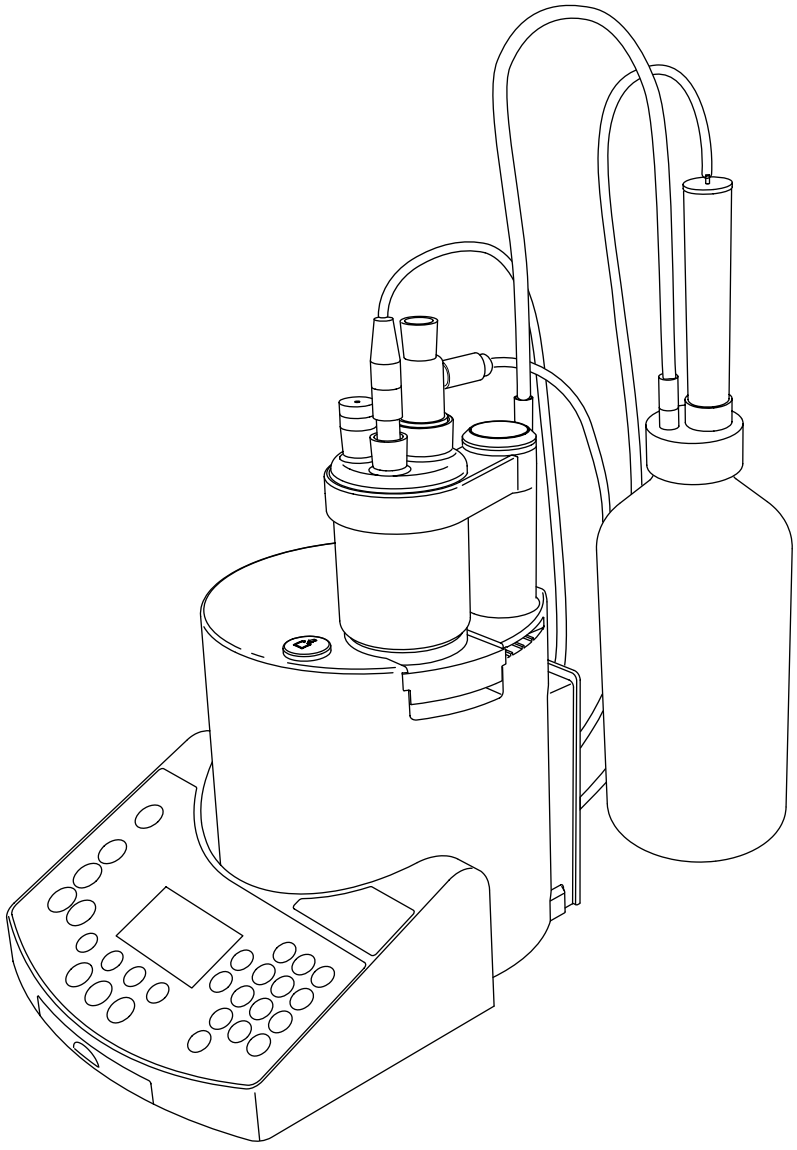
Operating Instructions



KF Coulometer

DL32 / DL39

Contents

1 The KF-Coulometer DL32/DL39

The METTLER TOLEDO DL32/DL39 coulometers are microprocessor controlled analytical instruments which you can use to perform coulometric Karl-Fischer and bromine index determinations simply, quickly and dependably.

You can attach a balance, the METTLER TOLEDO GA42 printer and a computer to the appropriate RS-232C interfaces; an EPSON- or HP-compatible printer can be attached to the Centronics interface and the METTLER TOLEDO drying oven Stromboli to the TTL-interface of the DL39.

The coulometers have a built-in tutorial, which allows you to quickly become acquainted with the instrument's operation and method.

The two coulometers are equal in operation. Differences in hardware and software are mentioned in the corresponding sections.

These **Operating Instructions** correspond to software version 1.1 or higher.

1.1 Where can you find what information?

These **Operating Instructions** and the Help texts integrated in the titrator provide a complete description of the method of functioning of the two titrators. Explanations of parameters contained in the Help text are supplemented here when necessary.

On the **memo card** you can find a short overview of menus and methods.

The **Application Brochure** explains the theoretical fundamentals of the coulometric Karl-Fischer titration as well as the METTLER methods that are in the DL39`s memory.

The **Help texts in the coulometer** provide you with more information or refer you to the Operating Instructions or the Application Brochure.

You will find a detailed description of the communication between the titrator and a computer in the **Description for the computer interface**.

1.2 Coulometric determination of water - principle of measurement

When determining the water content according to Karl Fischer, water reacts with iodine and sulphur dioxide in the presence of an alcohol and a base according to the following reaction:

$H_2O + I_2 + SO_2 + CH_3OH + 3\ RN \rightarrow [RNH]SO_4CH_3 + 2\ [RNH]I$ (1).

For a volumetric titration, iodine is added as titrant. In the case of a coulometric titration, the iodine is generated electrochemically by oxidation at the generator electrode:

$2\ I^- \rightarrow I_2 + 2\ e^-$ (2).

As long as there is water in the anolyte, the generated iodine will react according to reaction (1). I_2 and H_2O react with each other on a 1:1 basis. According to Faraday's Law, the generated amount of iodine is proportional to the electric charge (10.72 mC ≙ 1 µg H_2O). Current consumption, therefore, is a measuring stick for the amount of water.

As soon as all water has been used for the reaction, a small surplus of iodine will develop in the anodic compartment. The iodine surplus is detected by the polarized measuring electrode, and the flow of current to produce iodine is stopped.

METTLER TOLEDO offers generator electrodes with or without diaphragms. In both cases, iodine generation and detection are equal. The various applicabilities are described in the Application Brochure.

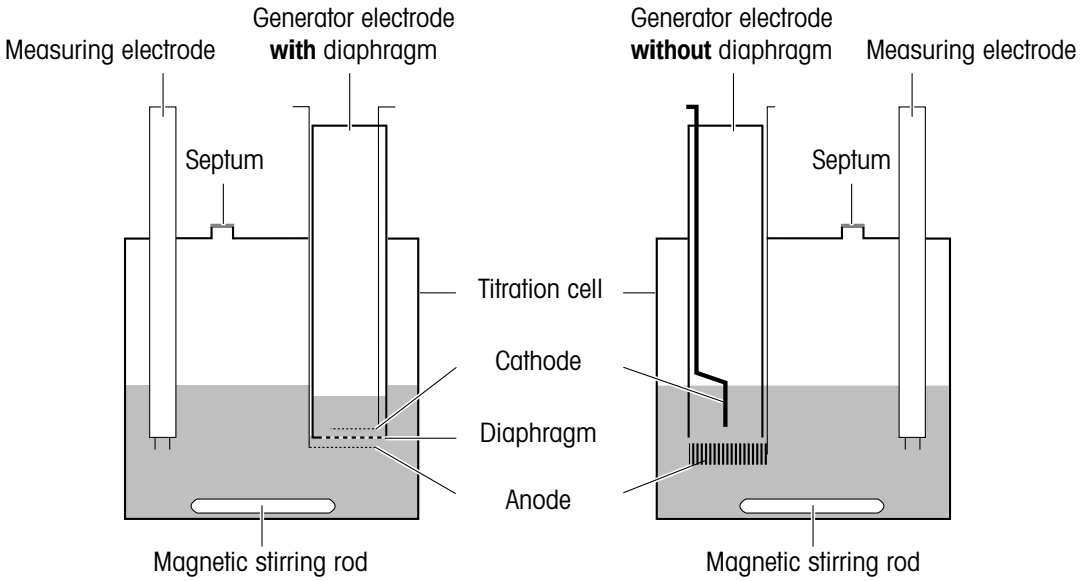
In coulometric bromine index determinations, electrochemically generated bromine reacts with the double bonds of organic compounds:

Br_2 + R1-C=C-R2 → R1-CBr-CBr-R2 (3).

Bromine is, thereby, produced at the anode of the generator's electrode:

$2\ Br^- \rightarrow Br_2 + 2\ e^-$ (4).

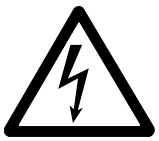
The bromine index [mg bromine / 100 g sample] indicates how much bromine is consumed in the transformation of a sample according to equation (3).



2 Safety Measures

The titrators have been tested for the experiments and intended purposes documented in these Operating Instructions. However, this does not absolve you from the responsibility of performing your own tests of the products supplied by us regarding their suitability for the methods and purposes you intend to use them for. You should, therefore, observe the following safety measures.

2.1 Measures for your protection



Risk of electric shock

- Ensure that you plug the power cable supplied into a receptacle outlet that is grounded! In the absence of grounding, a technical fault could be lethal.

Risk of explosion

- Never work in an environment subject to explosion hazards! The housing of the instrument is not gas tight (explosion hazard due to spark formation, corrosion caused by the ingress of gases).
- When using chemicals and solvents, comply with the instructions of the producer and the general lab safety rules!

All Karl Fischer reagents are readily flammable and toxic.

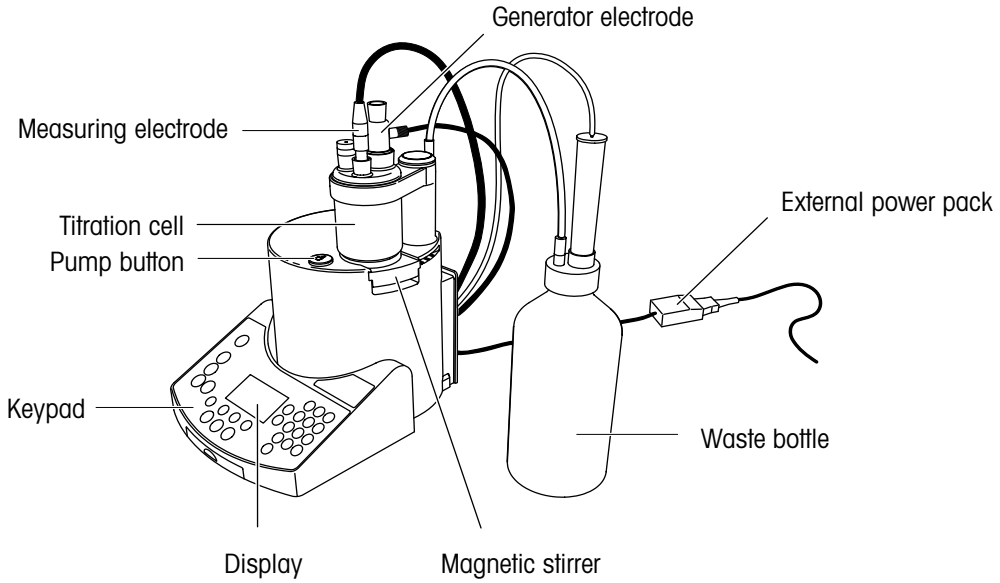
- In the case of skin contact, immediately wash off with copious amounts of water!
- If eye contact occurs, rinse intensively with copious amounts of water and consult a physician!

2.2 Measures for operational safety

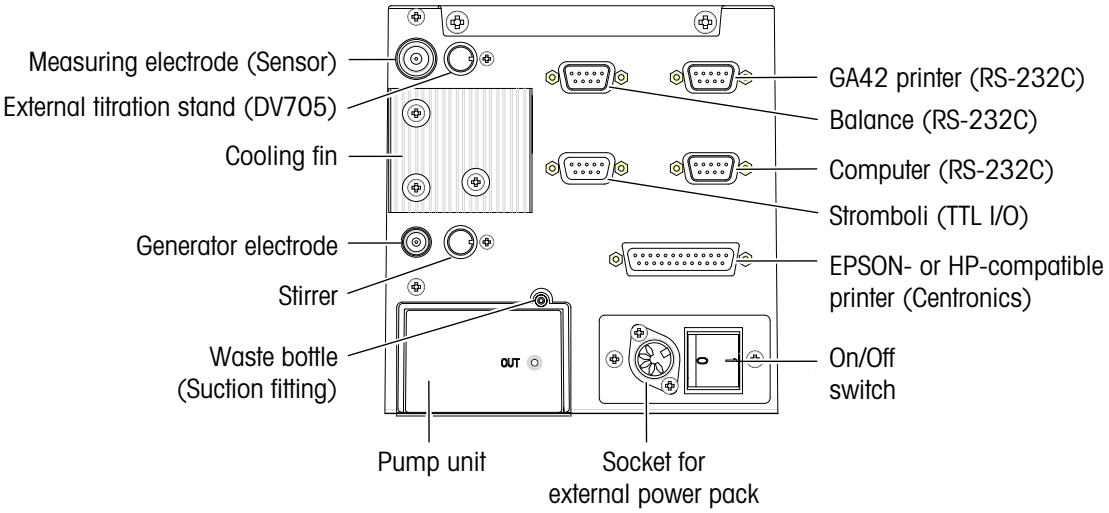
Caution

- Have the instrument serviced by METTLER TOLEDO Service only!
- Always wipe off splashed liquids immediately! The instrument is not waterproof.
- Exclude the following environmental influences:
  - powerful vibrations,
  - direct sunlight,
  - atmospheric humidity greater than 80%,
  - temperatures below 5 °C and above 40 °C,
  - powerful electric or magnetic fields!

3 The Coulometer

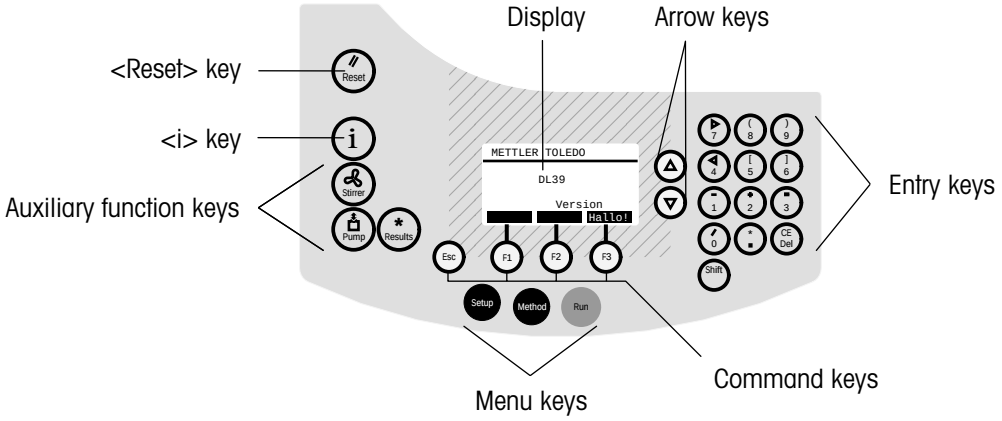


Rear view of instrument with connection diagram



3.1 Putting into operation

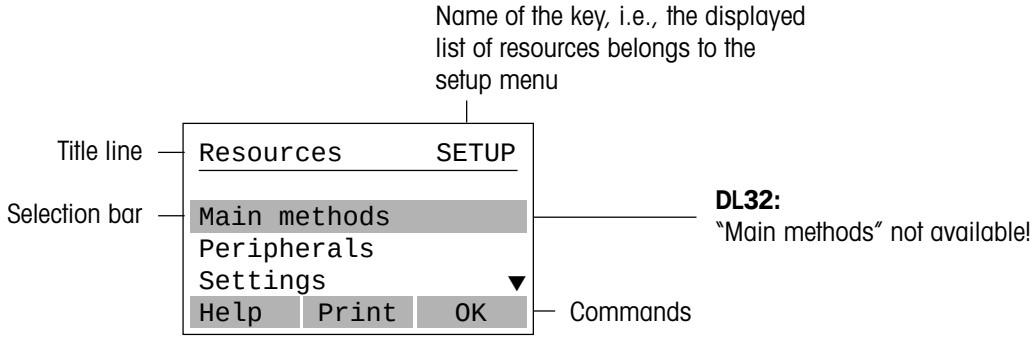
- Connect the supplied external power pack; switch on the coulometer. A self-test is performed before the name of the coulometer appears on the display (example DL39).



