `#01 m(H20) XXXX ug -B`
`w(H20) XXXX ppm or %`

display: CONT.-B XXXX PPM or P.C.

» 20) Key board: depress **extr**

display: EXTRACT 0

21) Key board: depress **clear, ·, 1, 2, enter**

display: CONT.-B XXXX PPM or P.C.

22) Key board: depress **extr**

display: EXTRACT 0.12

» 23) Key board: depress **GO**

display: ADD SAMPLE and switch resistor switch-box immediately to 3250 Ω

display: EXTRACT . | XXXXX ↓

. 0.06[5] .

. 0.00

counts in intervals of 1 s towards 0 | value changes continuously, also when EXTRACT time is elapsed

24) Resistor switch-box to 2250 Ω

'beep'

printer: `#02 m(H20) XXXX ug -B`

display: WATER-B XXXXX

---

[5] The time runs also during 'ADD SAMPLE'

» 25) Tastatur: **extr** drücken

Anzeige: EXTRACT 0.12

26) Tastatur: **–, enter** drücken

Anzeige: WATER-B XXXXX
(Im Wiederholungsfalle kann auch 'DRIFT' angezeigt werden.)

27) Tastatur: **extr** drücken

Anzeige: EXTRACT – 0.12

28) Tastatur: **GO** drücken

Anzeige: ADD SAMPLE und sofort Dekade auf 3250 Ω umschalten

Anzeige: EXTRACT

.	0
.	↓
–0.06[5]	
.	
.	
–0.00	
zählt im Sekundentakt gegen 0	bleibt 0 bis EXTRACT-Zeit abgelaufen, dann laufende Änderung

29) Dekade auf 2250 Ω

'piep'
Drucker: `#03 m(H20) XXXX ug -B`

Anzeige: WATER-B XXXXX

» 30) Tastatur: **blank** drücken

Anzeige: BLANK 1

31) Tastatur: **5, 6, 7, 8, 9, enter**

Drucker: `#03 BLANK ERROR ug`

Anzeige: BLANK ERROR
(Blindwert > Wasserwert)

» 32) Dekade auf 1300 Ω

---

[5] Die Zeit läuft auch während 'ADD SAMPLE'

» 25) Key board: depress **extr**

display: EXTRACT 0.12

26) Key board: depress **–, enter**

display: WATER-B XXXXX
(In case of repetition 'DRIFT' may be displayed.)

27) Key board: depress **extr**

display: EXTRACT – 0.12

28) Key board: depress **GO**

display: ADD SAMPLE and switch resistor switch-box immediately to 3250 Ω

display: EXTRACT

.	0
.	↓
–0.06[5]	
.	
.	
–0.00	
counts in intervals of 1 s towards 0	remains 0 until EXTRACT time is elapsed, then continuous change

29) Resistor switch-box to 2250 Ω

'beep'
printer: `#03 m(H20) XXXX ug -B`

display: WATER-B XXXXX

» 30) Key board: depress **blank**

display: BLANK 1

31) Key board: **5, 6, 7, 8, 9, enter**

printer: `#03 BLANK ERROR ug`

display: BLANK ERROR
(blank value > water value)

» 32) Resistor switch-box to 1300 Ω

---

[5] The time runs also during 'ADD SAMPLE'

33) Tastatur: **GO** drücken

Anzeige: ADD SAMPLE
(nach 6 Sekunden)
SAMPLE UNFIT

34) Indikatorelektrode ausziehen [6]

Anzeige: IND ELECTRODE
(piep)

35) Indikatorelektrode einstecken

Anzeige: BLANK ERROR

» 36) Tastatur: **extr** drücken

Anzeige: EXTRACT – 0.12

Tastatur: **clear, enter** drücken

Anzeige: BLANK ERROR

» 37) (Dekade auf 1300 Ω)

38) Potentiometer 'EP voltage' auf 'low'
(Linksanschlag)

39) *Falls keine Widerstandsdekade vorhanden, bei Punkt 39 den Wert 2250 Ω verwenden und Hinweise Seite 20 beachten!*

Tastatur: **GO** drücken

Anzeige: ADD SAMPLE und sofort
Dekade auf >2000 Ω (jedoch
<10'000 Ω)

Anzeige: XXXXX
.....
Wert ändert laufend

40) Generatorelektrode ausziehen [6]

Anzeige: GEN ELECTRODE
(piep)

41) Generatorelektrode wieder einstecken

Anzeige: BLANK ERROR

Netz AUS

33) Key board: depress **GO**

display: ADD SAMPLE
(after 6 seconds)
SAMPLE UNFIT

34) Unplug indicator electrode [6]

display: IND ELECTRODE
(beep)

35) Plug in indicator electrode

display: BLANK ERROR

» 36) Key board: depress **extr**

display: EXTRACT – 0.12

key board: depress **clear, enter**

display: BLANK ERROR

» 37) (Resistor switch-box to 1300 Ω)

38) Potentiometer 'EP voltage' to 'low'
(left stop)

39) *If no resistor switch-box available, use value 2250 Ω in step 39 and note hints on page 20!*

Key board: depress **GO**

display: ADD SAMPLE and switch
resistor switch-box immediately
to >2000 Ω (but <10 000 Ω)

display: XXXXX
.....
value changes continuously

40) Unplug generator electrode [6]

display: GEN ELECTRODE
(beep)

41) Plug in generator electrode again

display: BLANK ERROR

power OFF

---

[6] Achtung: Stecker sind verriegelt. Bitte an der Hülse ziehen.

