Application Bulletin 445/1

Installation instruction: MVA-25 – 884 Professional VA fully automated for the determination of antioxidants with automatic sample preparation

The «MVA-25» is a fully automated system for the determination of antioxidants in lubricants, including automatic sample preparation. The only manual operation needed is to pipette the reference oil or the in-service oil sample into a vial and place it on the rack of the sample changer. All other steps of the analysis procedure are carried out automatically.

Important features:

- Automatic sample preparation.
  - Addition of electrolyte into the sample vial.
  - Mixing of reference oil or in-service oil sample with sand and electrolyte.
- Calibration and determination of a series of samples.
  - Automatic addition of electrolyte into the measuring vessel for the blank determination.
  - Automatic transfer of the extraction solution from the sample changer to the measuring vessel.
  - Automatic calculation of the calibration curve for a reference oil or the remaining antioxidant content for an in-service oil sample.
  - Automatic rinsing of transfer tubing and measuring vessel.
- Applications:
  - Determination of aromatic amine type antioxidants based on ASTM D6971 [**1**].
  - Determination of hindered phenol type antioxidants based on ASTM D6810 [**2**].
  - Combination of ASTM D6971 and ASTM D6810 into one determination requiring only one sample preparation procedure per sample.

Figure 1. Components of an MVA-25 system.

Content

Version 09/2024

1 Instruments and accessories

1.1 Instruments

Quantity	Article no.	
1	2.884.0010	884 Professional VA
1	6.1256.040	RDE measuring head high resistance
1	2.858.0130	858 Professional Sample Processor for Antioxidants
2	2.800.0020	800 Dosino
1	2.843.0230	843 Membrane Pump Station (peristaltic) for Professional VA/CVS systems
2	6.1608.030	Round glass bottle 1 L
2	6.1805.120	FEP tubing 100 cm
1	6.2055.100	Bottle holder
1	6.2141.300	Remote cable 843 Pump Station to Sample Processor
2	6.3032.220	Dosing Unit 20 mL
1	6.5339.100	VA electrode equipment for antioxidants
1	6.6065.30x	**viva** 3.0

Amongst other accessories, the following electrodes are part of the VA electrode equipment for antioxidants (6.5339.100):

WE	Glassy carbon electrode tip Driving axle for RDE	6.1204.600 6.1204.510
RE	Separate Pt rod electrode	6.0343.000
AE	Separate Pt rod electrode	6.0343.000

1.2 Reagents

- Acetone, $w(CH_3COCH_3) \geq 99.5\%$, for analysis, CAS 67-64-1
- Ethanol (denatured or pure), $w(CH_3CH_2OH) \geq 96\%$, for analysis, CAS 64-17-5
- Lithium perchlorate, $LiClO_4$, for analysis, CAS 7791-03-9
- Sodium acetate trihydrate; $CH_3COONa * 3\ H_2O$, CAS 6131-90-4
- Sodium hydroxide solution, $w(NaOH) = 30\%$ in water, for analysis, CAS 1310-73-2
- Nitric acid, $w(HNO_3) = 65\%$, for analysis, CAS 7697-37-2
- Quartz sand, 0.2–0.3 mm ± 0.1 mm, CAS 14808-60-7, e.g. Supelco 1.07711, Sigma-Aldrich 274739, Acros 393302500, or similar
- Soda lime, CaO / NaOH, CAS 8006-28-8, for adsorber tube (6.1619.000)

1.3 Solutions

Electrolyte neutral	$c(CH_3COONa) = 0.002$ mol/L $c(LiClO_4) = 0.05$ mol/L, w(Ethanol) = 30% w(Acetone) = 70% Dissolve 0.272 g sodium acetate trihydrate and 5.32 g lithium perchlorate in 300 mL ethanol. Make up to 1000 mL with acetone.
Electrolyte alkaline	c(NaOH) = 0.1 mol/L w(Ethanol) = ≥ 96% While stirring, slowly add 10 mL sodium hydroxide solution