After the coulometer has been switched on, the command key <F3>, "Hello!", the <i> key and all menu and auxiliary function keys can be activated.

3.2 The operating concept

- Press, e.g., the setup key:



Now you can also activate the <Reset> key as well as the arrow and command keys.

OK (Press <F3>): The list of selected resources appears.

Print (Press <F2>): The list of selected resources is printed (if a printer has been selected and defined).

Help (Press <F1>): Information about the selected resource appears.

3.2.1 The arrow keys

▲▼ The arrow appears in the display when there are more lines to the list than are visible. When you press the arrow keys (∇Δ) next to the display, the lines are scrolled downwards or upwards. The selection bar is fixed. By pressing <Shift>, ∇ or <Shift>, Δ the lines are moved a page at a time. The commands that can be executed always refer to the line highlighted by the selection bar.

3.2.2 The command keys

The commands, which can be triggered with <F1> … <F3> change according to the selected menu item. The following commands require an explanation:

Hello! When the instrument is delivered, the <F3> command in the initial mask "METTLER TOLEDO…" is assigned to a tutorial menu. This is deleted when you have performed the first titration with the tutorial.

Note You can call up the tutorial at any time with the <i> key.

OK This command is always a confirmation for what you

- wish to view,
- have viewed or entered,
- wish to adopt from a selection.

Modify When this command appears, a

- submenu can appear, which can or must be modified,
- a selection menu appears from which you can or must accept values or names,
- an existing parameter value or name can be directly replaced.

If a value can be modified or entered only with the keypad, the "Modify" command is missing.

ABC This command always appears when you can select letters or characters, e.g., for a name. In this case, you cannot enter numbers until you have confirmed "ABC" (press<F1>).

Help Information about the selected resource appears.

The <Esc> key

If you have made changes in the current menu or submenu, they are discarded, i.e., the original values/names remain. <Esc> returns you to the previous display.

3.2.3 The <Reset> key

The initial mask "METTLER TOLEDO..." reappears: <Reset> is used to terminate analyses or other actions. Data that is not stored is lost.

3.2.4 The <i> key

The value of the current electrolyte capacity, the last drift determination, the last blank value determination for Stromboli (METTLER method 912), the "Hello!" tutorial, and a menu for testing the titrator hardware are accessible with this key.

3.2.5 The menu keys

In order to analyze a sample automatically, the required data must be stored. On the coulometer, this data is assigned to task areas (the menus), and can be accessed with the menu keys. Only the interaction between these menus makes automatic analysis possible.

All resources required for titration such as "Peripherals" and "Settings" are stored in the <SETUP> menu and can be changed.

The sample is determined with the aid of a method. All methods necessary for the different analyses are stored in the <METHOD> menu and can be changed. All resources defined in the <SETUP> menu are available for these methods.

DL32 Only one method can be stored.

DL39 Fifty user methods can be stored.

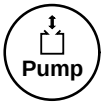
The titration is performed in the <RUN> menu. The method called up determines the analysis sequence.

Note Each menu is subdivided into task areas (submenus), which are designated to menus, lists or masks in these Operating Instructions.

3.2.6 The auxiliary function keys

To activate the stirrer, the pump or to recalculate results, the required commands are also assigned to menus. As they are independent of a sample analysis, but can support it, they are called auxiliary functions. They are accessible under the corresponding keys.

You can switch the stirrer on or off and change the stirring speed.



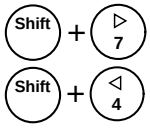
You can siphon off electrolyte from the cell into the waste bottle. By pressing the <Pump> and <F3> keys, "Start" or "Stop" resp., the value of the electrolyte capacity is reset to its initial value.

You can view the result list of analyzed samples, perform recalculations, change the statistical evaluation of a series (DL39 only!) and print out additional reports.

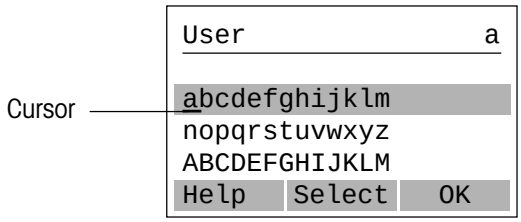
3.2.7 The enter keys

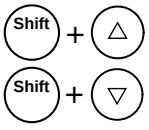
The <Shift> key activates the characters above the numbers.

CE You delete all entered numbers/characters/letters.
Del You delete the number/character/letter last entered.



You move the cursor to the right or left (only if letters/characters are selected), see example:

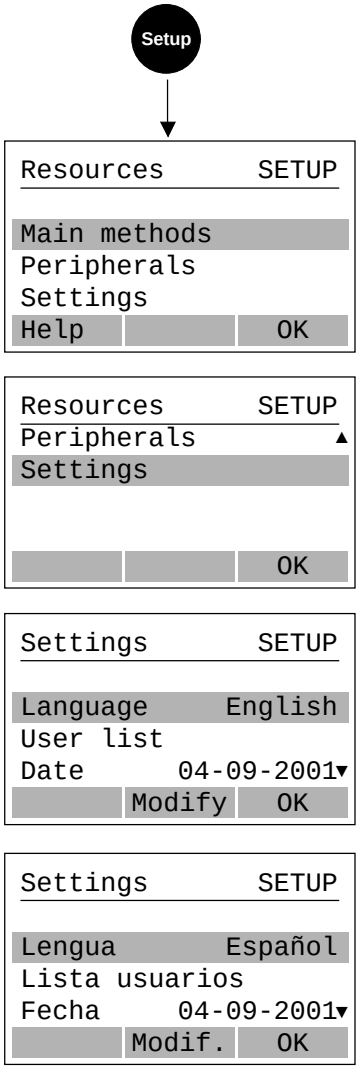




moves the display up by 3 lines,
moves the display down by 3 lines.

3.3 Changing the language

All texts on the coulometer are stored in German, English, French, Spanish, Italian and Russian. If you have not run the tutorial and understand one of the available languages better than the one displayed, you should select it:



– Press the <Setup> key.

– Press <Shift> and the arrow key (-) at the same time in order to scroll down by two lines, so that "Settings" is selected.

– Press <F3>, "OK".

– Press <F2>, "Modify" repeatedly until, e.g., "Español" appears (example).

Pressing "OK" or <ESC> returns you to the "Resources" mask.

OK Spanish text appears.

Esc English text reappears.

4 Setup

In order to perform titrations and to enable data transmission to the peripherals, your coulometer needs to be setup with the necessary resources. In this menu, you define and store these resources.

When you press the <SETUP> key, the list of resources appears:

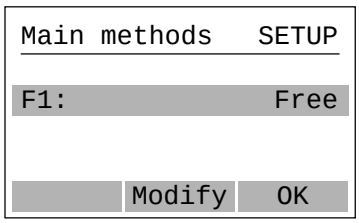
```
Main methods (DL39 only)
Peripherals
Settings
```

You can select the resources with the arrow keys and open the submenu with <F3>, "OK".

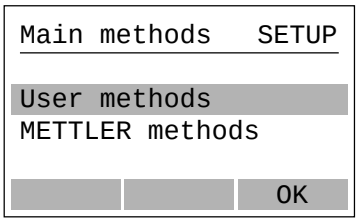
4.1 Main methods (DL39 only)

When the titrator is delivered, the <F3> command is assigned to the "Hello!" tutorial, i.e., you can select its sequence immediately. In this menu you can assign methods to command keys <F1>...<F3> or delete "Hello!".

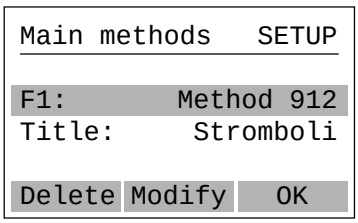
With <F3>, "OK", the following appears (example on delivery of the titrator):



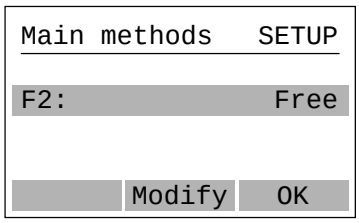
With <F2>, "Modify", the following appears:



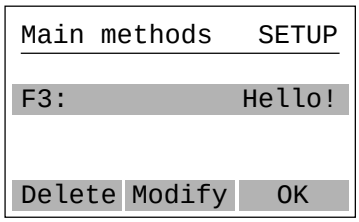
You can select a method from the user methods, if available, or from the METTLER methods (e.g., "METTLER 912 Stromboli":



With <F3>, "OK", the following appears:



You can select a method to configure the <F2> command (Press <F2>, "Modify"). If you confirm this display with <F3>, "OK", the following appears:



You can either delete "Hello!" with <F1> or overwrite it with another method (press <F2>, "Modify").

4.2 Peripherals

With <F3>, "OK", the names of the peripherals you can attach to the coulometer via the RS-232C interfaces or the Centronics interface appear. You must define these and possibly change the preset settings.

```
Printer          None
Balance          None
Titrn stand  Internal
Computer    Not def.
```

4.2.1 Printer

With <F3>, "OK", the name of the printer you connected to the coulometer appears.

```
HP
GA42
EPSON
None
```

If you select the METTLER TOLEDO GA42 there is no need for any further settings. If you select an EPSON- or HP-compatible printer, you must enter the following settings (standard settings for the printer are printed in **bold**).

	HP-compatible	EPSON-compatible
Type	**PCL3+** or PCL3	**LQ/Stylus** or LX/SX
Paper	**Single sheet**	**Single sheet** or Fanfold
Format	**A4** or 81/2 * 11"	**A4**, 81/2 * 11" or 81/2 * 12"
Automatic feed	**Yes**	**Yes** or No

Type Select "PCL3+", "PCL3", "LQ/Stylus" or "LX/SX".

Paper Select "Single sheet" or "Fanfold.

Format
- A4 (width= 21 cm, length= 29,7 cm)
- 81/2 * 11" (width= 81/2 inches, length = 11 inches)
- 81/2 * 12" (width= 81/2 inches, length= 12 inches)

Automatic feed Select "Yes" or "No".

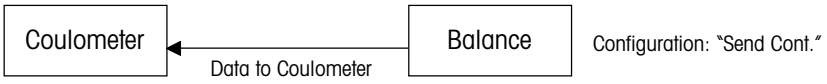
Yes Each report starts on a new page;
with "Paper: Single sheet", a footer is printed out on each page.

No The individual reports are separated by a distance of 2 lines.

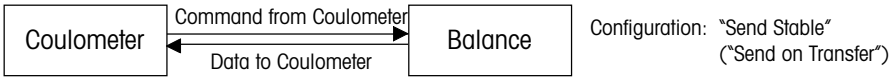
4.2.2 Balance

```
Unidirect.
Bidirect.
None
```

Unidirectional The weight, the balance continuously transfers the current weight value.



Bidirectional On requesting the weight, the balance transfers the current weight value when ordered by the titrator.



For METTLER TOLEDO balances AB, AG, AT and AX always select "Bidirectional".

4.2.3 Titration stand

```
Internal
External
```

You can attach the METTLER TOLEDO DV705 KF titration stand as an external titration stand. Its magnetic stirrer and pump are controlled via the DV705. For use of the coulometric measuring cell on the external titration stand, the titration arm must be exchanged (see optional equipment).

4.2.4 Generator electrode

For the generator electrode (with or without diaphragm) there is no need for any further settings.

Note The maximum value of the current pulses of the generator electrode is 400 mA. If the conductivity of the electrolyte is low and this value can no longer be reached for this reason, the coulometer limits the current pulses to 200 mA.

4.2.5 Computer

```
Defined
Not defined
```

If you connect a computer, you must select "Defined" and possibly change the settings.

Default settings for the computer

```
Baudrate        4800
Parity          Even
Number of data bits8
Number of stop bits1
Character set  ASCII
Start/End     '{'/CR
```

Baudrate Select 1200, 2400, 4800 or 9600.

Parity Select "Even", "Odd" or "None".

Data bits Select 7 or 8 bits .

Stop bits Select 1 or 2 bit(s).

Character set Select "ASCII" or "DL".

Note If you select "DL", you must specify 8 for the number of data bits.

Start/End Select "'{'/CR" or "STX/ETX".

Note You can find additional information on the communication between coulometer and the computer in the "Description for the Computer Interface".

4.2.6 Oven sample changer Stromboli

If you have an oven sample changer Stromboli connected to the DL 39, no further entries are necessary.

4.3 Settings

You can select or define the following settings for the coulometer:

```
Language     English
User list
Date      26-08-2001
Time           10:20
Titrator-ID
Access for    Expert
Beep             Yes
Capacity [mg]     80
Pumping time [s]  60
```

Language Select English, German, French, Spanish, Italian or Russian.

User list Press <F2>, "Modify", and a list of defined names and an empty line appears ("...") where you can enter a new name.

Pres "ABC" and you can enter your name. Erase a selected name with "Delete".

You can then select your name for both the development of a method and the performance of the analysis.

Date You can set the date and select the format.

```
Day               26
Month              8
Year            2001
Format    31-08-2001
```

Format Select "31/08/2001", "08-31-2001", "31-Aug-2001" or "Aug/31/2001".

Time You can set the time and select the format.

```
Hour              10
Minute            20
Format         24 h
```

Format Select between "24 h" or "am/pm".

Titrator ID To enter an identification for your coulometer , press <F1>, "ABC". The ID is always reported.

Access for You can decide whether all persons who work with the coulometer should also have access to the "Setup" and "Method" menus, i.e., have the right to modify resources or methods.

Expert When the coulometer is delivered, you have access to all menus. To change this, select "Routine".

Routine You can:

- in the "Setup" menu, only print out the defined resources and view the list of settings
- in the "Method" menu only print out the list of methods (DL39 only) and each method.
- not perform any recalculations or change any statistical data.
- under the <i> key, select neither the "Tutorial" nor the "Hardware test" .

Renewed access for experts is described on the last page of these Operating Instructions.

Beep You can select:

```
Yes
Minimum
No
```

Yes In addition to those cases described below under "Minimum", a beep also sounds after each keystroke.

Minimum A beep sounds on transition from pretitration to standby, on display of the results and in the case of error messages.

Capacity You can perform several titrations consecutively in the same anolyte. Its capacity, however, is limited. In the vicinity of the capacity limit the reaction rate decreases.

You should enter the value for capacity that the producers of the reagents recommend. When this value is surpassed the message "Capacity exhausted" appears.

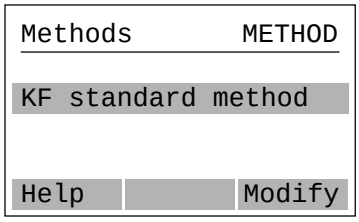
The amount of water (in mg) that has been titrated during the analyses and pretitrations is added up. The difference between the value entered and the titrated water is displayed under the <i> key. Pressing the <Pump> and <F3> keys, "Start" or "Stop" resp., reset the value to its initial setting.

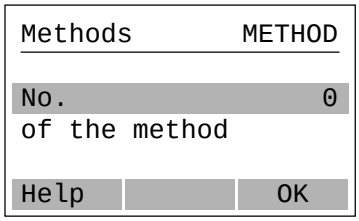
Pumping time The defined time is a safety criterion: the pump will shut off after this time if you, e.g., leave the coulometer while the pump is running.

5 Methods

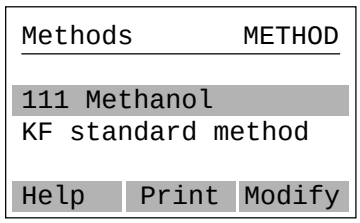
The coulometer automatically performs analyses with the help of predefined methods. On delivery of the instrument

in the **DL32**, the KF standard method specified by us is stored. You can modify this method and save it under a number.