[6] Please mind: The plugs are locked. Please pull at the sleeve.

42) Ausdruck mit nachfolgendem Muster vergleichen

```
#01 m(H2O)   118 ug
#01 m(H2O)   118 ug     w(H2O)   9.5 ppm
#01 m(H2O)   118 ug
#01 m(H2O)   117 ug -B
#01 m(H2O)   117 ug -B  w(H2O)   9.4 ppm
#02 m(H2O)   193 ug -B
#03 m(H2O)  54.7 ug -B
#03 BLANK ERROR ug
```

Die unterstrichenen Zeichen sind Resultate. Sie müssen nicht mit dem Muster übereinstimmen.

42) Compare the print out with the following pattern

What is underlined are individual results that need not be identical with the actual ones.

43) Potentiometer 'EP Voltage' wieder auf die vorgefundene Position einstellen.

43) Set potentiometer 'EP Voltage' to the original position again.

Hinweis für den Fehlerfall

Sollte trotz positiver Diagnose die Funktionstüchtigkeit des Gerätes angezweifelt werden, so bestehen noch 2 Fehlermöglichkeiten, nämlich

a) fehlerhafte Generatorelektrode oder

b) fehlerhafter Generatorelektrodenstrom, d. h. Fehler im Gerät.

Aufschluss hierüber gibt die Wiederholung der Diagnose mit einer anderen, guten Elektrode.

Sollte keine zweite Elektrode vorhanden sein, so kann ein Elektrospezialist (Elektroniker oder Betriebselektriker) den Elektrodenstrom überprüfen.

Zusätzlich benötigte Hilfsmittel:

- Servicekabel 3.496.5080 oder 2 gewöhnliche Laborkabel mit Klemmen für den Anschluss am Sockel "Gen. El" im Innern des Gerätes nach Abheben des Deckbleches (2 Schrauben M4)
- Universalinstrument oder Ampèremeter für Messwert 357 mA dc
- Widerstandsdekade oder Einzelwiderstand 6-10 kΩ

Vorgehen:

- Messinstrument mittels Kabel (s. oben) an "Gen. El." anschliessen. dc-Strombereich wählen.
- Punkte 1 bis 4 der Diagnose ausführen
  Anzeige: WAIT XXXXX (Zahlenwert positiv)
  Das Ampèremeter registriert Stromimpulse
- Widerstand an "Ind. El." auf einen beliebigen Wert zwischen 6 und 10 kΩ erhöhen:
  Das Ampéremeter registriert einen konstanten Strom von 357 mA (± 1 mA; Toleranz des Messinstrumentes mitberücksichtigen)
  Richtiger Stromfluss (bei falschem Resultat) deutet auf einen Fehler in der Generatorelektrode hin.

Hint in case of trouble

If the instrument's correct function is called in question despite of faultless diagnosis results, two possible faults are still remaining:

a) faulty generator electrode or

b) incorrect current through the generator electrode i.e. fault inside the unit

Repetition of the diagnosis with another, correct electrode gives the required information.

If there is no second electrode available, an electro specialist (e.g. staff electrician) may check the analytic current.

Additional equipment required:

- Service cable 3.496.5080 or 2 ordinary laboratory cables with clamps to be connected to the "Gen. El." socket inside the unit. This is accessible after removing the cover sheet (2 screws M4)
- Multimeter or ammeter for value 357 mA dc
- Resistor switch-box or individual resistor 6 to 10 kΩ

Procedure:

- Connect measuring instrument to "Gen. El." input by means of cable (see above). Select dc current range.
- Carry out items 1 to 4 of the Diagnosis
  Display: WAIT XXXXX (positive numerical value)
  The ammeter shows current pulses
- Increase the resistance at "Ind. El." to any value between 6 and 10 kΩ
  The ammeter shows a constant current of 357 mA (± 1 mA; note also tolerance of the measuring instrument).

  Correct current (but false result) means faulty generator electrode.