	(w(NaOH) = 30% or c(NaOH) = 10 mol/L) into 1000 mL ethanol. Make sure that possible precipitations of NaOH are dissolved directly after the addition. Always keep this solution in a closed glass bottle to prevent formation of poorly soluble carbonates.
Ethanol for rinsing	σ(HNO_3) = 0.1 mL/L Per 1 L ethanol add 0.1 mL w(HNO_3) = 65%.
Acetone for rinsing station	w(acetone) ≥ 99.5%

2 System setup

In addition to this Application Bulletin, it is recommended to have the following documents available.

8.807.8002xx	Manual 807 Dosing Unit [**3**] In the following chapters it will be referred to as *807 Manual*
8.843.8003xx	Manual – 843 Pump Station with peristaltic pump [**4**] In the following chapters it will be referred to as *843 Manual*
8.858.8002xx	Manual – 858 Professional Sample Processor [**5**] In the following chapters it will be referred to as *858 Manual*
8.884.8003xx	Manual – 884 Professional VA [**6**] In the following chapters it will be referred to as *884 Manual*

2.1 Electrical connections

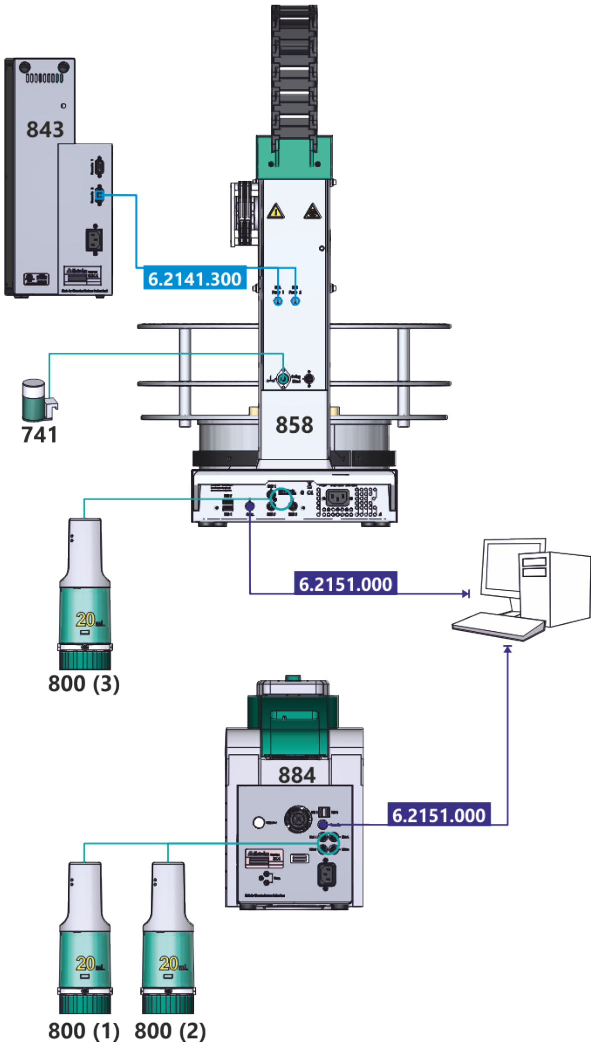


Figure 2. Electrical connections.

- The cable 6.2141.300 must be connected to «Remote 2» of the 843 Pump Station.
- The 800 Dosinos can be connected to any of the MSB ports. The indicated number is only used to distinguish the 807 Dosing Units in this document.
- The controller cables 6.2151.000 from the 884 Professional VA and the 858 Professional Sample Processor should be directly connected to the PC. The connection should not be cascaded via the USB hub in the rear of the instruments. In case the PC has an insufficient number of USB connections, it is recommended to use an external USB hub with power supply.