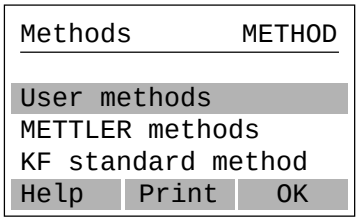




When you have modified and saved the method, the following appears (example):

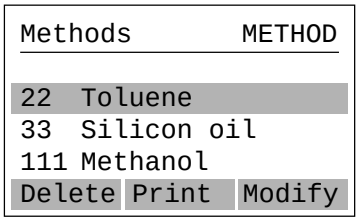


in the **DL39** the KF standard method specified by us and 5 METTLER methods are stored. You can modify these methods and save them as user methods.



Print The list of methods you have developed is printed out.

OK The user methods with their defined numbers and titles appear (example):



A complete titration method comprises sample preparation, mixing and wait times, the actual titration, result calculation and a report. These partial steps are defined in the coulometer as parameters which determine the progress of an analysis.

You modify a method
by changing its parameters.

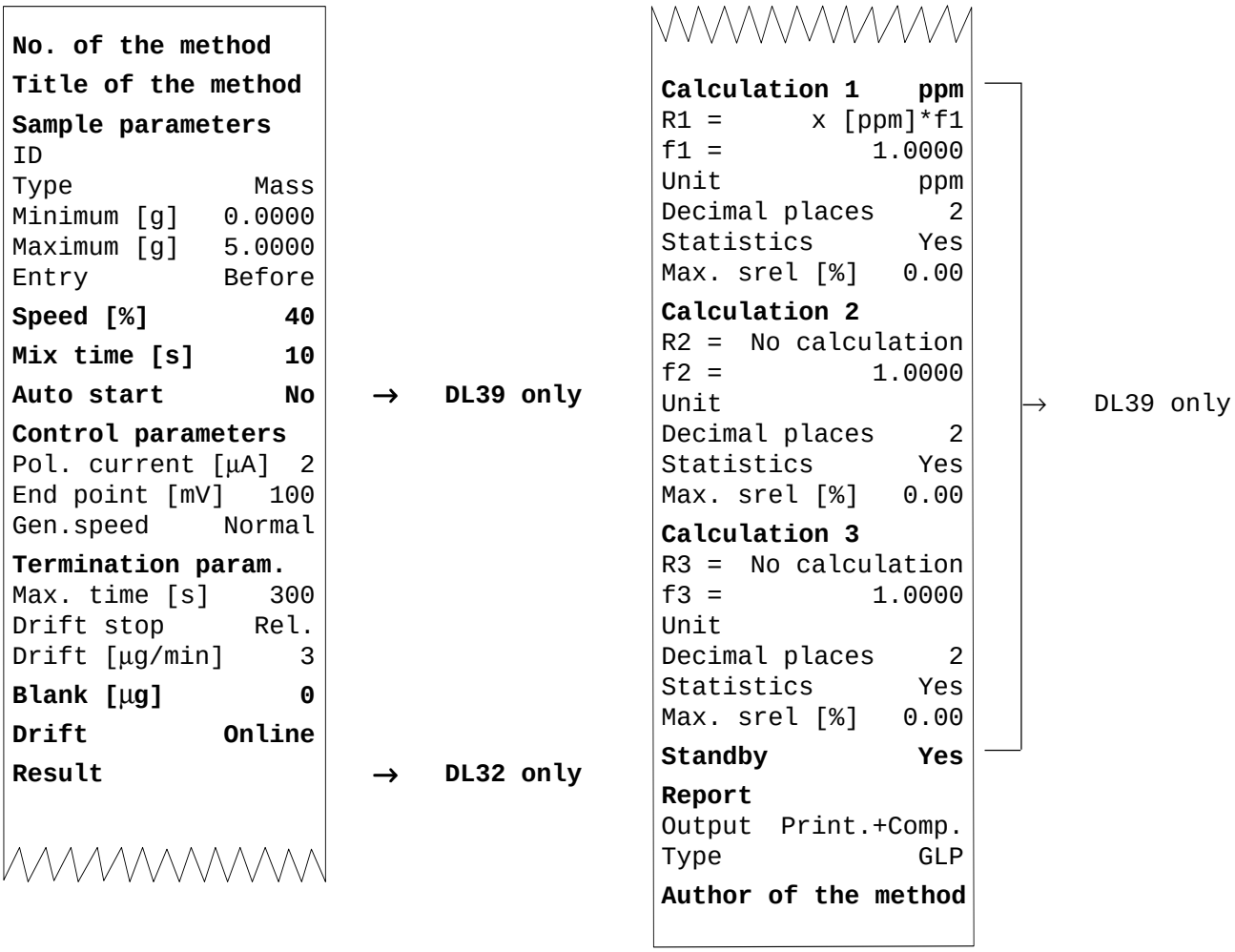
5.1 The KF standard method

You can use the KF standard method to develop your own method. In this you are guided from one parameter to another in the specified order. Exceptions are sample, control, termination and report parameters, which are shown as a group in a mask. In the case of the DL39, this also applies to the calculation parameters.

With the user and METTLER methods, all parameters appear as a list in a mask. Exceptions are again the above-mentioned groups.

The last parameter of a method, "Author of a method", always appears in its own mask.

The method is always shown with the following default parameters.



5.2 KF method parameters

The following parameters can be changed. This will either cause some parameters to appear or disappear. The METTLER methods 911 – 915 and specific parameters for automation with the METTLER TOLEDO oven sample changer Stromboli are described in a separate chapter.

5.2.1 No. (of the method)

The method is stored under the number. The numbers 911 – 915 are reserved for METTLER methods.

5.2.2 Title (of the method)

You can give the method a specific name.

5.2.3 Sample parameters

ID You can enter an identification for the sample(s) now or just before the titration ("Request") for every sample.

Type Select "Mass", "Fixed mass", "Volume", "Fixed volume", "Pieces" or "Fixed pieces".

Minimum/Maximum appears when "Mass", "Volume" or "Pieces" is selected. The unit depends on the type of sample: [g], [mL] or [pcs]..

Help You can calculate and enter values for a fixed or variable amount of sample.

Entry of the amount of sample "Before" or "During" the actual titration. "Entry" appears when "Mass", "Volume" or "Pieces" is selected.

DL39: If you select "Yes" for the parameter "Auto start" (see below), "Before" is automatically converted to "During" when storing.

Density appears when "Volume" or "Fixed Volume" is selected.

Weight appears when "Fixed Mass" is selected.

Volume appears when "Fixed volume" is selected.

Number appears when "Fixed pieces" is selected.

5.2.4 Speed

Stirring should guarantee quick and thorough mixing of the electrolyte. We recommend the setting: 40 %. The magnetic stirring rod should not "jump".

Only use the magnetic stirring rod included in the delivery (see equipment).

5.2.5 Mix time

The time is an empirical value and can be entered individually for the samples ("Request").

5.2.6 Auto start (DL39 only)

Yes The DL39 begins analysis as soon as a sample has been added. The time for adding a sample may not exceed 30 seconds or the instrument will revert to its "Standby" mode.

5.2.7 Control parameters

Pol. current Select 1,2 or 5 µA for polarization current.

End point For the end point we recommend a value of 100 mV.

The recommended values for both types of generator electrodes (with or without diaphragm) are in **bold** print.

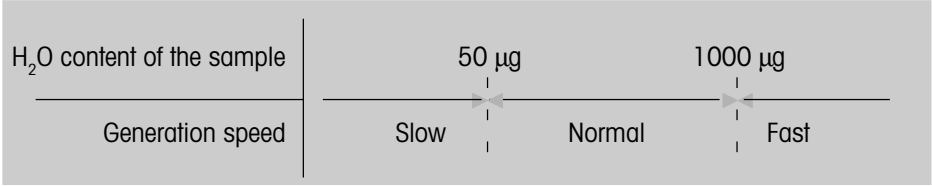
Pol. current [µA]	1	**2**	5
End points [mV]	100	**100**	100

Gen. speed Select "Normal", "Fast" or "Slow" for the titrant generation (iodine or bromine).

Normal This setting is optimized for the determination of water in the µg and lower mg range.

Fast Select this setting for larger amounts of water in order to shorten the analysis.

Slow Select this setting for smaller amounts of water.



5.2.8 Termination parameters

To terminate the titration, you must define "Max. time [s]" **and** "Drift stop" ("Delay" respectively) as a condition. After reaching the end point, the titration is terminated when the first of the selected conditions is met.

Max. time As a safety measure, you must enter a value for the maximum time of analysis. If no end point can be found, the analysis will be terminated after this time has run out.

Drift stop Select "Absolute", "Relative" or "No".

Relative Termination when actual drift is less than the drift measured before the titration(D_0) plus the entered value (D_i): $D < D_0 + D_i$.

Absolute Termination when the drift is less than the entered value (D_i): $D < D_i$.

No "Drift [µg/min]" disappears and "Delay [s]" appears.

Delay If you enter "0" for the delay time, the titration is terminated as soon as the end point is reached. This could result in premature termination of the titration.

5.2.9 Blank

For the entry of a correct value, you should perform a determination. You can enter the value specific to the sample ("Request").

[mg] You can enter a value in the method.

Request Before each titration, the value is requested individually for each sample.

5.2.10 Drift

The drift value is needed for calculation of the result. You can enter a value ("[µg/min]") in the method or just before every titration ("Request") or have it entered automatically:

[µg/min] You can enter a value in the method.

Request Before each titration, the value is requested individually for each sample.

Online The moisture that enters the titration vessel is continuously measured, evaluated and displayed in the standby mode.

Determination Some standard operating procedures require insertion of the value of a drift determination. If you have performed a drift determination, the result is stored under the <i> key and used in the calculation.

5.2.11 Result (DL32 only)

The water content is calculated with the appropriate formula by selection of the unit: [mg], [µg], [%], [ppm], [mg/pc], [mg or µg] and [% or ppm].

[mg or µg], [% or ppm] With the following limit values, the result is automatically set from one unit to the other.

mg		µg	**%**		**ppm**
smaller than 0,1	→	99,..	smaller than 0,1	→	999,..
0,1..	← larger than	100	0,1..	← larger than	1000

5.2.12 Calculation 1 (DL39 only)

R1 Result of the first calculation: The water content is calculated with the appropriate formula by selection of the unit: [mg], [µg], [%], [ppm], [mg/pc], [mg/g], [min], [ppm]ext.extr., [ppm]ext.soln., [%]ext.extr., [%]ext.soln.

[min] Duration of the titration.

[ppm]ext.extr., [ppm]ext.soln., [%]ext.extr., [%]ext.soln. Special calculation for samples that are used after an external extraction or external dissolution. The second and third calculations are needed. See Application Brochure.

Unit You can enter a user-defined unit (e.g., "g" if you define a factor of 0.001 for the calculation of the H_2O content in [mg]) .

Statistics To obtain the mean value $\bar{x}$, the standard deviation s and the relative standard deviation srel, of a sample series, you must select "Yes". You can terminate a sample series using the auxiliary function "Results".

Max. srel If the entered value for the max. relative standard deviation is exceeded, a message appears.

5.2.13 Calculation 2 / Calculation 3 (DL39 only)

The available parameters are the same as for calculation 1. Instead of a formula, you can select "No calculation". The water content is calculated with the appropriate formula by selection of the unit:
[mg], [µg], [%], [ppm], [mg/pc], [mg/g], [min].
The following units are missing: [ppm]ext.extr., [ppm]ext.soln., [%]ext.extr., [%]ext.soln.

Note You cannot determine samples from an external extraction or dissolution in the routine mode as you must enter the amount of sample for the extraction/dissolution and the amount of solvent under calculation 2 and 3.

5.2.14 Standby

Yes After a titration, the cell is kept anhydrous. We recommend allowing the standby titration to run even during lengthy pauses so that you can start the next titration at any time.

No After a titration the start mask of the analysis menu reappears.

[min] After the sample determination, a switch is made to the standby mode and the subsequent rate of consumption is displayed and printed out every minute for the defined time.

5.2.15 Report

Output Select "Printer", "Computer" or "Print.+Comp." as output device.

Type

DL32 Select "GLP", "None" or "Short-form.

DL39 Select "GLP", "GLP+curves", "None" or "Short-form". Curves can only be printed out on an EPSON or HP compatible printer.

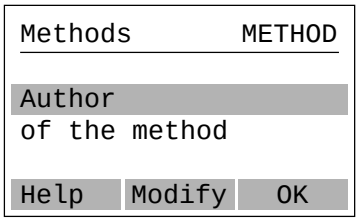
(GLP report: All data which is required by the rules of Good Laboratory Practice.)

5.2.16 Author of the method

By selecting your name from the user list, you can document that you are responsible for the development of the method.

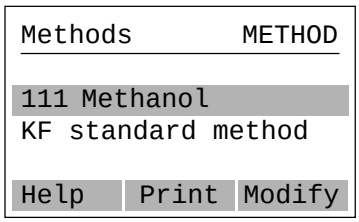
5.3 Storage procedures

The following always appears as the last parameter of a method:

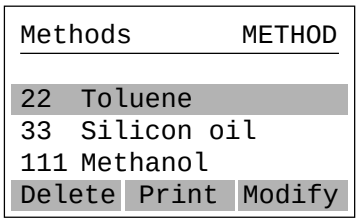


The modified method is stored when you confirm by pressing <F3>, "OK". Examples:

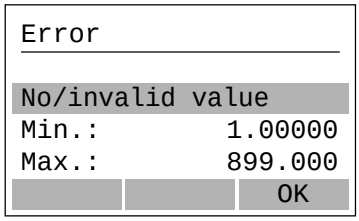
DL32



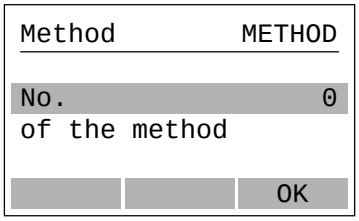
DL39



If you have not entered any or a wrong method no., the following appears:

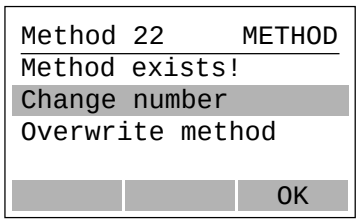


– Confirm the error message by pressing <F3>, "OK".



– Enter the number and confirm by pressing <F3>, "OK". The method is stored.

If you have entered a method no. that already exists (DL39 only), the following appears:



Change number The mask "No. of the method" reappears. You can now enter a new number.

Overwrite method The new or modified number is stored. The old method with the same number is overwritten.

While you are modifying a user or a METTLER method, you can press the <Run> key in order to start an analysis (the <Setup> and <Auxiliary functions> keys are blocked).

- If you have not yet modified any parameter of the method, the start mask of the "Analysis" menu appears.
- If you have already modified a parameter of the method, the mask "Author of the method" appears. The method is stored with <F3>, "OK", and the start mask of the "Analysis" menu is displayed.

5.4 User and METTLER Methods (DL39 only)

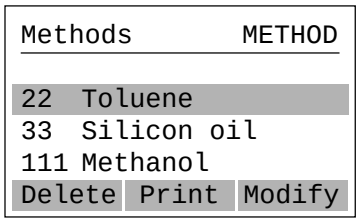
The following methods have been developed by us and can be performed immediately (see Application Brochure):

```
911     Standard 1.0
912        Stromboli
913        Ext.Extr.
914         Br Index
915         Br Blank
```

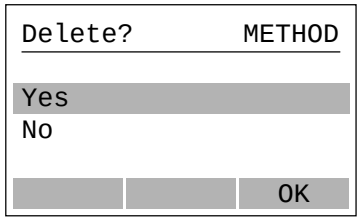
You can modify METTLER methods, but in this case you must always give them a new number (1 – 899) so that they are stored as **user methods**.

You can print out the selected methods by pressing <F2>, "Print".

User methods can be deleted (only in expert mode).



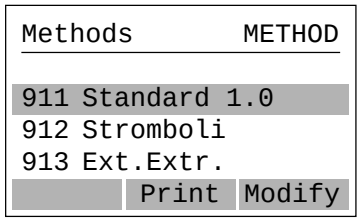
If you press <F1>, "Delete", the following appears:



Yes Pressing <F3>, "OK", will delete the method.