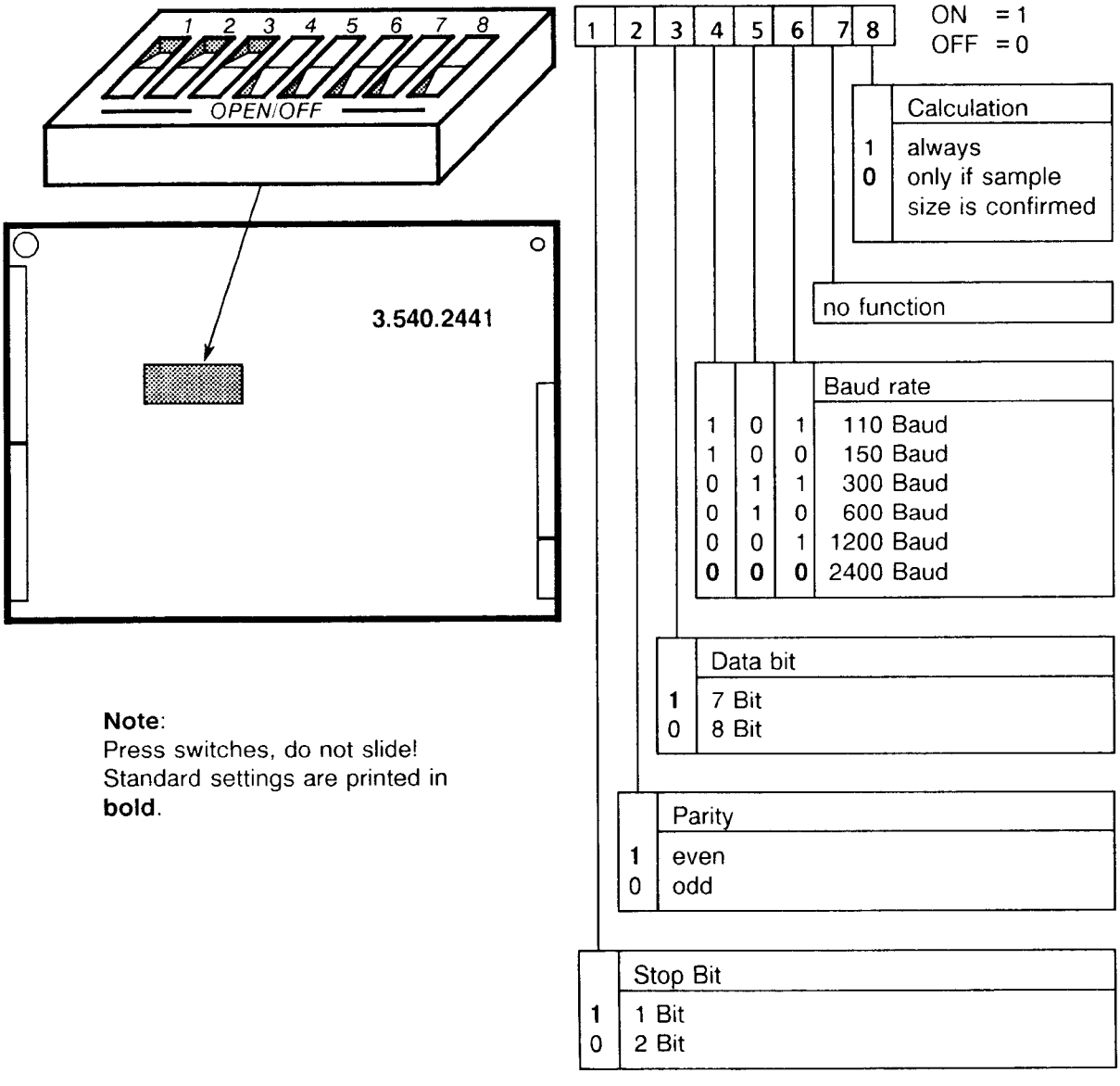
7. 3.540.2441 RS232 interface

7.1 Technical specifications

The interface is configured as DTE (Data Terminal Equipment). Its specifications are according to EIA standard RS 232C (DIN 66020 page 1).