2.2 Mounting Rinsing Station and 741 Stirrer

For proper operation, both the rinsing station and the stirrer must be mounted in the correct position on the assembly rail of the 858 Professional Sample Processor. The following procedure is recommended for the adjustment:

1. Make sure the rack is not installed on the turntable.
2. Install the sample needle as described in the *858 Manual* [**5**] chapter 3.8.
3. Temporarily attach the rinsing station and the stirrer to the assembly rail as shown in **Figure 3**.
4. Place the rack on the turntable.
5. Connect the sample changer to the software.
6. Configure the tower and rack parameter as specified in 3.2 Devices – 858 Professional Sample Processor.

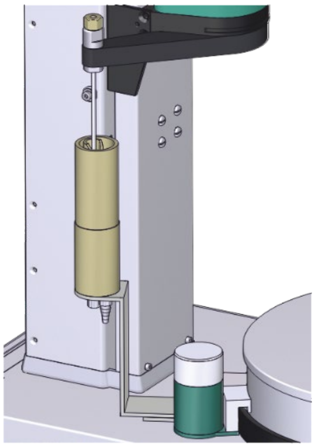


Figure 3. Position of rinsing station and magnetic stirrer.

2.2.1 Positioning of Rinsing Station

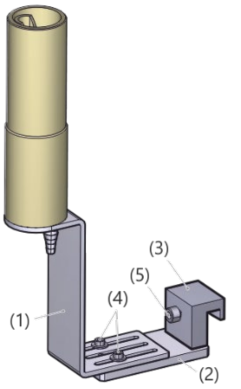


Figure 4. 6.2841.110 Rinsing Station

The holder of the Rinsing Station (**Figure 4**) consists of a double angled support bracket (1), a base plate (2) and a clamping fastener (3). Two 2.5 mm Allen® screws (4) fasten the support bracket to the base plate and allow the adjustment of the rinsing station in axial direction. The 4 mm Allen® screw (5) on the clamping fastener is used to fix the position of the rinsing station on the assembly rail.

Procedure for adjustment:

1. In the **viva** software, go to «Manual control».

   Select «Tower 1» » of the 858 Professional Sample Processor and swing the robotic arm to «External 1».
2. Remove the rack from the sample changer.
3. Loosen the two 2.5 mm Allen® screws of the Rinsing Station to allow free movement between the baseplate and support bracket.
4. Adjust the position of the Rinsing Station in such a way that the sample needle points into the center of the inner tube.
5. Secure the axial distance by tightening the two 2.5 mm Allen® screws.
6. Secure the position along the assembly rail by tightening the 4 mm Allen® screw on the clamping fastener.

Testing the positions:

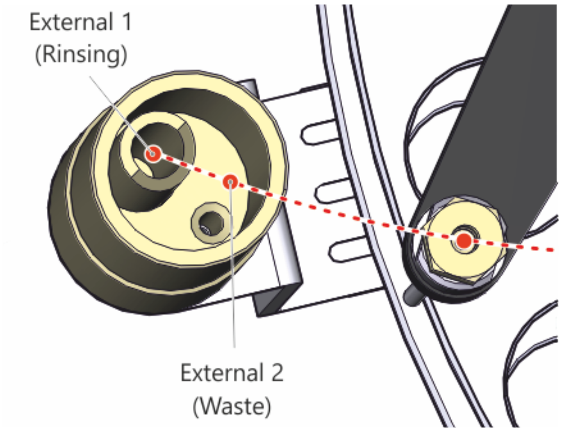


Figure 5. External positions.

- Place the sample rack back on the turntable.
- In the **viva** software, go to «Manual control».
- External position 2 (Waste)
  - Swing to «External 2»
  - Lift to «Work position»

  - See **Figure 5** for position. The sample needle tip should be located approximately 1 cm below the edge of the outer tube.
- External position 1 (Rinsing)
  - Swing to «External 1»
  - Lift to «Work position»
  - See **Figure 5** for position. The sample needle tip should go down to the bottom of the inner tube.