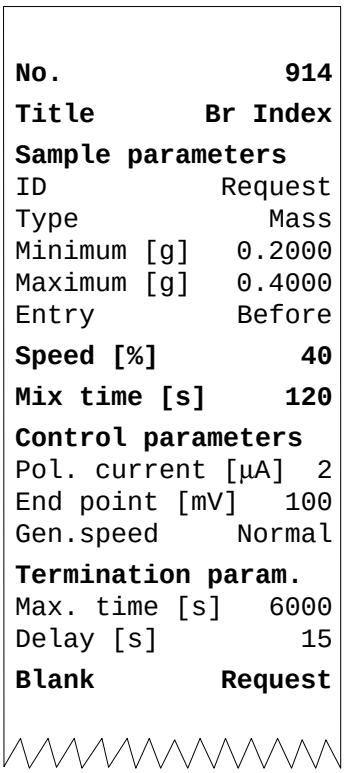
No Pressing <F3>, "OK", will bring up the list of methods. The method is not deleted.

METTLER methods **cannot** be deleted.

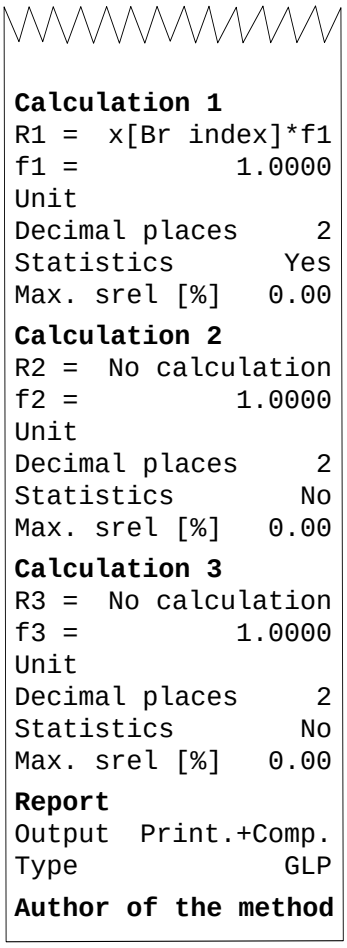


5.5 METTLER methods “914 Br index” and “915 Br Blank” (DL39 only)

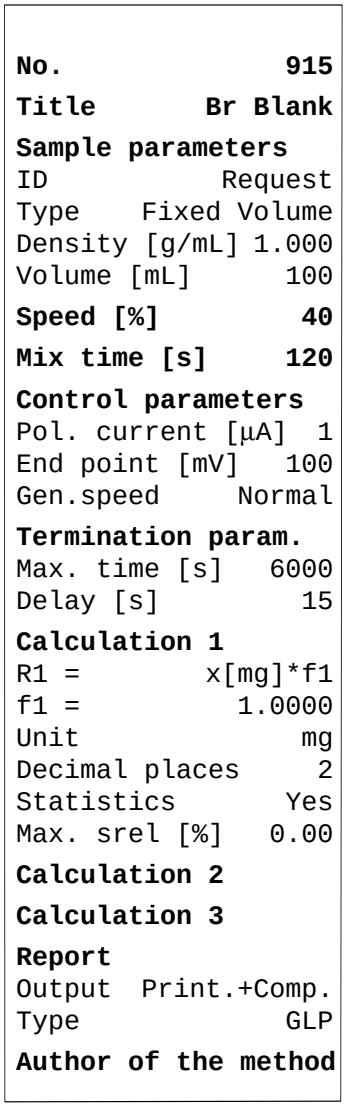
If you wish to develop a bromine index determination to meet your requirements, you can modify METTLER method 914 and 915 and store them as user methods.



No.	**914**
Title	**Br Index**
Sample parameters	
ID	Request
Type	Mass
Minimum [g]	0.2000
Maximum [g]	0.4000
Entry	Before
Speed [%]	**40**
Mix time [s]	**120**
Control parameters	
Pol. current [µA]	2
End point [mV]	100
Gen.speed	Normal
Termination param.	
Max. time [s]	6000
Delay [s]	15
Blank	**Request**



Calculation 1	
R1 =	x[Br index]*f1
f1 =	1.0000
Unit	
Decimal places	2
Statistics	Yes
Max. srel [%]	0.00
Calculation 2	
R2 =	No calculation
f2 =	1.0000
Unit	
Decimal places	2
Statistics	No
Max. srel [%]	0.00
Calculation 3	
R3 =	No calculation
f3 =	1.0000
Unit	
Decimal places	2
Statistics	No
Max. srel [%]	0.00
Report	
Output	Print.+Comp.
Type	GLP
Author of the method	



No.	**915**
Title	**Br Blank**
Sample parameters	
ID	Request
Type	Fixed Volume
Density [g/mL]	1.000
Volume [mL]	100
Speed [%]	**40**
Mix time [s]	**120**
Control parameters	
Pol. current [µA]	1
End point [mV]	100
Gen.speed	Normal
Termination param.	
Max. time [s]	6000
Delay [s]	15
Calculation 1	
R1 =	x[mg]*f1
f1 =	1.0000
Unit	mg
Decimal places	2
Statistics	Yes
Max. srel [%]	0.00
Calculation 2	
Calculation 3	
Report	
Output	Print.+Comp.
Type	GLP
Author of the method	

Pretitration This parameter is not applicable.

Autostart This parameter is not applicable.

Pol. current Measurement results and endurance of the measuring electrode are ideal at a polarization current of 1µA.

Gen. rate The speed of bromine generation at the anode of the generator electrode. For bromine determinations the setting is fixed at “Normal”.

Delay Desired time of delay [s] after reaching the end point. Drift and driftstop are not applicable.

Blank The value determined as a blank (METTLER method “915 Br Blank”) can be determined before the start of an analysis in the method, or it can be entered before the titration (“Request”).

Drift This parameter does not apply because bromine determinations do not have a drift.

R1 Result of the first calculation: the bromine index [Br-Index] is calculated according to the selected formula.

Unit The bromine index and the bromine number are quantities without dimension.

The bromine index is the amount of bromine in [mg] reacting with 100 g of sample.

The bromine number is the amount of bromine in [g] reacting with 100 g of sample.

Standby This parameter does not apply.

Author "Author of the Method" only appears if you change the method.

Specific parameters for the blank determination with "915 Br Blank".

Type Select "Fixed volume" because the measuring cell is filled with 100 mL of solvent.

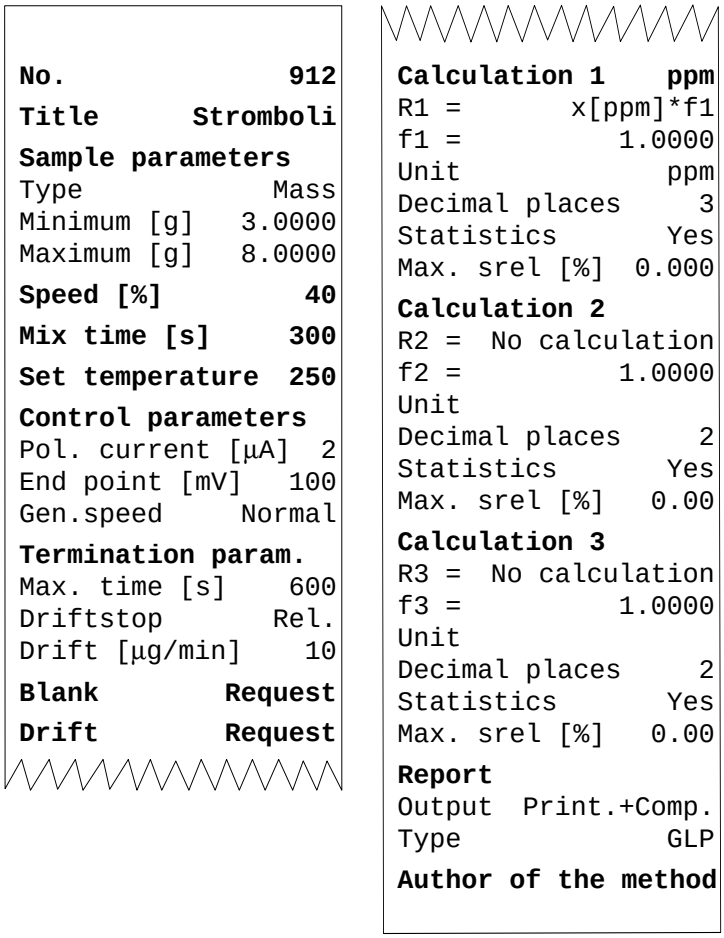
Volume Select "100" because the measuring cell is filled with 100 mL of solvent.

Blank This parameter does not apply.

R1 The blank value is measured in [mg] and is needed for the calculation of the bromine index.

5.6 METTLER Method “912 Stromboli” (DL39 only)

If you wish to develop an automatic determination of the water content of thermally stable liquids or solids, you can modify the METTLER method "912 Stromboli" and store it as a user method.



No. 912
Title Stromboli
Sample parameters
Type Mass
Minimum [g] 3.0000
Maximum [g] 8.0000
Speed [%] 40
Mix time [s] 300
Set temperature 250
Control parameters
Pol. current [µA] 2
End point [mV] 100
Gen.speed Normal
Termination param.
Max. time [s] 600
Driftstop Rel.
Drift [µg/min] 10
Blank Request
Drift Request

Calculation 1 ppm
R1 = x[ppm]*f1
f1 = 1.0000
Unit ppm
Decimal places 3
Statistics Yes
Max. srel [%] 0.000
Calculation 2
R2 = No calculation
f2 = 1.0000
Unit
Decimal places 2
Statistics Yes
Max. srel [%] 0.00
Calculation 3
R3 = No calculation
f3 = 1.0000
Unit
Decimal places 2
Statistics Yes
Max. srel [%] 0.00
Report
Output Print.+Comp.
Type GLP
Author of the method

Sample parameters The sample parameter "ID" and "Entry" are not applicable.

Mix time The time (in seconds) during which the water in the sample evaporates completely and dissolves into the solvent in the measuring cell.

Autostart This parameter is not applicable because the sequence of the sample series is controlled automatically.

Set temperature Enter the set temperature in °C at which the H_2O determination is to be performed. The set temperature can be selected anywhere between 50 and 300 °C. This value cannot be changed within a series. The set temperature is noted in the titration report.

Blank The blank value [µg] is made up of the H_2O content of the carrier gas (time dependent) and the H_2O content of the sample vial (time independent). The termination is like a "normal" sample determination with defined method parameters and, therefore, can be integrated into the sequence of a series. Drift is deducted from the result making the blank an absolute value independent of time. The blank value for Stromboli can be viewed at any time by pressing the <i> key.

Determination The value is automatically determined before the sample series and stored for calculating the results.

Request The value is requested before the series.

No The most recently stored value is used.

Note For a onetime blank determination for various sample series the blank value can be determined individually. To do this, a method is built selecting "Determination" for the blank parameter. When prompted to enter the number of samples under the sample parameters, enter "0". The resulting blank value is stored, i.e., it is available for all following sample series and can be viewed at any time by pressing the <i> key."

Drift The drift can be determined manually in the standby mode at any time (press <F1>, "Drift"), or automatically before each series.

Determination Value is determined automatically before the sample series and stored for the calculation of the results.

Request Value is requested before the series.

No The most recently stored value is used.

Standby This parameter is not applicable because no post consumption measurement is performed.

Report The results are printed at the end of a series.

Author "Author of the Method" only appears if you modify the method.

At the beginning of a sample series, the following parameters are required as long as "Request" has been selected for them in the method.

Blank [µg]

Drift [µg/min]

ID (text)

Number of samples (max. 13)

Sample parameter (mass, volume, pieces, etc.)

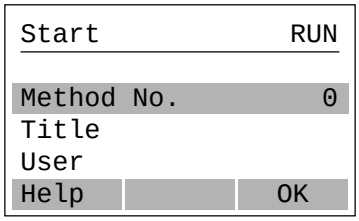
6 Analysis (Run)

You perform titrations with a selected method. The required data is stored in the "Method" and "Setup" menus. While an analysis is running, all menus and auxiliary functions are blocked.

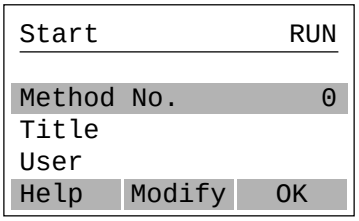
6.1 Starting a method

When you press the <Run> key, the start mask appears:

DL32



DL39



The method number

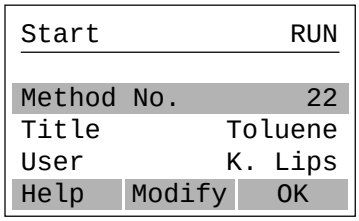
- of "0" is entered if no method (**DL32**) or no user method (**DL39**) is stored.
- of the stored method (on the **DL32**) is always automatically entered together with the title.
- on the **DL39** is always the number you either entered directly or accepted from a METTLER or user method.

Notes

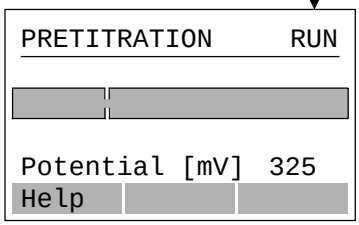
- You can select the user name. The name that was selected in the analysis last performed remains stored.
- **DL39:** The start mask always shows the number of the method with which an analysis was last performed, e.g., method no. 22. If you delete this, "Method not available" appears when you confirm the mask with "OK".

6.1.1 Menu sequence up to standby mode (KF methods)

Example:



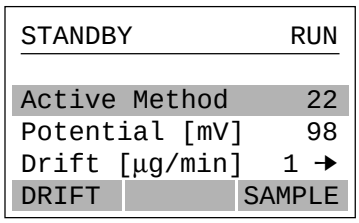
You start the pretitration by pressing <F3>, "OK", (DL32: "Modify" is missing).



Pretitration is always executed with the control parameters of the selected method. The electrolyte is titrated until anhydrous.

The actual potential is displayed.

Transition to standby mode is automatic.



The arrows beside the drift value indicates the drift status:

↘ Wait. Drift is decreasing!

→ This arrow indicates that you can start a determination.

↗ Wait. Drift is increasing!

Start a drift determination by pressing <F1>, "DRIFT".

Start a sample determination by pressing <F3>, "SAMPLE".

Note If the pretitration lasts longer than 30 minutes, a message appears. After confirmation with "OK", the pretitration starts again. In such a case, you should check whether, e.g., all connections of the titration stand and cell are tight.

6.1.2 Standby mode

During standby, the following menus are blocked or selectable:

Blocked <Setup>, <Pump> and, via the <i> key: "Hello!" and "Hardware test".

Selectable <Stirrer>, <Results>, <Method>, <RUN> and <i> key (except "Hello!" and "Hardware test".

Stirrer

You can change the speed of the stirrer. This is reported for the subsequent sample determination.

Results

The menu is not shown until you have performed the first measurement or a result is available.

Method

You can modify all methods. Within the **active** method, you **cannot** modify the following parameters:

- Polarization current
- End point

The modified parameters are adopted for the next sample. For documentation conforming with GLP, you should print out the method before you switch back to the "Run" menu.

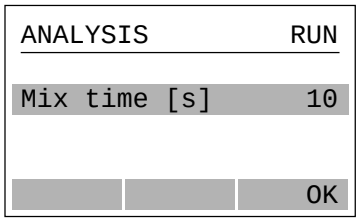
Note (DL39 only) If you change parameters of an active method, the sample series will be terminated. If you restart a method, the results of the current series are deleted.

6.2 Sample determination

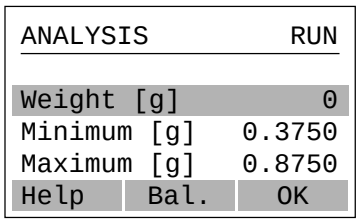
With <F3>, "OK", or <Run> you start a sample determination. According to the selected method, the following masks may appear.

In succession, specific parameters are requested if defined in the method as "Request".