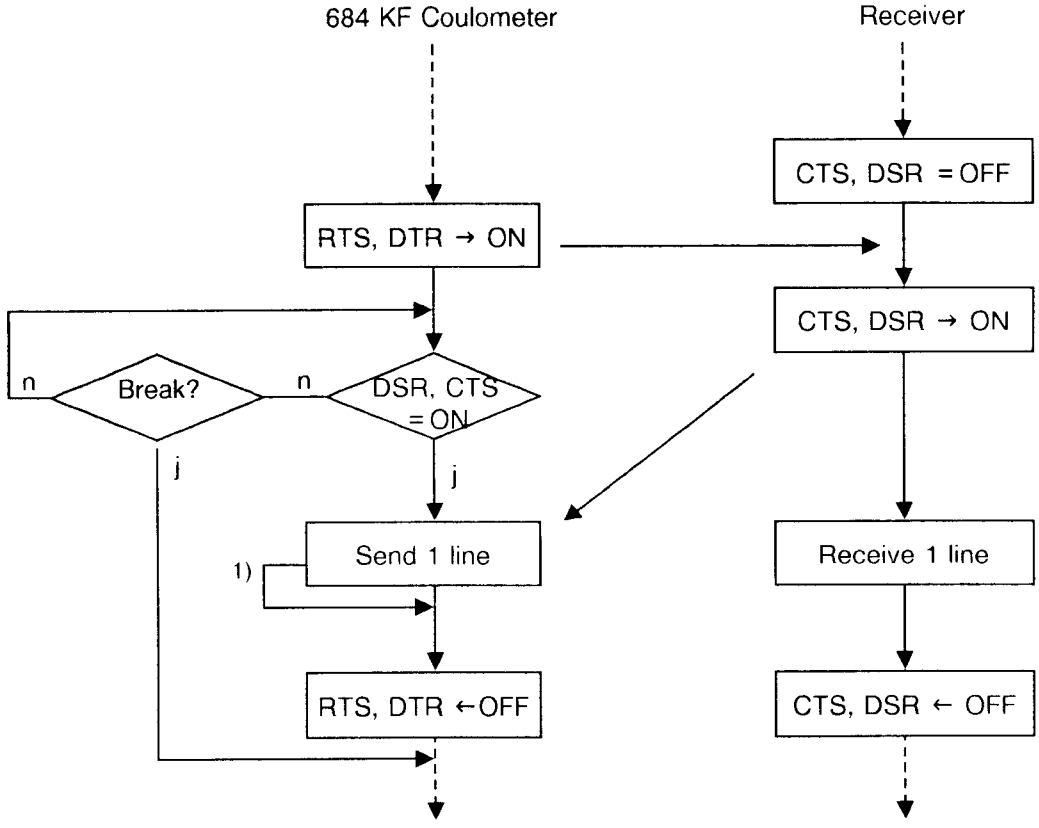
Code:	ISO-7-Bit (ISO 646-1973)
Baud rates:	110, 150, 300, 600, 1200, 2400 (selectable) tolerance < ± 0.9 %
Parity:	even or odd (selectable)
Stop bit:	1 or 2 (selectable)
Data bit:	7 or 8 Bit (selectable)
End of transmission:	C_R and L_F
Cable lengths:	maximal app. 20 m

7.2 DIP switch settings



Note:
Press switches, do not slide!
Standard settings are printed in **bold**.

7.3 Program structure: 684 emits one line



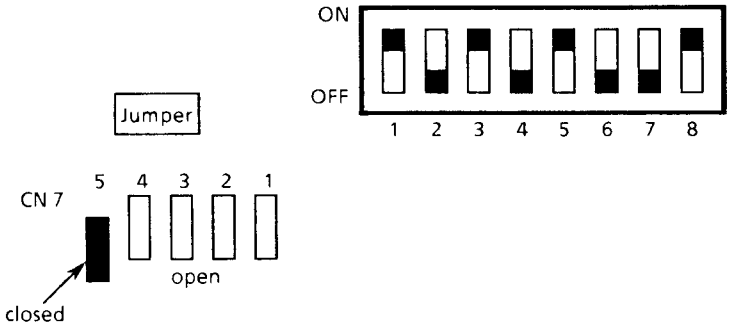
1): Exit if DSR = OFF
All designations (DSR, CTS etc.) are referred to the 684 KF Coulometer as sender.
"Break?" with <clear>, see error messages page 19.

7.4 Examples for the connection of peripheral units

7.4.1 Citizen iDP-560 RS Printer

Cable: 3.980.3550

DIP switch settings at the printer for standard settings on 3.540.2441 interface (see page 30):



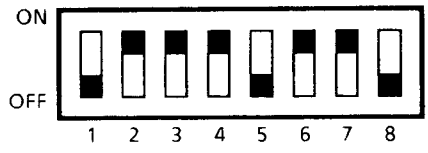
Parameters

Baud rate:	2400
Data bit:	7
Stop bit:	1
Parity:	Even

7.4.2 EPSON P40/P80 Printer

Cable: 3.980.3401

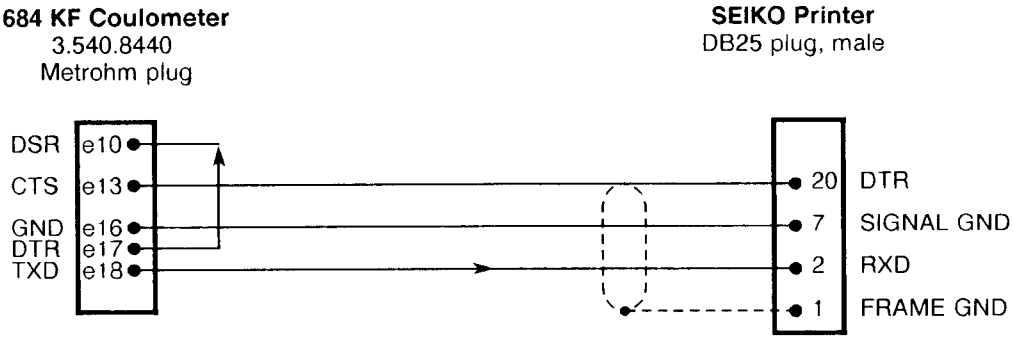
DIP switch settings at the printer for standard settings on 3.540.2441 interface (see page 30):



Parameters	
Baud rate:	2400
Data bit:	7
Stop bit:	1
Parity:	Even

7.4.3 Seiko DPU-411 Printer

Cable:



7.4.4 IBM® PC/XT/PS-2/AT or compatible

Cable: 3.980.3480; for AT with additional 6.2125.010 Adaptor

Example of a data transfer program in GWBasic:

```
100 CLS
110 PRINT "Data Transfer 684 Coulometer ==> PC"
120 PRINT "Cable : 3.980.3480"
130 PRINT "Press <send> key on 684; red lamp must be on"
140 PRINT "Release data transfer by pressing <water> on 684"
150 PRINT "Press <ESC> key on computer keyboard to quit"
160 PRINT
200 OPEN "COM1:1200,E,7,1,CD0,DS0,LF" FOR INPUT AS 1
210 WHILE INKEY$<>CHR$(27)
220   IF EOF(1) THEN 260
230     INPUT #1,A$
240     PRINT A$
250     B$=INPUT$(1,1)                'Remove LF character from COM buffer
260 WEND
270 CLOSE
280 CLS
290 END
```

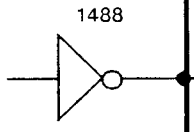
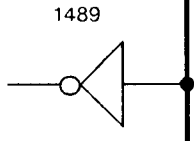
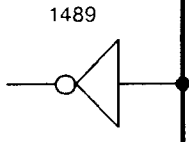
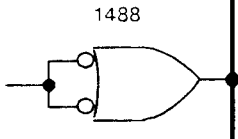
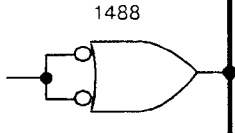
7.4.5 Other peripheral units

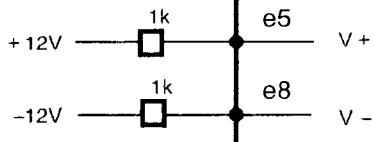
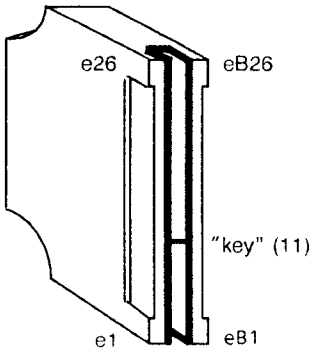
HP calculator with 82939A serial interface	3.980.2810 cable
EPSON Printer with #8148 serial interface	3.980.3550 cable

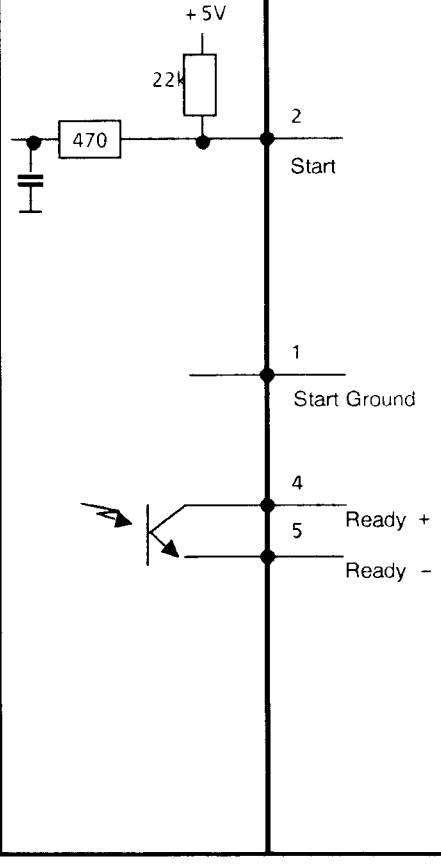
7.4.6 Wiring for operation without handshake

Connect RTS with CTS and DTR with DSR in Metrohm 3.540.8440 plug.
The program receives lines continuously.

7.5 Pin assignment

	3.540.2441	extern
EIA RS-232 C Schnittstelle **EIA RS-232 C Interface**		
Sendedaten (TxD). Erfolgt keine Datenübertragung, wird die Leitung im Zustand EINS" gehalten Daten werden nur gesendet, wenn CTS, DSR, RTS und DTR im "EIN"-Zustand sind. **Transmitted Data (TxD).** TxD is held in marking condition if there is no data transfer. A data transfer occurs only if CTS, DSR, RTS and DTR are in ON condition.		e18 Transmitted Data
Sendebereitschaft (CTS) EIN-Zustand: Gegenstation ist bereit, Daten zu empfangen. **Clear to Send (CTS)** ON condition: The connected device is ready to accept data.		e13 Clear to Send
Betriebsbereitschaft (DSR) EIN-Zustand: Die Übertragungsleitung ist angeschlossen. **Data Set Ready (DSR)** ON condition: Communication channel is connected.		e10 Data Set Ready
Sendeteil einschalten (RTS) EIN-Zustand: Interface ist bereit, Daten zu senden. **Request to Send (RTS)** ON condition: Interface is ready to send data.		e20 Request to Send
Interface bereit (DTR) EIN-Zustand, wenn Interface sendebereit (initialisiert). **Data Terminal Ready (DTR)** ON condition as soon as the Interface is ready to send.		e17 Data Terminal Ready
Betriebserde **Schutzerde.** Direkte Verbindung vom Kabelstecker zur Schutzerde des Gerätes. **Signal Ground** **Protective Ground.** Direct connection from the cable plug to the protective ground of the device.		e16 Signal Ground