2.2.2 Positioning of 741 Stirrer

To guarantee proper stirring of the sample, the stirrer must be positioned underneath the particular sample. To find the correct position proceed as follows:

Procedure for adjustment:

1. Put a stirrer bar 6.1903.010 into a vial 6.2747.010 and place both in position 24 of the rack.
2. In the **viva** software, go to «Manual control».

   Select «Tower 1» of the 858 Professional Sample Processor and move the rack to «Rack position» 24.
3. Shift the 741 Stirrer on the assembly rail until it is located exactly under rack position 24.

Test the positioning:

- In the **viva** software, go to «Manual control».

  Select «Stirrer 1» of the 858 Professional Sample Processor.
- Set stirrer rate to «8» and start the stirring.
- The stirrer is positioned correctly when the stirring starts easily, and the stirrer bar rotates smoothly.

2.3 Tubing connections with one electrolyte for sample preparation

This is the recommended setup for the determination of aromatic amine and hindered phenol using the combined method «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol». If sample preparation with «Electrolyte alkaline» is also required, please refer to the optional setup described in chapter 2.5.

2.3.1 Overview

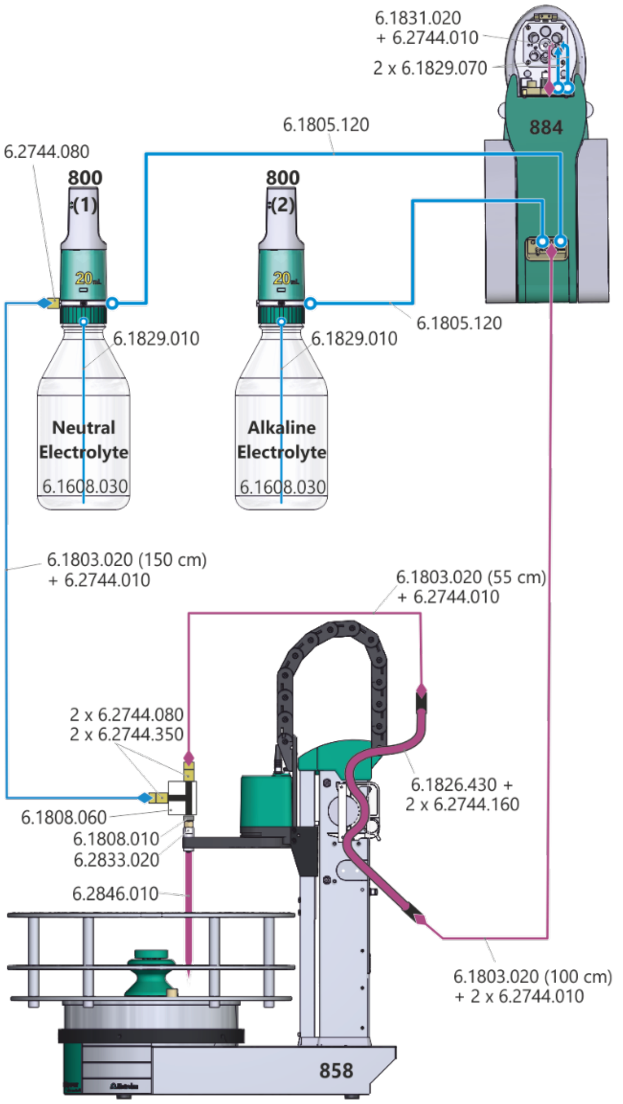


Figure 6. Tubing connections with one electrolyte for sample preparation.

Please refer to *858 Manual* [**5**] chapter 3.12 for the installation of the peristaltic pump. The coupling with security device (6.2744.160) should be used for the connection of the pump tubing (6.1826.430).

2.3.2 Details 858 Professional Sample Processor – Swing head

The handling of one electrolyte for sample preparation requires one T connector (6.1808.060) attached to the robotic arm of the 858 Professional Sample Processor (see **Figure 6** and **Figure 7**).