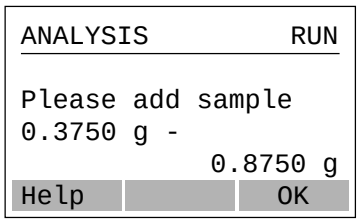
Example:



Then one of the following mask appears:



The mask for the sample entry appears if a variable amount of sample is defined with "Entry: Before".



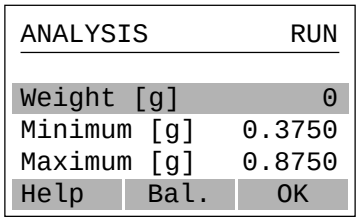
The mask for sample addition appears if a variable amount of sample is defined with "Entry: During" (example: mass)

Note

- If you take longer than five minutes for the entry of samples or sample-specific parameters, the coulometer switches back to the standby mode.
- If you have selected "Autostart: Yes" in the method, the sample must be added within 30 seconds. Otherwise, the coulometer returns to the standby mode.
- If you accidentally add a sample while the titrator is in the standby mode, the coulometer will begin a "Pretitration", i.e., it will titrate all the water out of the sample. You can salvage the situation ("Emergency analysis") by pressing the <RESET> key first and then the <SHIFT> and <RUN> keys simultaneously. One of the above displays will appear, i.e., pretitration and standby mode are skipped. Thus, your sample is not "lost".

Sequence of sample determination

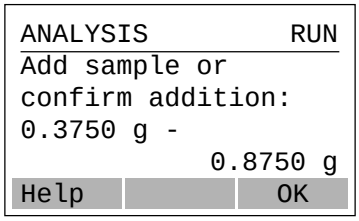
Example (with "Weight: before"):



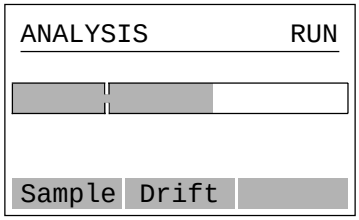
The values and the limits for the weight are adopted from the defined sample parameters of the method.

If you have attached a balance, you can transfer the value displayed on the balance (weight of the sample) by pressing <F2>, "Balance".

Pressing <F3>, "OK", will bring up the following mask appear.

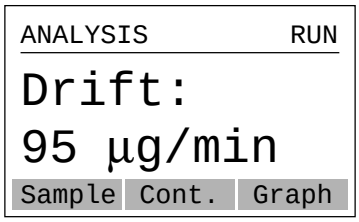


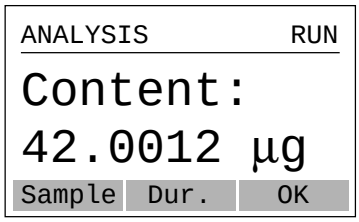
Pressing <F3>, "OK", confirms addition of the sample and starts the analysis.

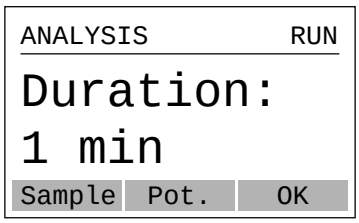


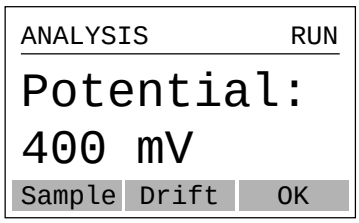
It is possible to enter the amount of the sample during analysis. Pressing <F1>, "Sample", the parameter "Weight [g]" or "Volume [mL] is displayed for you to enter the value.

During titration you can switch to four different displays:









Drift Current generation rate.

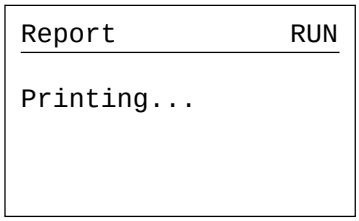
Content H_2O content titrated so far.

Duration Measuring time from beginning of data logging (excluding mixing time!).

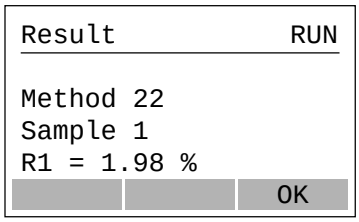
Note The time value printed in the report includes mixing time!

Potential Potential measured at the measuring electrode.

Titration is ended in accordance with the defined termination parameters. In the background, the coulometer goes back into the standby mode.



The result is printed out and displayed.

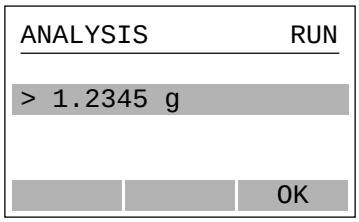


If you confirm with "OK", one of the following is displayed:

- the standby mask (method parameter "Standby: Yes"), or
- the start mask ("Standby: No"), or
- the post consumption mask (method parameter "Standby: [min]).

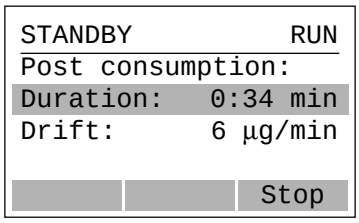
The result is now stored under the auxiliary function "Results" so that you can, e.g., perform recalculations.

6.2.1 Weight transfer from a balance



If you press <F2>, "Balance", in the corresponding mask, the value displayed on the balance appears. It is accepted with "OK".

6.2.2 Post consumption

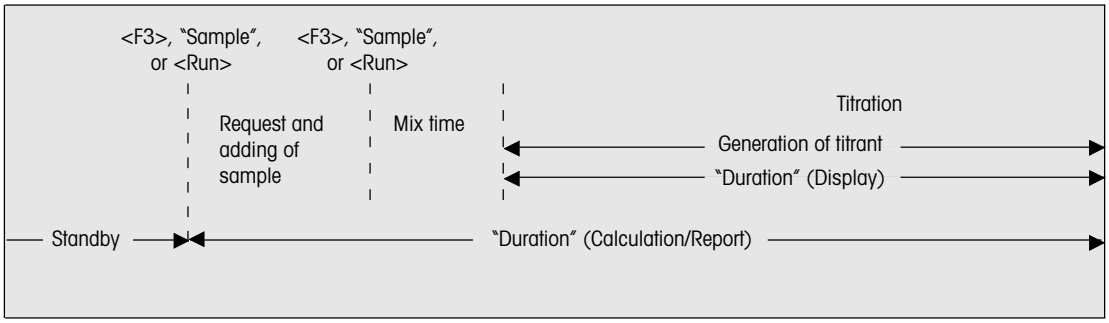


If you have selected "Standby: [min]" in the method, the subsequent measurement of the drift is performed directly after the sample determination, and a drift value is automatically printed out every minute.

6.2.3 Calculations

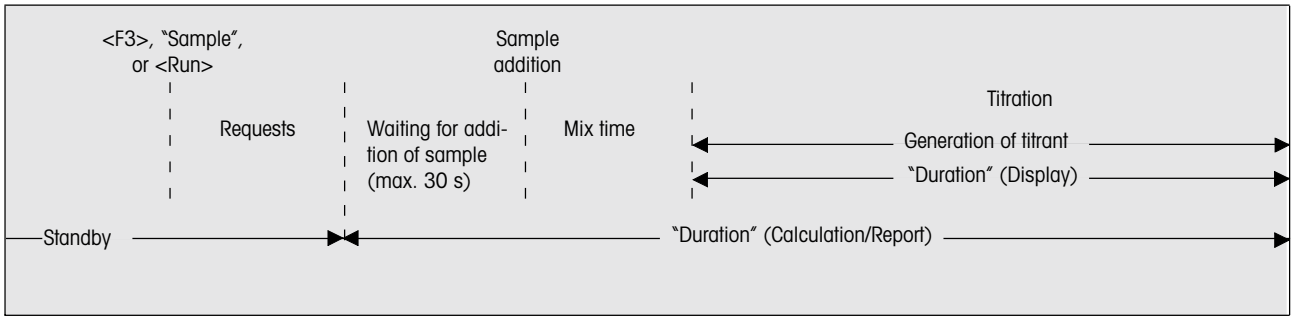
DL32 (without Auto start) / DL39 ("Auto start: No")

If you press <F3>, "Sample", or the <Run> key in the standby mode, measurement of the time needed for calculation of the drift compensation starts. It is stopped as soon as the titration has ended.



DL39 ("Auto start: Yes")

In the case of an automatic start of the titration ("Autostart: Yes"), measurement of the time ("Duration") needed for the calculation of the drift compensation starts with the request for the sample. It is stopped as soon as the titration has ended.



H_2O content in µg

H_2O [µg] = (consumption [mC] / 10.72 [mC/µg]) – (drift [µg/min] ∗ duration [min]) – (blank [µg])

To get the H_2O content in mg, divide by 1,000.

H_2O content in %

$$H_2O\ [\%] = \frac{((\text{consumption [mC]} / 10.72\ [\text{mC}/\mu\text{g}]) - (\text{drift [}\mu\text{g/min]} * \text{duration [min]}) - (\text{blank[}\mu\text{g]})) * 100\ [\%]}{\text{mass [g]} * 10^6\ [\mu\text{g/g}]}$$

To get the H_2O content in ppm, multiply the formula by 10,000,
for the H_2O content in g/kg, multiply by 10.

H_2O content per piece

$$H_2O\ [\mu\text{g/pc}] = \frac{(\text{consumption[mC]} / 10.72\ [\text{mC}/\mu\text{g}]) - (\text{drift [}\mu\text{g/min]} * \text{duration [min]}) - (\text{blank [}\mu\text{g]})}{\text{number of pieces [pcs]}}$$

These parameters are listed on every GLP report to allow you to double-check the result.

6.2.4 Sample series with statistics (DL39 only)

If you have selected "Statistics: Yes" in the method under Calculation 1, 2 or 3, results and statistical data of the sample or concentration determinations are stored under the auxiliary function "Results".

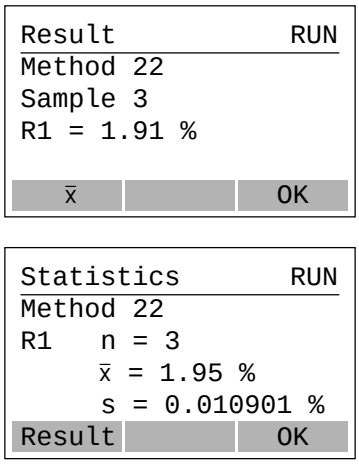
The series is terminated, if you

- enter the corresponding command in the auxiliary function "Results",
- change the method parameters of the active method,
- select a different method,
- switch off the coulometer.

The series is **not** terminated if you stop a determination by pressing <Reset> and perform the next determination under the same method.

Note You can perform a series with a maximum of 99 samples. The last 60 results are stored.

After, e.g., the third sample determination, the following appears:



<F1> Allows you to toggle between displaying results or statistics.

Note The mean is calculated after two samples; after three samples, the absolute and relative standard deviation are computed.

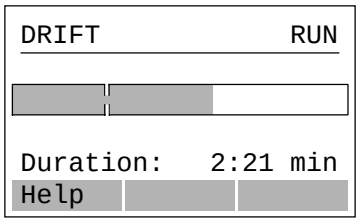
6.3 Blank determination

If you have dissolved a sample in a solvent with a H_2O-content unknown to you, run an analysis with only the solvent and without the sample. The obtained value can be entered as a blank before each titration ("Request") or can be entered automatically ("Determination"). This blank value is included in the calculations.

The blank value of the METTLER method "912 Stromboli" is stored under the <i> key.

6.4 Drift determination

You must determine the drift when "Drift: Determination" is defined in the method. By pressing <F1>, "DRIFT", the following appears:

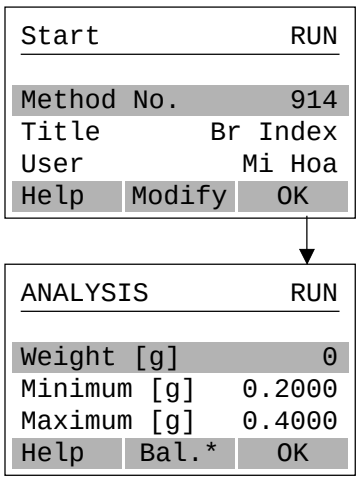


The bar will fill according to the time elapsed. After 3 minutes, the result is printed and displayed. Simultaneously, the value is stored under the <i> key.

6.5 Determination of bromine index (DL39 only)

The bromine index distinguishes itself from a KF titration by different method parameters and the missing display of "Drift", "Content" and "Duration" during the analysis. Because the determination of the bromine index does not have a drift, it cannot be used as a termination parameter.

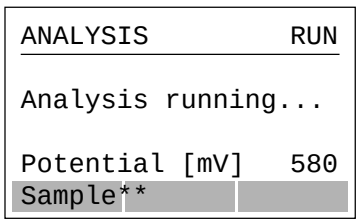
Note Because it is easier to clean we recommend using a generator electrode without diaphragm for bromine index determinations.



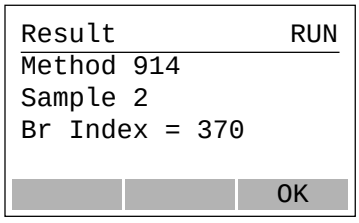
If the parameters of the method have been defined with "Request", they are displayed before the screen to enter the sample appears (example "Mass" and "Entry: Before").

* only appears if a balance has been defined.

After you have confirmed the sample addition with <F3>, "OK", the titration will begin.



** only appears if you have not entered the sample size. Press <F1>, "Sample", the parameter "Weight [g]" appears for you to enter the value.



After the titration, the result is recorded before it is displayed.

Pressing <F3>, "OK", will return you to the starting screen.

Calculation formula

$$\text{Bromine index} = \frac{100 * (0{,}0008281\ [\text{mg/mC}] * \text{consumption [mC]} - \text{blank[mg]})}{\text{weight of sample [g]}}$$

$$\text{Blank [mg]} = 0{,}0008281\ [\text{mg/mC}] * \text{consumption [mC]}$$

$$\text{Bromine number [g Bromine / 100 g sample]} = \frac{\text{bromine index [mg Bromine / 100 g sample]}}{1000}$$

Note Bromine molar mass: 79,9 [g/mol]
Faraday constant: 96485 [C/mol]

$$\frac{79{,}9}{96485} = 0{,}0008281\ [\text{mg/mC}]$$

6.6 Sample determination with the oven sample changer Stromboli (DL39 only)

The oven sample changer Stromboli is used in combination with the DL39 coulometer for the automatic determination of H_2O content of thermally stable liquids and solids. In order to do this, the sample is heated in the oven and the evaporated water is transported into the measuring cell by means of a dry inert gas stream. The DL39 controls all of Stromboli's functions via the METTLER method "912 Stromboli". Using this method as point of departure, user methods can be developed allowing automatic determination of sample series with up to 13 samples as well as drift and blank determinations. Prior to determination, Stromboli automatically inserts the sample vials on the sample rack into the oven.

The result of a sample determination with Stromboli is made up of H_2O content of the sample, blank value (H_2O content of an empty sample vial), and drift value (H_2O content of the carrier gas).

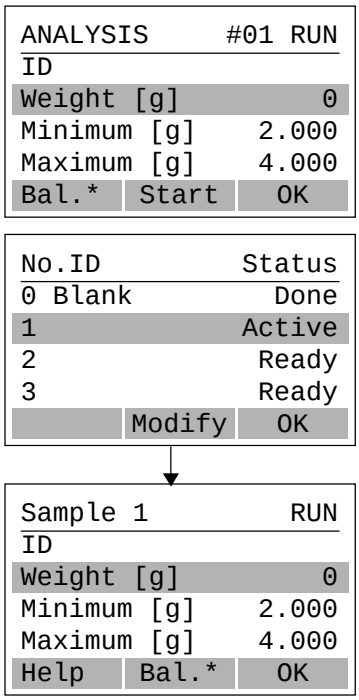
A drift determination is automatically performed if "Drift: Determination" was selected in the method. The drift can also be determined manually at any time in the standby mode (Press <F1>, "Drift"). In both cases, the determination is performed with the sample vial in the "Drift" position. The vial is inserted into the oven and the determination is performed for three minutes after reaching the set temperature entered in the method. The result is stored (i.e., it is available for subsequent sample series) and can be viewed by pressing the <i> key (including date and time of determination).