	3.540.2441	extern
RS-232 C (Forsetzung) **RS-232 C** (continued from sheet 1) **V+, V-** Für festverdrahtete Kontrollsignale (CTS, DSR). For hardwired Control signals (CTS, DSR). $I_{IH\ 1489A}$ 3 mA (V_{IH} = 12 V), 0.5 mA (V_{IH} = 3 V) $I_{IL\ 1489A}$ -3 mA (V_{IL} = -12 V), -0.5 mA (V_{IL} = -3 V)		
Kontaktanordnung am GS-Direktstecker: **Contact configuration at the PCB direct connector:**  3.540.8440		
Nicht belegte Anschlüsse: **Unused connections:**	e1...e4, e6, e7, e11, e12, e15, e19, e21...e26 eB1...eB26	
Treiber / Driver 1488 Empfänger / Receiver 1489 gemäss EIA RS-232 C Spezifikation in conformance with the specifications of EIA standard № RS-232 C		

	3.540.2441	extern
RS-232 C (Fortsetzung) **RS-232 C** (continued from sheet 2) **Polaritätszuordnung der Signale** - Datenleitungen (TxD) Spannung negativ (<–3 V): Signalzustand "EINS" Spannung positiv (> +3 V): Signalzustand "NULL" - Steuer- oder Meldeleitungen (CTS, DSR, RTS, DTR) Spannung negativ (<–3 V): AUS-Zustand Spannung positiv (> +3 V): EIN-Zustand Im Uebergangsbereich von +3 V bis –3 V ist der Signalzustand undefiniert. **Definition of Signal States** - data interchange circuits (TxD) negative voltage (<–3 V): marking condition positive voltage (> +3 V): spacing condition - timing and control interchange circuits (CTS, DSR, RTS, DTR) negative voltage (<–3 V): OFF condition positive voltage (> +3 V): ON condition The function is not defined for voltages in the transition region between +3 V and –3 V.		
5-polige Buchse **5 pin socket** **Start** Signal muss min. 1.1 s lang anstehen und spätestens 1 s vor Titrationsende zurückgesetzt werden. Set signal for at least 1.1 s and reset signal at the latest 1 s before the titration ends. low level: U <0.2 V I <0.6 mA **Start Ground** **Ready +, Ready –** Aktiv wenn Konditionierung ok, keine Titration gestartet. Nicht aktiv wenn Konditionierung nicht ok oder Titration läuft. Active if conditioning ok, no titration in progress. Not active if conditioning not ok or titration in progress. Aktiv/active: I_C = 12 mA U_{CE} <1.5 V Nicht aktiv/not active: I_C < 10 µA U_{CE} max.30 V		

8. Appendix

8.1 Scope of delivery and ordering designations

KF Coulometer with cell **with diaphragm**: **2.684.0030**
including the following accessories

1	Magnetic Stirrer	1.728.0010
1	Stand rod, 25 cm	6.2016.030
1	Stand rod base for Stirrer	6.2001.040
1	Clamping ring, 10 cm	6.2013.010
1	Connecting cable for stirrer	6.2108.100
1	Titration vessel, 200 ml	6.1415.310
1	Titration vessel lid	6.1414.040
1	Set of O-rings	6.1454.000
1	Double platinum electrode	6.0338.100
1	Electrode cable	6.2104.020
1	Generator electrode	6.0339.000
1	Drying tube	6.1403.030
1	Molecular Sieve 250 g, pore diameter 3 Å (0.3 nm)	6.2811.000
3	Screw nipple	6.2730.010
2	Sets of septa (5 pieces each)	6.1448.010
1	Stirring bar, 16 mm	6.1903.020
1	Stirring bar, 25 mm	6.1903.030
1	Gas inlet tube	6.1617.010
1	Screw cap for sealing gas inlet tube	6.1446.040
1	PTFE connection tube, 10.5 cm	6.1805.070
1	Sleeve for SGJ 19 on Drying tube	6.2713.020
1	Funnel	6.2738.000
1	Syringe, 1 ml	6.2816.000
1	Needle for syringe	6.2816.010
1	Mains cable with plug according to specifications:	
	Typ SEV 12 (Switzerland...)	6.2122.010
	Typ CEE(7), VII (Germany...)	6.2122.030
	Typ NEMA/ASA (USA...)	6.2122.060
1	Plastic dust cover	6.2723.250
1	Instructions for Use for 684 KF Coulometer	8.684.1013

KF Coulometer with **cell without diaphragm** **2.684.0140**
including the following accessories