If the additional option for sample preparation with «Electrolyte alkaline» is required, please refer to the setup described in 2.5 Optional: tubing connections with two electrolytes for sample preparation.

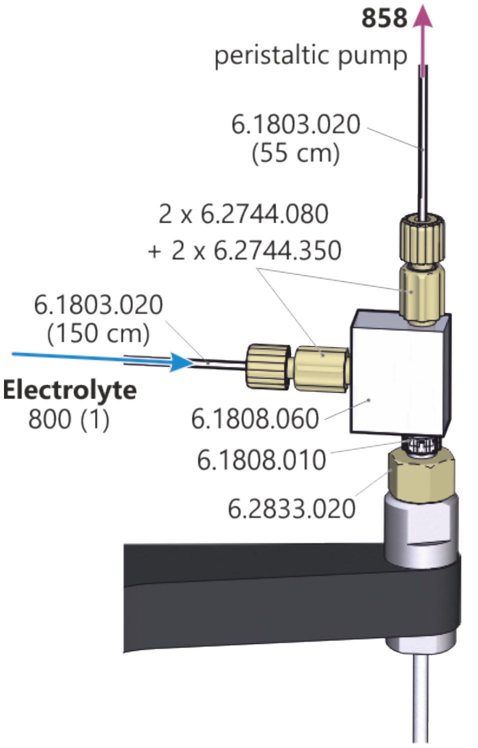


Figure 7. Details of the T connector 6.1808.060 on the robotic arm with one electrolyte for sample preparation.

One junction of the T connector is fixed to the needle holder (6.2833.020) on the robotic arm by means of the M6/M6 adapter (6.1808.010). The opposite side of the T connector is connected to the peristaltic pump of the 858 Professional Sample Processor for transferring the extracted sample from the sample vial to the measuring vessel of the 884 Professional VA.

The third junction is connected to the 807 Dosing Unit on 800 Dosino (1) for the addition of «Electrolyte neutral» to the sample vial. The 807 Dosing Unit with «Electrolyte alkaline» does not need to be connected to the 858 Professional Sample Processor.

Both capillaries (6.1803.020), i.e., the one coming from the 807 Dosing Unit with «Electrolyte neutral» and the one connected to the peristaltic pump, should run through the guide chain of the 858 Professional Sample Processor.

2.3.3 Details 884 Professional VA

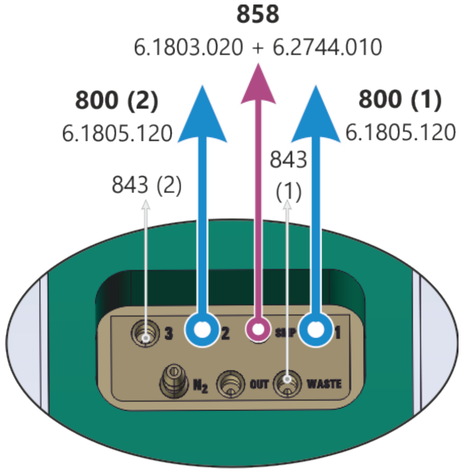


Figure 8. Details of the tubing connections for solution transfer on the tubing connector on the back of the measuring head arm.