A blank determination is automatically performed if "Blank: Determination" was selected in the method. The determination is performed with the sample vial in the "Blank" position (empty sample vial). The determination is performed like a normal sample determination and, therefore, can be integrated into the sequence of a series. The blank value is defined as sample "0" without any content parameters and the default parameter "ID: Blank". The result of the blank determination is stored and can be seen under the sample number "0" in the titration report or viewed by pressing the <i> key (including date and time of determination).

Sequence of a sample series

When starting a method from the idle state, the entered, set temperature is conveyed to the oven. The sample vial in position "Drift" is inserted into the oven and the oven heats up to the set temperature during pretitration, i.e., in the standby mode. The temperature display flashes on the Stromboli, and the display alternates between current temperature and set temperature.

After reaching a constant drift at the set temperature, the sample series can be started from the standby mode by pressing <F3>, "Sample". The analysis will only begin when the oven has reached the set temperature. Until the set temperature has been attained (can take several minutes), the message "Waiting for Stromboli" appears.



* only appears if a balance has been defined.

When starting a sample series, the parameters that have been set to "Request" in the method, are asked for. The entries are stored with <F3>, "OK" and the display for the next sample (#...) appears. Pressing <F2>, "Start", starts the sample series even if the sample data have not all been entered yet.

By pressing <F3>, "Sample" during a titration, the state (ready, active, done) of the samples is displayed. Pressing <F2>, "Modify", allows you to change the entries or to complete them respectively. After each sample, the results are calculated and recorded, and the series is continued without displaying the results. If a printer is installed, the results are printed after each sample.

At the end of a series, the results of the last sample and the statistics for the series (press <F1>, "$\bar{x}$") are displayed. In the standby mode, the results can be viewed by pressing the <Results> key.

Important Results and statistics of a series are automatically deleted at the start of the next series as soon as the message "Series aborted!" has been confirmed with <F3>, "OK".

Note

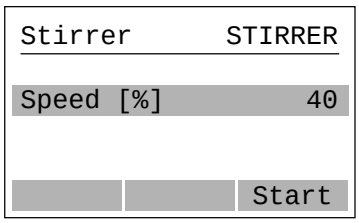
- If an analysis has been terminated by the termination parameter "Max. time", even though water has been detected in the measuring cell of the coulometer, the sample rack is returned to its base position (position "Drift" is below the oven) and remains there even during pretitration for the next sample. Stromboli only changes to the next sample, when the DL39 goes into the standby mode.
- As soon as a Stromboli connected to the DL39 is switched on, any titration will start automatically, regardless of whether "Autostart" "Yes" or "No" was selected. Therefore, the Stromboli must be switched off for a KF method with "Autostart...No" and without a Stromboli.
- When using automatic sample determination with Stromboli, the coulometer only starts running the timer when the sample has reached the set temperature.
- In the following cases, the sample series is interrupted. The message has to be confirmed by pressing <F3>, "OK" on the titrator in order to continue the sample series.
  - Appearance of one of the following messages: "Weight [g] 0", "No titration!", "Capacity exhausted".
  - The calculated value of "srel" is above the value entered in the method.
  - Sampling and entering of the parameters pertaining to the sample take more than 5 minutes.

7 Auxiliary Functions (Stirer, Pump, Results)

With the auxiliary functions keys, you can access menus that allow you to execute functions that are independent of a titration method, but support or expand it. While an analysis is running, all auxiliary functions are blocked: in standby mode you can activate only the functions of the <Stirrer> or <Results> keys.

7.1 Stirrer

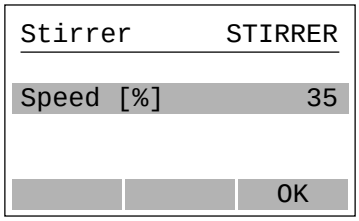
You can switch the stirrer on and off and change its speed.



Stirring can be started and stopped by pressing <F3>, "Start" or "Stop". The stirrer stirs at the defined speed.

To change the speed in the standby mode during a titration,

– press the <Stirrer> key and change the speed.

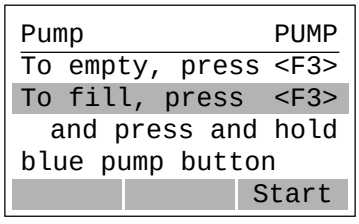


– Confirm with <F3>, "OK".
  The stirrer stirs at the new speed.

– Press the <Run> key to return to the "Analysis" menu.

7.2 Pump

With the aid of the pump, you can empty the anodic and cathodic compartments.



The pump is switched on or off by pressing <F3>, "Start" or "Stop". While the pump is running, you can switch on the stirrer with <F2>, "Stir".

Emptying

– Connect the silicon tubing from the top of the waste bottle to the pump inlet (back of the titrator) of the pump unit.
– Push the waste tube of the waste bottle to the bottom of the cell.
– Press <F3>, "Start", and empty the cell.
– Pull the waste tube out of the cell while the pump is still running. Repeat for cathodic chamber if generation electrode with diaphragm is being used.
– Press <F3>, "Stop".
– Empty the waste bottle when full.

Note

- The pump will switch off automatically when the pumping time defined in the "Setup" menu has run out.
- Each pumping operation resets the electrolyte capacity to the value defined in the "Setup" menu.

7.3 Results

the following functions are available in this menu:

```
All results
Recalculation
Calculations (DL39 only)
Statistics (DL39 only)
Report
Statistics series (DL39 only)
```

"All results" is accessible when at least one result is available.

"Statistics" are accessible when at least two results of a sample series are available.

"Report" is accessible when a drift determination has been performed or a result is available.

"Statistics series" is accessible when the first result of a sample series is available.

In order to change, e.g., results of KF determinations in the standby mode,

– press the <Results> key, change the result under "Recalculation" and confirm with "OK".
– press the <Run> key to return to the "Analysis" menu.

7.3.1 All results

You can view the results generated in the titration of a sample or sample series. You can also print out the results. The data in the result memory is deleted when you switch off the coulometer.

DL32 The results of the last 20 determinations are stored.

DL39 You can perform a sample series with 99 samples. The results of the last 60 samples remain stored, i.e., the results of sample 1 are deleted when you start to titrate sample 61.

Calculations of statistical data is always based on the last 60 samples.

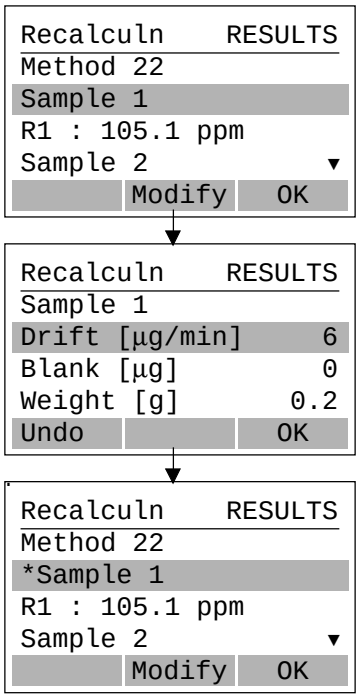
Note

- Samples terminated with the error message "No titration!" are also stored.
- The result of a determination you terminated with <Reset> is also stored.

7.3.2 Recalculation

You can recalculate existing results by changing the following values for each sample:

- in a KF sample determination: Drift, blank value and/or amount of sample.
- in a bromine index determination: Blank value and/or amount of sample.



If you change one of the values, you can nullify it with <F1>, "Undo". With "Undo", the changed values are always reset to the original values.

The sample with the changed result is marked by an asterisk (*).

Note

- The values obtained in the determination always remain stored so that you can also nullify changes later.
- Under "All results" you can print out the recalculated results. The changed and the original values are reported.
- **DL39** The changed results are also taken into account for the statistical data.

7.3.3 Report

At the end of every determination, you can print out a (additional) data report or send it to the computer.

```
Report          RESULTS

Output   Print.+Comp.
Type                GLP

Help     Modify   Start
```

Note If you have changed the result of the last determination beforehand, it will be printed out marked with an asterisk (*).

7.3.4 Calculations (DL39 only)

At the end of every titration, you can perform additional calculations for this sample.

```
Calculations RESULTS

R =           x [µg]*f
f =             1.0000
Unit                µg
Help     Modify   OK
```

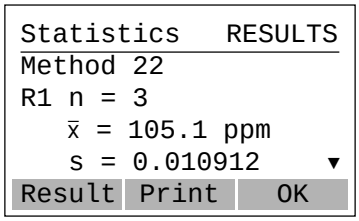
With <F3>, "OK", the result is displayed and can be printed out.

7.3.5 Statistics (DL39 only)

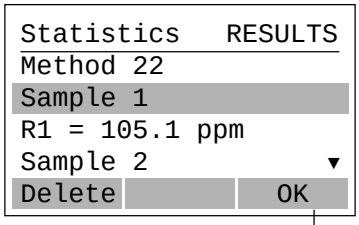
If you have selected "Statistics: Yes" in the method under calculation 1, 2 or 3, the mean is calculated in a series of 2 samples. For more than 2 samples the absolute and relative standard deviation are additionally calculated. You can print out these results here and modify the statistical evaluation by eliminating outliers.

In its statistical calculations the **DL39** does not incorporate results that were obtained after a "Reset" or after the message "No titration!".

Example of a statistical evaluation of 3 samples

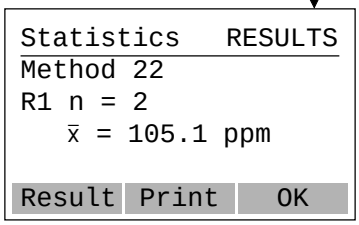


Using the list of results, you decide which sample result is an outlier and then delete it.



If you delete "Sample 1" with <F1>, "Delete", "Undo" is displayed to allow you to nullify the command. Simultaneously sample 1 is marked as "Deleted".

By pressing <F3>, "OK", the following appears:

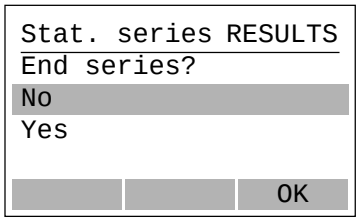


The statistical data based on the changed number of samples (e.g.: sample 1 is deleted) is calculated. You can delete several sample results and print out the statistics each time.

As long as the result list of this sample series is stored, you are able to nullify the deletion operation.

7.3.6 Statistics series (DL39 only)

With the help of this function you can terminate a sample series. This clears all data in the result memory. A subsequent analysis with the same method restarts with "Sample 1".



8 Information Menu (<i> key)

The measured values and menus below are stored under the <i> key:

```
Capacity [mg]     80
Drift [µg/min]     0
Blank [µg]         0
Hello! (Tutorial)
Hardware tests
```

Capacity The anolyte capacity defined in the "Setup" menu is entered as an initial value. After each titration, the difference between the initial value and the amount of analyzed water is displayed. If "0" is reached or exceeded, an error message appears.

Note As soon as you press the pump button, the value defined in the "Setup" menu is reentered.

Drift The value of the last drift determination performed is stored here and automatically adopted for the drift compensation if you have defined "Drift: Determination" as a method parameter.

Blank The value of the last blank determination performed is stored here and automatically adopted for calculations (only for method with Stromboli).

Hello! In this tutorial, you can acquaint yourself with the coulometer step by step.

Hardware tests Here, there are functions at your disposal allowing you to test the hardware of the coulometer. For these tests you need the connector set (see optional equipment).

9 Error Messages and Malfunctions

9.1 Error messages from the coulometer

Error messages that refer to this section or that are not self-explanatory are explained here.

A. After the coulometer has been switched on, the following errors could be displayed

- ERROR
- RAM x test ERROR(Q) "x" represents a number
- ERROR –> HW version
- ERROR –> DCB
- ERROR –> application
- No application found

The messages refer to a faulty hardware component.

– Press any key: The coulometer attempts to continue the booting procedure; this may be successful, but it does not guarantee proper functioning.

Measures

– Note the displayed text.

– Note the serial number and software version (can be found on every report).

– Notify METTLER TOLEDO Service of these points as well as of the attached peripheral units and the defined configuration.

B. If the following three displays appear, parts of your hardware may be defective

```
Internal error: x

xxxxxxxxxxxxxxxxxxxxxxxx
xxxxxxxxxxxxxxxxxxxxxxxx
xxxxxxxxxxxxxxxxxxxxxxxx
SYSTEM IS BLOCKED!
See manual: Errors
```

```
OS ERROR: x
P1: xx
P2: xx
D1: xx
D2: xx
SYSTEM IS BLOCKED!
Please call METTLER
TOLEDO service
```

```
ERROR: x

SYSTEM IS BLOCKED!
Please call METTLER
TOLEDO service
```

"x" represents letters and/or numbers

Measure

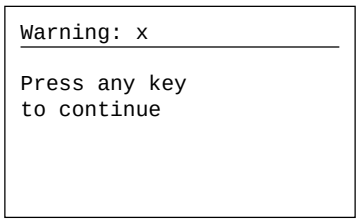
– Apart from the text or error (e.g., "ERROR: 1000), also note the procedure that triggered the error.

– Note the serial number and software version (can be found on every report).

– Switch off the coulometer.

– Notify METTLER TOLEDO Service of these points as well as of the attached peripheral units and the defined configuration.

C. If the following warning appears, you have to consider the current procedure as failed and repeat it



"x" represents a number

Measures

– Press any key: The coulometer can continue to function.
– On no account consider the result of a determination terminated in this manner!
– Should the warning appear frequently, take the measures mentioned under point B.

D. Faulty data deleted!

• The coulometer has only saved parts of a method if, e.g., the power fails while the method is being saved. This will delete the method completely. It also possible that several methods have been deleted.

Measures

– Confirm the message.
– Check which methods have been deleted and re-enter them.

• The coulometer has only saved parts of the parameters of a resource if, e.g., the power fails while the parameters are being saved. All data defined in the "Setup" menu will be deleted.

Measures

– Confirm the message. The coulometer then loads the default parameters of the "Setup" menu, i.e., all the data that was stored on delivery.
– Switch the coulometer off and then on again.
– Check whether the default parameters are active again. Re-enter the names and values saved before the power failure.

If you receive this error message frequently, the battery is discharged! The battery must be changed by METTLER TOLEDO Service.

E. Method not stored!

• The coulometer can no longer save a method if the user data memory is full.

Measures

– Confirm the message.
– Delete one or more unused methods.
– Reenter the new method and save it.

9.2 Other errors and malfunctions

The following collection of errors and malfunctions that are not reported by the coulometer will help you correct the fault yourself in many cases so that you do not have to rely on the METTLER TOLEDO Service (referred to in the table as "Service").

You can also check some malfunctions with the hardware test ("Information" menu, <i> key) first before you contact Service.

Error	Possible cause	Remedy
No display on coulometer	Device not connected to power supply.	Connect to power supply, otherwise, contact Service.
Several points on the display are missing		Contact Service.
Display and keys do not match		Contact Service.
Transmission error to attached peripheral device	Peripheral device defective or switched off.	Check attached devices for correct functioning.
Device (printer, balance, computer) does not respond	Device not switched on wrong settings and/or configuration (switch positions wrong); wrong cable.	Switch on device; settings and configuration must match; check cable.
Pump does not work	Suction tube not connected; defective pump.	Connect suction tube and check connections; check pump.
TTL inputs or outputs do not function	Defective inputs.	Check inputs/outputs.
Magnetic stirring bar does not rotate	Cable of magnetic stirrer not plugged in properly; wrong magnetic stirring bar.	Check magnetic stirrer, change magnetic stirrer; Use delivered magnetic stirring bar.
No hydrogen production at the generator electrode	Missing or bad contacts; connectors interchanged.	Check contacts or call Service; check connectors (colors!).
"Conductivity too low! Titration terminated"	Current pulse of generator electrode < 200 mA	Confirm message with <F3> (instrument performs a "Reset")

9.3 Checking hardware

The menu "Hardware tests" is stored under the <i> key and you can use it to check whether, e.g., the stirrer and pump of the coulometer are functioning correctly. If you order the connector set for the interface check, you can also test the interface and the TTL input and outputs of the coulometer

9.3.1 User interface

Display test

Five displays appear in succession, four with different patterns, the last without a pattern. This allows you to detect faulty pixels on the display. The test mode automatically switches off after approx. 20 seconds.