1	Double platinum electrode with SGJ 14/15	6.0341.100
1	Generator electrode with SGJ 29/22	6.0342.100
1	Drying tube with SGJ 19/17	6.1403.030
1	Glass stopper with SGJ 14/15	6.1437.000
1	Inlet/outlet tube with SGJ 14/15	6.1439.010
1	Stopper with thread M6 for work with the KF Oven	6.1446.060
2	Stoppers with thread M8 for work with a Pump	6.1446.080
2	Sets of septa (5 items each)	6.1448.020
1	Titration vessel, 200 ml, amber glass with SGJ	6.1455.313
1	Tubing connection M6, 10.5 cm, for work with the KF Oven	6.1805.070
1	Tubing connection M8, 50 cm, for work with a Pump	6.1805.200
1	Stirring bar, 25 mm	6.1903.030
1	Titration vessel holder	6.2047.000

1	Electrode cable, plug F, 1 m, for indicator electrode	6.2104.020
1	Electrode cable, plug H, 1 m, for generator electrode	6.2104.120
1	Screw cap	6.2701.040
3	PTFE ground joint sleeves SGJ 14	6.2713.000
1	PTFE ground joint sleeve SGJ 29	6.2713.010
1	PTFE ground joint sleeve SGJ 19	6.2713.020
1	Stopper with nipple	6.2730.030
1	Funnel	6.2738.000
1	Bottle of molecular sieve, 250 g	6.2811.000
1	Syringe, 1 ml	6.2816.000
1	Needle for syringe	6.2816.010
1	Mains cable with plug according to specifications:	
	Type SEV 12 (Switzerland ...)	6.2122.010
	Type CEE(7),VII (Germany...)	6.2122.030
	Type NEMA/ASA (USA...)	6.2122.060
1	Plastic dust cover	6.2723.250
1	Instructions for Use for 684 KF Coulometer	8.684.1013

Options

Ti Stand; compact titration stand with built-in stirrer and pump for aspirating used solution and adding fresh electrolyte	2.703.0010
KF Oven	
707 KF Oven with automatic control of sample boat and built-in air pump	2.707.0010
Connecting cable 684 KF Coulometer – 707 KF Oven	6.2141.000
688 KF Oven	
220...240 V	2.688.0014
100...120 V	2.688.0015
Pump Unit for aspirating of used solution and for producing a dry stream of air for work with the KF Oven	2.661.0010
Measuring cell without diaphragm, complete	6.5405.000
Pump Unit for aspirating used solution and adding fresh electrolyte	
100...120 V, US plug	2.681.0021
220...240 V, Euro plug	2.681.0024
100...120 V, Euro plug	2.681.0025
RS232 interface for connection of a printer or as data transfer interface	3.540.2441
Connecting cable for Citizen iDP-560 RS Printer	3.980.3550
Connecting cable for Epson P40 or P80 Printer	3.980.3401
Connecting cable for Epson Printer with #8148 serial interface	3.980.3550
Connecting cable for IBM® PC/XT/PS-2	3.980.3480
Connecting cable for IBM® AT	3.980.3480 + 6.2125.010
Connecting cable for HP calculator with 82939A serial interface	3.980.2810
Connecting cable for EPSON HX20 calculator	3.980.2890

8.2 Technical specifications

Endpoint indication	voltametric
Titration speed	max. 2 mg/min, near the endpoint the speed is reduced automatically
Range of determination	
Technically possible	1 ... 65 535 µg of water
Usual in practice	10 ... 10 000 µg of water
Resolution	
$m(H_2O) \leq 99{,}9$ µg	0.1 µg
$m(H_2O) \geq 100$ µg	1 µg
Measuring errors	
$m(H_2O) \leq 1000$ µg	≤ app. 5 µg
$m(H_2O) \geq 1$ mg	≤ app. ± 0.5%
Mains supply	
Voltage	100, 117, 220, 240 V ± 10%, with selector switch
Frequency	50 or 60 Hz; for 60 Hz insert bridge no. 1 on print 3.540.2140
Power consumption	app. 40 VA
Fuses	0.4 A (slow) for 100 and 117 V 0.2 A (slow) for 220 and 240 V
Safety specifications	Constructed according to IEC 348, safety class I
Dimensions B × H × T	570 mm × 290 mm × 520 mm
Weight	app. 8.5 kg

8.3 Warranty

The warranty regarding our products is limited to rectification free of charge in our workshops of defects that can be proved to be due to material, design or manufacturing faults which appear within 12 months from the day of delivery. Transport costs are chargeable to the orderer.

For day and night operation, the warranty is valid for 6 months.

Glass breakage in the case of electrodes or other glass parts is not covered by the warranty. Checks which are not a result of material or manufacturing faults are also charged during the warranty period. For parts of outside manufacture insofar as these constitute an appreciable part of our instrument, the warranty stipulations of the manufacturer in question apply.