Keyboard test

When you press a key, a numeric code assigned to this key appears. This allows you to recognize a faulty key (see following table).

– Press the <Esc> key to quit the test mode.

Key codes

Key ..... Code	Key ..... Code	Key ..... Code
Reset 23	F1 17	3 3
i 30	F2 18	4 4
Stirrer 28	F3 19	5 5
Pump 27	∇ 11	6 6
Burette 29	Δ 12	7 7
Results 26	Shift 10	8 8
Setup 25	0 0	9 9
Method 24	1 1	Del 31
Run 21	2 2	 33

Beep test

used to test the internal beeper

9.3.2 Peripheral interfaces

Interface test

– Before the test
  - plug the test plug 51107288 into the balance, computer or GA42 interface.
  - plug the Centronics cable into the Centronics interface and the test plug 51107287 into the Centronics socket of the cable.

After the testing phase, either "Test successful" or "Test failed" will appear.

Balance test

This menu option is not displayed if no balance is defined in the "Setup" menu.

– The weight displayed on the balance must appear on the coulometer display.

Printer test (GA42, EPSON or HP)

The appropriate printer must be attached. If the error message "Printer: No connection" appears, you can quit this error message with <Esc>. With "OK" the coulometer tries to set up the connection to the printer again.

– The letters and characters available in the coulometer must be printed out.

9.3.3 Inputs and outputs

TTL I/O (DL39 only)

– Before the test, connect the test plug 51107723 to the TTL I/O interface.

After the testing phase, either "Test successful" or "Test failed" appears.

Internal stirrer

Here, you test the rotational movement (counterclockwise) and change in the speed of the magnetic stirring bar.

External stirrer

Here, you test the rotational movement and change in the speed of the magnetic stirring bar on the connected DV705 titration stand.

Internal pump

To test whether the pump functions.

– A "noise" must be heard.

– It must be able to siphon off when the waste bottle is attached properly.

External pump

To test whether the pump on the optional external DV705 titration stand functions (see "Internal pump").

Note Always press the upper key (⇑ arrow) to siphon off.

10 Installation and Maintenance

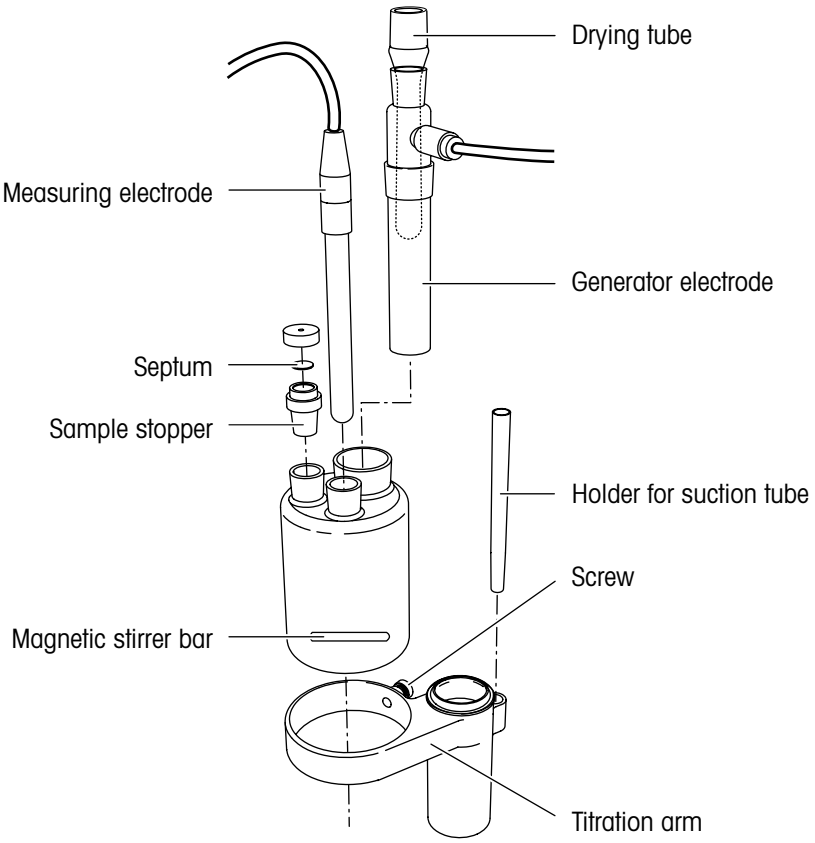
10.1 Equipping the titration stand

After setting up your coulometer in an appropriate location you can equip the titration stand. The arm of the titrator can be turned in both directions.

– Carefully slide the magnetic stirring bar included in the delivery into the cell.

Note Only the original magnetic stirring bar will guarantee the specifications of your coulometer's magnetic stirrer.

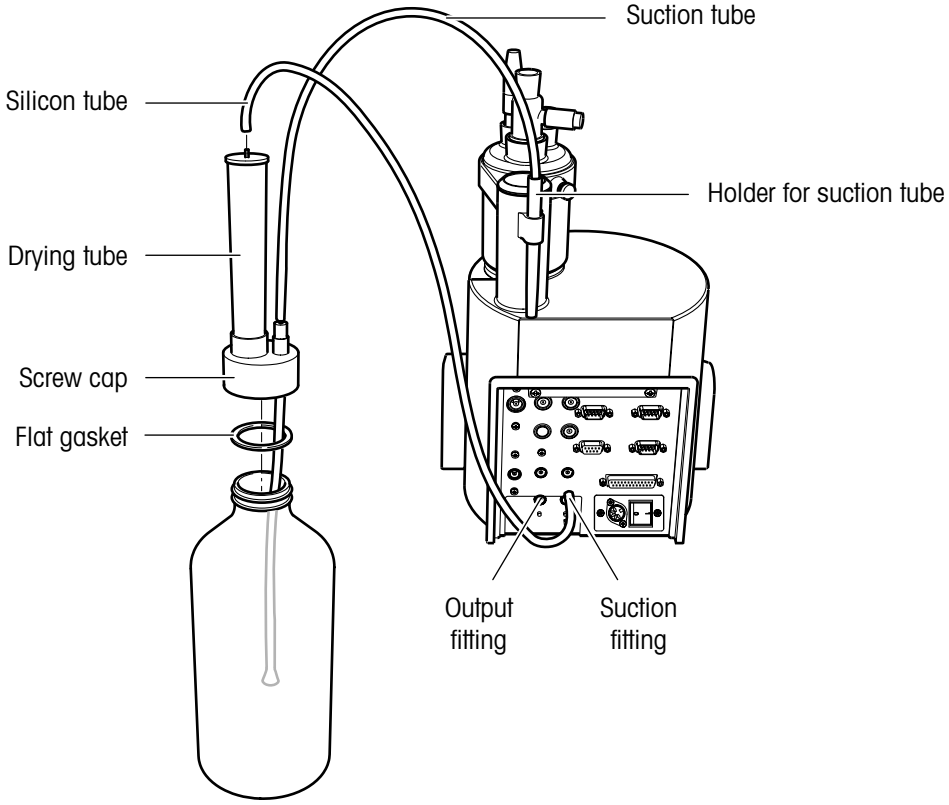
– Place the cell in the titration stand and fasten it with the screw.
– Grease the ground joints with the included grease (see delivery note).
– Place the sample stopper with the septum into the opening in the cell.
– Place the measuring and generator electrodes in their respective openings in the cell.
– Fill the drying tube with desiccant and place it in the generator electrode.
– Insert the holder for the tip of the waste bottle.



10.2 Installing the waste bottle

Install the waste bottle to empty the cell (included in the delivery) as follows:

– Push the suction tube tip first from underneath through the collar of the screw cap and place the tip into the holder for the suction tube on the titration stand.
– Place the flat gasket on the waste bottle and screw on the screw cap.
– Slide the silicone tube onto the drying tube of the bottle, connect the other end to the suction fitting on the rear of the coulometer.

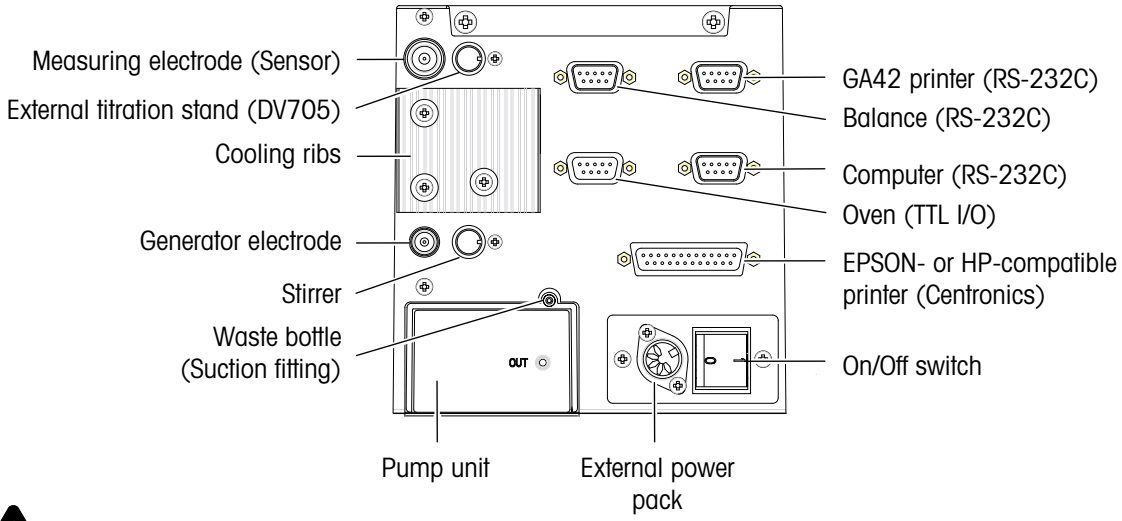


Notes

- You can connect a tube to the output fitting in order to carry solvent fumes to a suitable place.
- Check all connections for a tight fit in order to ensure the system's tightness.

10.3 Attaching the magnetic stirrer, electrodes and devices

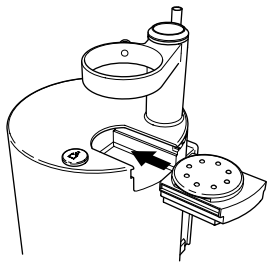
– Attach the devices used to the corresponding connectors/sockets on the rear side of the coulometer (see diagram).



– The stirrer output is not inherently short-circuit proof! Damaged pins of the cable connector could cause a short circuit that will damage the coulometer, rendering it useless.

Magnetic stirrer

On delivery, the magnetic stirrer is pushed into the casing on the upper side of the coulometer.



– Attach its cable to the stirrer output. The arrow on the miniDIN connector must point towards the screw.

Measuring electrode

– Connect the electrode to the triaxial cable. Plug the cable into the measuring electrode input (Sensor) and insert the electrode into the top of the cell.

Generator electrode

– Connect the electrode to the triaxial cable. Plug the cable into the generator electrode input and insert the generator electrode into the top of the cell.

Balance, printer, computer, TBox DR42

Attach all peripheral devices to the same plug connector (phase) to which the coulometer is connected! Otherwise, equalizing currents could flow across the cables.

METTLER TOLEDO and SARTORIUS balances are compatible with these coulometers.

10.4 Maintenance and servicing

All Karl-Fischer reagents are easily combustible and poisonous.

- In the case of skin contact, rinse immediately with a lot of water.
- In the case of eye contact, rinse immediately and thoroughly with water, then consult a doctor.

Cleaning

– You can clean the coulometer with a cloth moistened with alcohol

– If necessary, grease ground joints.

Clean the cell as follows

– Empty the anode and cathode compartments using the waste bottle and pump.

– Rinse thoroughly with methanol. Persistent contamination can be removed by using a common cleanser (cleanser for lab equipment).

– Dry with a lint-free cloth.

– Dry in drying oven over night at 70 - 80 °C.

– If necessary, grease ground joints.

Clean the measuring and generator electrode as follows

– Rinse thoroughly with methanol.

– Dry with a lint-free cloth.

– In case of a contaminated diaphragm:
  – Over night, soak the electrode in a suitable solution (preferably methanol).
  – Dry in the drying oven at 70 - 80 °C.
  – An electrochemical cleaning of the electrodes can be performed as follows:
    – Fill the generator electrode with methanol and place it in a vessel filled with methanol. Connect the generator electrode to a DC power source of 30 V / 1 A (if available, use a lab power pack with 30 V / 2 A).
    – Reverse the polarity of the current after 5 minutes and permit it to react for another 5 minutes.
    – Rinse well with methanol and dry in the drying oven at 70 – 80 °C for several hours.

Note Use of a fritt cleanser is not recommended.

Waste bottle

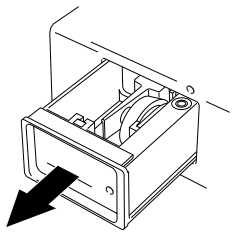
– The tubing should be replaced when the Teflon seal no longer seals properly (wear and tear).

Molecular sieve

– If the drift remains too high you should fill the drying tubes with fresh molecular sieve.

Note You can regenerate molecular sieve in a drying oven at 160 - 300 °C for at least 24 hours.

Pump unit



If the diaphragm pump no longer functions, you can replace it:

– Pull out the pump unit and insert the new one.

Magnetic stirrer

If the magnetic stirrer is defective, you can replace it:

Battery

The battery installed in the coulometer has a service life of approx. 5 years. The battery may be changed only by METTLER TOLEDO Service.

Disposal

Contact your METTLER TOLEDO dealer if you have to dispose of the coulometer.

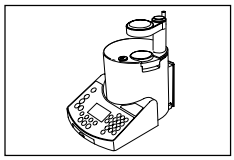
10.5 Using TTL inputs and outputs (DL39 only)

You can only connect the METTLER TOLEDO oven sample changer Stromboli to this TTL socket.

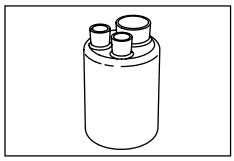
11 Standard and optional equipment

You can order each part listed with an **order number** from METTLER TOLEDO.

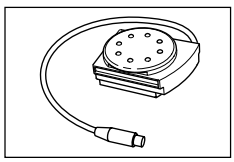
11.1 Standard equipment



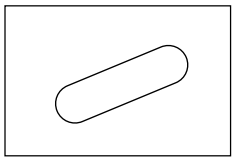
Coulometer



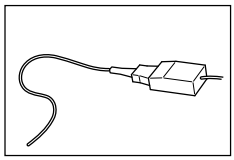
Titration cell
51108732



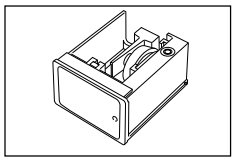
Magnetic stirrer
51108750



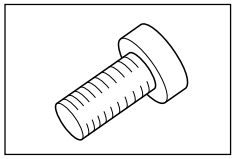
Magnetic stirrer bar
51191159



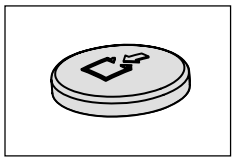
External power pack
100 - 240 VAC
51107777



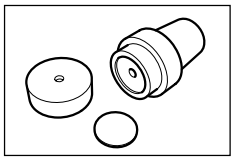
Pump unit
51107479



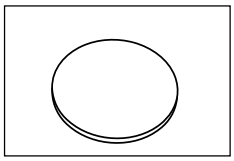
Fastener screw for titration cell (PTFE)
51108752



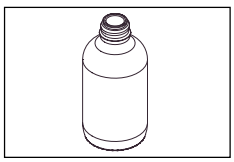
Pump button (blue)
51107600



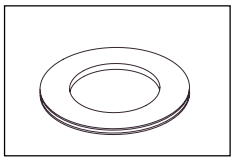
Sample stopper (PTFE) with septum
51108741



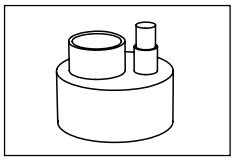
Septum (12 pieces)
51108740



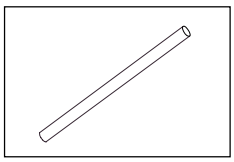
Brown glass bottle 1L
71296



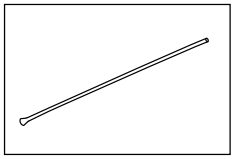
Gasket
23981



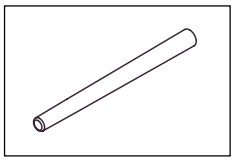
Screw cap
23937



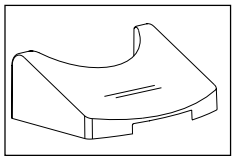
Silicon tube
Length: 0.45 m
51107490



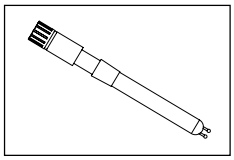
Suction tube (PTFE)
Length: 0.8 m
23936



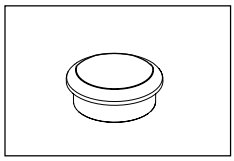
Holder
23960



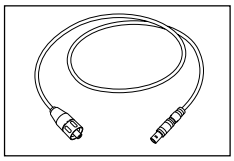
Keypad cover
1 piece



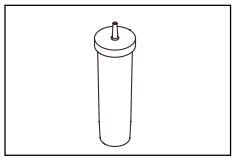
Measuring electrode DM143-SC
(double platinum pin electrode)
51107699



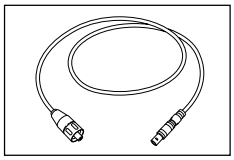
Seal (drying tube of titration stand)
51107492



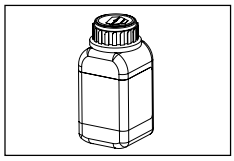
Cable for DM143-SC
(LEMO - SC)
Length: 0.6 m
89601



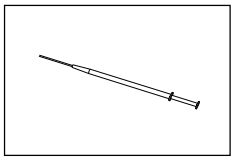
Drying tube with cover
23961



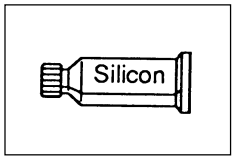
Cable for generator electrode
51107830



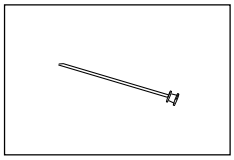
Bottle with molecular sieve
71478



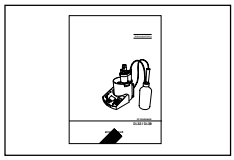
Syringe, 1 piece



Silicon grease
71300

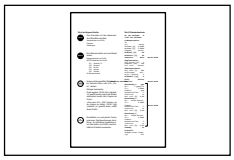


Injection needle (80 x 0.8 mm),
1 piece



Operating Instructions

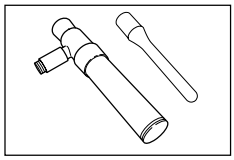
German	**51710107**
English	**51710108**
French	**51710109**
Spanish	**51710110**
Italian	**51710111**



Memo card

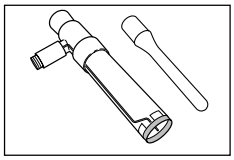
German	**51710112**
English	**51710113**
French	**51710114**
Spanish	**51710115**
Italian	**51710116**

DL32 D / DL39 D



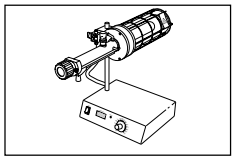
Generator electrode **with**
diaphragm with straight
drying tube
51108751

DL32 X / DL39 X

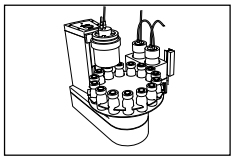


Generator electrode **without**
diaphragm with straight
drying tube
51108753

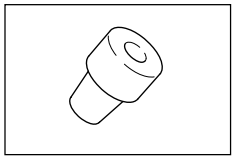
11.2 Optional equipment



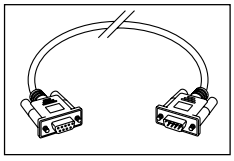
Drying oven
DO307



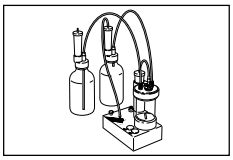
Oven sample changer Stromboli
with DL39D or DL39X only
Stromboli



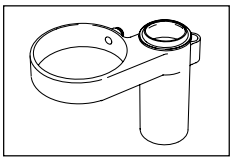
Adaptor for DO307
51108761



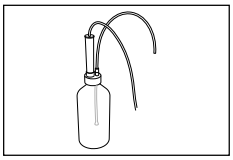
Connection cable for Stromboli
(DL39 only)
51190589



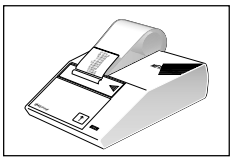
External titration stand
DV705



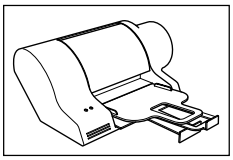
Titration arm, without screw, without holder
51108729



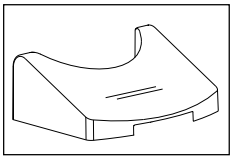
Waste bottle complete
51108745



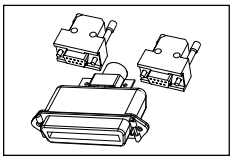
Printer
GA42



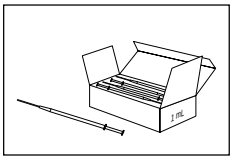
Olivetti Artjet printer
US version **51190986**
EU version **51190985**



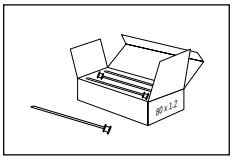
Keypad cover
3 pieces
51107666



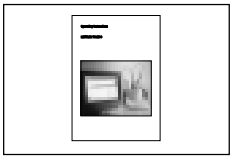
Connector set
for hardware tests
51107790



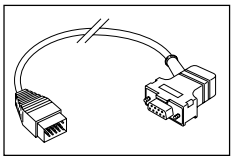
Syringe, 100 pieces
1 mL **71492**
10 mL **71482**



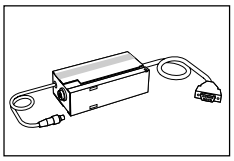
Injection needle, 12 pieces
80 x 1.2 mm **71483**
80 x 0.8 mm **71484**



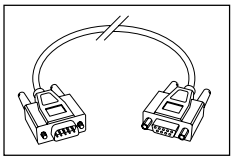
Description of the interface
German **51709875**
English **51709876**



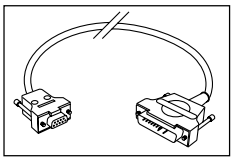
Connection cable for
METTLER TOLEDO balance
AM, PM, AT, AX
229029



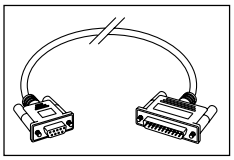
Connection cable for
METTLER TOLEDO balance
AG, AB, PB, PG (LC interface)
229065



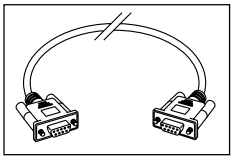
Connection cable for
METTLER TOLEDO balance
AB, PB, PG-S (RS9 interface)
11101051



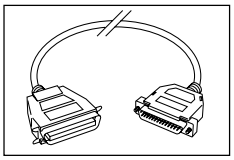
Connection cable for
METTLER TOLEDO balance
AE with option 011
59759



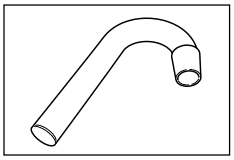
Connection cable for
SARTORIUS balances
51190363



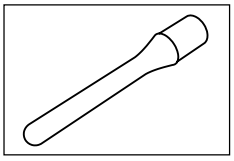
Connection cable for
GA42 printer
51190362



Connection cable for
EPSON/HP compatible printer
(i.e. Olivetti Artjet)
51107780



Drying tube, bent,
for DO307
51108639



Drying tube, straight,
51108733

12 Technical Data

Power supply (External power pack)

Voltages	100 – 240 VAC ± 10 %
Frequency	50/60 Hz
Power consumption	45 VA
Fuse	T3,15H250V (not interchangeable)
Voltage	24 V 0,8 A / 5 V 1,2 A

Dimensions

Width	240 mm
Depth	305 mm
Height	370 mm
Weight	approx. 3.5 kg

Materials

Housing	Polypropylene
Titration stand	Polypropylene
Keypad	Polyester
Titration cell	Glass
Suction tube	PTFE

Ambient conditions

Ambient temperature	+5 °C ... +40 °C
Atmospheric humidity	max. 80 % at 40 °C
Use	indoors
Overvoltage category	II
Pollution degree	2

Measurement system

KF input	Triaxial socket
Pol. current (Sensor)	1 µA, 2 µA or 5 µA
End point	100 mV
Generator current	60 mA, 100 mA, 200 mA, 400 mA (automatic steps)
Generator voltage	28 V (pulsating)
Max. permissible errors	< 0.2 %

Outputs

Output	8-pin socket (mini DIN)
Magnetic stirrer type	Stepper motor
Speed	Software controlled (1–100%)
Power	2 W (24 V)
Max. speed	1050 rpm (40 % ≈ 600 rpm, 70 % ≈ 1050 rpm)
Output	5-pin socket (mini DIN)
Magnetic stirrer type	DC motor
Speed	Software controlled (1–100%)
Voltage range	0 bis 18 VDC (max. 300 mA)
Pump	
Voltage	24 VDC (max. 400 mA)

Magnetic stirrer (stepper motor)

Max. Speed	1050 rpm
Power consumption	2 W

Diaphragm pump

Voltage	24 VAC (4 W)
Pressure buildup	approx. 150 mbar

Display

Liquid crystal display	6 lines, 20 characters per line, backlit
Languages	German, English, French, Spanish, Italian and Russian

Memories

KF standard method	1
Tutorial method	1
METTLER methods	5 (DL39)
User methods	max. 50 (DL39) / max. 1 (DL32)

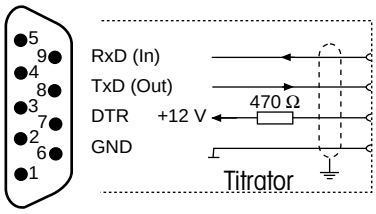
Interface

TTL I/O	D-sub connector 9-pin

Attachment possibilities for peripherals

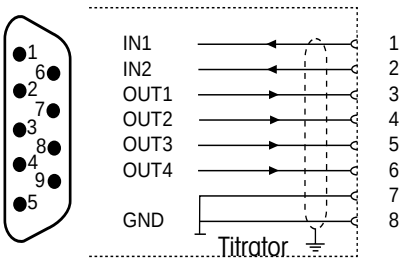
Balance	Attachment via RS232C interface (9-pin D-sub connector) for METTLER TOLEDO and SARTORIUS balances
Printer	Attachment via RS232C interface (9-pin D-sub connector) for GA42 printer Attachment via Centronics interface (25-pin D-sub socket) for commercial EPSON compatible printers with parallel interface
Computer	Attachment via RS232C interface (9-pin D-sub connector): full-duplex, short-circuit-proof, handshake: X on/off, no hardware handshake
Stromboli	Attachment via TTL I/O socket (9-pin D-sub)

RS232C connector (balance/GA42/computer)



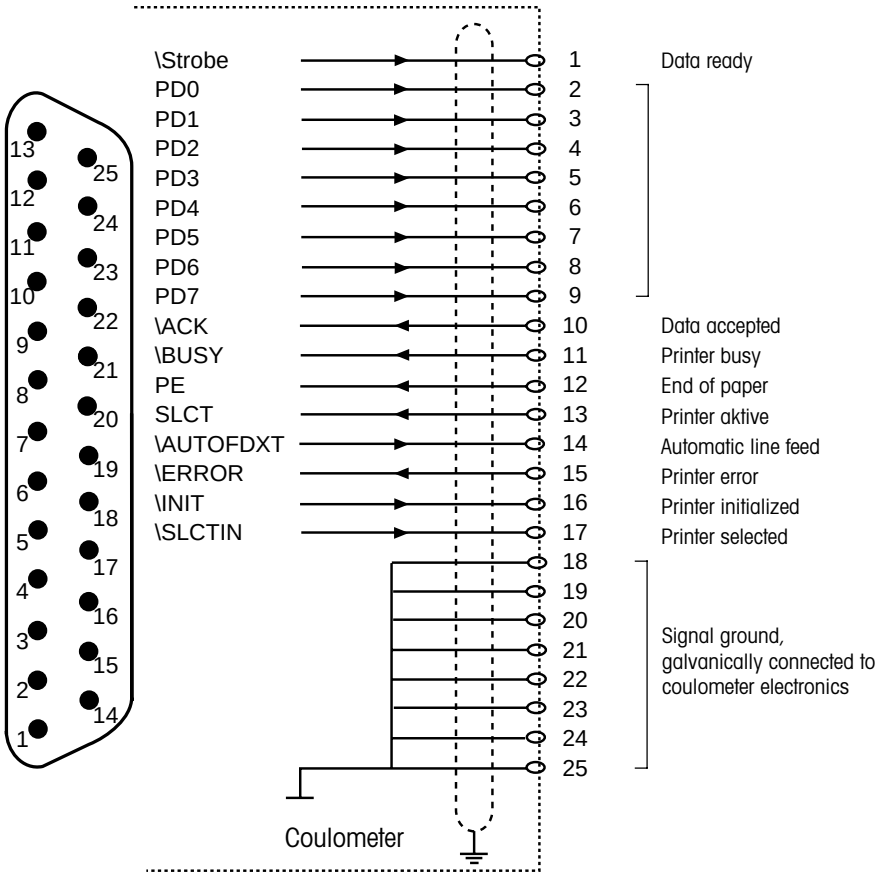
2	Data to coulometer
3	Data from coulometer
4	Handshake from coulometer fixed to operational readiness
5	Signal ground, galvanically connected to coulometer electronics

TTL I/O socket



In	TTL; short-circuit-proof; Pulse ≥150 ms (the input signal for the coulometer must be at least 150 ms)
Out	Open collector • Vce max. = 24 V • Ic max. = 20 mA
GND	Signal ground, galvanically connected to coulometer electronics

Centronics socket



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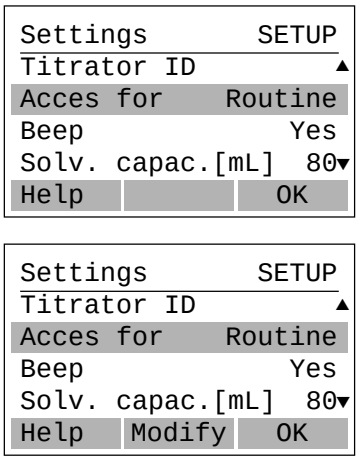
Switching from routine to expert mode



Select this line in the Setup menu.

– While holding down the Shift key, press key **1** three times:

"Modify" is assigned to <F2> allowing you to select "Expert".

– Confirm with <F3>, "OK" to save the change.

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METTLER TOLEDO Service assures the quality, measuring accuracy and preservation of value of all METTLER TOLEDO products for years to come. Please send for full details about our attractive terms of service. Thank you.

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P51710108

Subject to technical changes

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