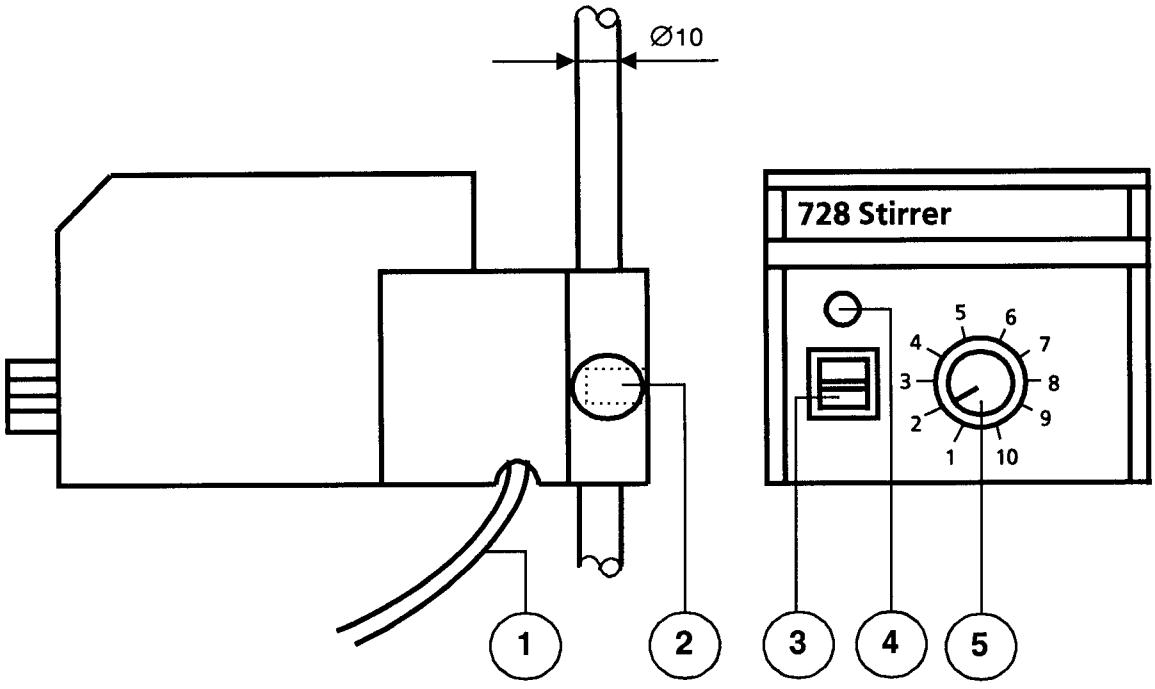
With regard to the guarantee of accuracy, the technical specifications in the Instructions for Use are authoritative.

Concerning defects in material, construction or design as well as the absence of guaranteed features, the orderer has no rights or claims except those mentioned above.

If damage of the packaging is evident on receipt of a consignment or if the goods show signs of transport damage after unpacking, the carrier must be informed immediately and a written damage report demanded. Lack of an official damage report releases METROHM from any liability to pay compensation.

If any instruments and parts have to be returned, the original packaging should be used if at all possible. This applies above all to instruments, electrodes, burette cylinders and PTFE pistons. Before embedment in wood shavings or similar material, the parts must be packed in a dustproof package (for instruments, use of a plastic bag is imperative). If open assemblies are enclosed in the scope of delivery that are sensitive to electromagnetic voltages (e.g. data interfaces etc.) these must be returned in the associated original protective packaging (e.g. conductive protective bag). (Exception: assemblies with built-in voltage source belong in a non-conductive protective packaging). For damage which arises as a result of non-compliance with these instructions, no warranty responsibility whatsoever will be accepted by METROHM.

8.4 Instructions for Use for 728 Magnetic Stirrer



(1) Connecting cable

(2) Fastening screw

(3) On/off switch

(4) Pilot lamp, supply

(5) Regulation of stirring speed

Fastening — The stirrer is mounted on a stand rod Ø = 10 mm. It is fixed at the appropriate height using screw (2) so that it can be swung out to the left or right from the working position.

Power supply — $U_{DC} \approx 8$ V

Stirring speed — stabilised, $n \approx 200$ ..... 1900 min^{-1} (without load)

Stirring bar — PTFE coating, magnetic core

	Length	Dimensions	Shape
6.1903.000	8 mm	Ø = 4 mm	O
6.1903.010	12 mm	Ø = 4 mm	O
6.1903.020	16 mm	Ø = 4 mm	O
6.1903.030	25 mm	Ø = 5 mm	O
6.1906.000	42 mm	-	Δ
6.1906.010	25 mm	-	Δ
6.1906.020	26 mm	-	oval

8.5 Index

Texts in display are designated with /   /, keys with < >.

Ionenanalytik • Analyse des ions • Ion analysis • Análisis iónico
684 KF Coulometer

CE

Metrohm

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EC Declaration of Conformity

The METROHM AG company, Herisau, Switzerland hereby certifies, that the instrument:

684 KF Coulometer

meets the requirements of EC Directives 89/336/EWG and 73/23/EWG.

Source of the specifications:

EN 50081-1	Electromagnetic compatibility, basic specification Emitted Interference
EN 50082-1	Electromagnetic compatibility, basic specification Interference Immunity
EN 61010	Safety requirements for electrical laboratory measurement and control equipment

Description of the instrument:

Instrument for coulometric water determinations according to Karl Fischer.

Herisau, December 6, 1995

Dr. J. Frank	Ch. Buchmann
Development Manager	Production and Quality Assurance Manager