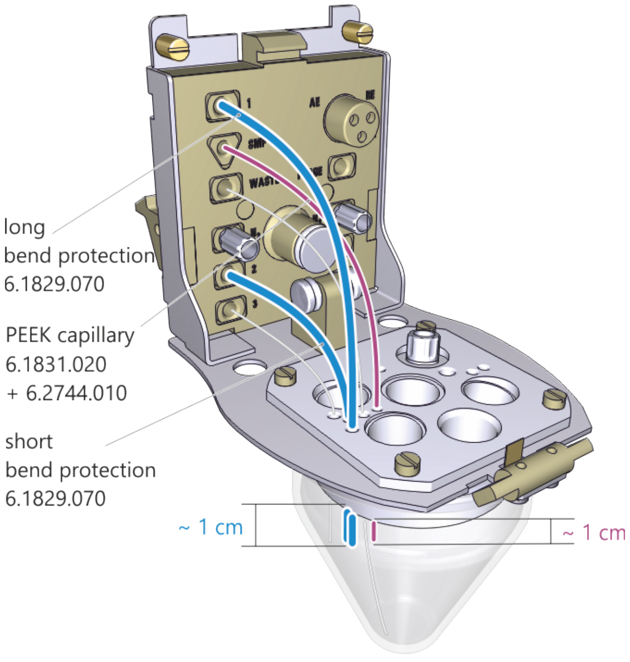


Figure 9. Details of the tubing connections for solution transfer in the measuring head.

The length of the FEP tubing (6.1829.070) and the PEEK capillary (6.1831.020) in the measuring head must be adapted by means of the capillary cutter (6.2621.080). All of this tubing must be shortened to approx. 1 cm measured from the bottom edge of the measuring head insert.

2.3.4 Details 807 Dosing Unit 20 mL for electrolyte

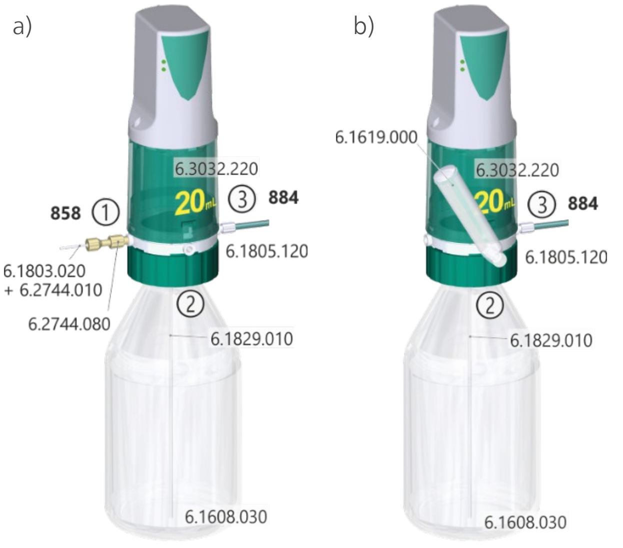


Figure 10. Setup of tubing connections of the 20 mL 807 Dosing Unit used for the addition of electrolytes, a) «Electrolyte neutral», and b) «Electrolyte alkaline».

The setup at port 1 depends on the intended use of the 807 Dosing Unit. If the 807 Dosing Unit is used to supply electrolyte to the sample vial, a capillary (6.1803.020) is connected using an M6 adapter (6.2744.080) and a PEEK pressure screw (6.2744.010) as shown in **Figure 10a**. In case of the setup with one electrolyte for sample preparation (see 2.3), this applies to the 807 Dosing Unit with «Electrolyte neutral». Nothing is connected to port 1 for 807 Dosing Unit «Electrolyte alkaline» in this setup (**Figure 10b**).

For the setup with two electrolytes for sample preparation (see 2.5), both 807 Dosing Units with «Electrolyte neutral» and «Electrolyte alkaline» are equipped with the capillary on port 1.

The aspiration tube (6.1829.010) for aspirating the electrolyte must be connected to port 2 of the 807 Dosing Unit. The 1 L glass bottle is to be filled with «Electrolyte neutral» or «Electrolyte alkaline».

The FEP tubing (6.1805.120) for supply of electrolyte to the measuring vessel of the 884 Professional VA must be connected to port 3 of the 807 Dosing Unit. The other end of this tubing must be either connected to the tubing connector 1 or 2 of the measuring head arm of the 884 Professional VA (see **Figure 8**).

Please note! The port VENT on the 807 Dosing Unit for «Electrolyte alkaline» must be equipped with an adsorber tube (6.1619.000) filled with soda lime for CO_2 adsorption. For the assembly, please refer to the *807 Manual* [3] chapter 3.3.

2.4 Tubing connections for rinsing and draining

2.4.1 Rinsing measuring vessel

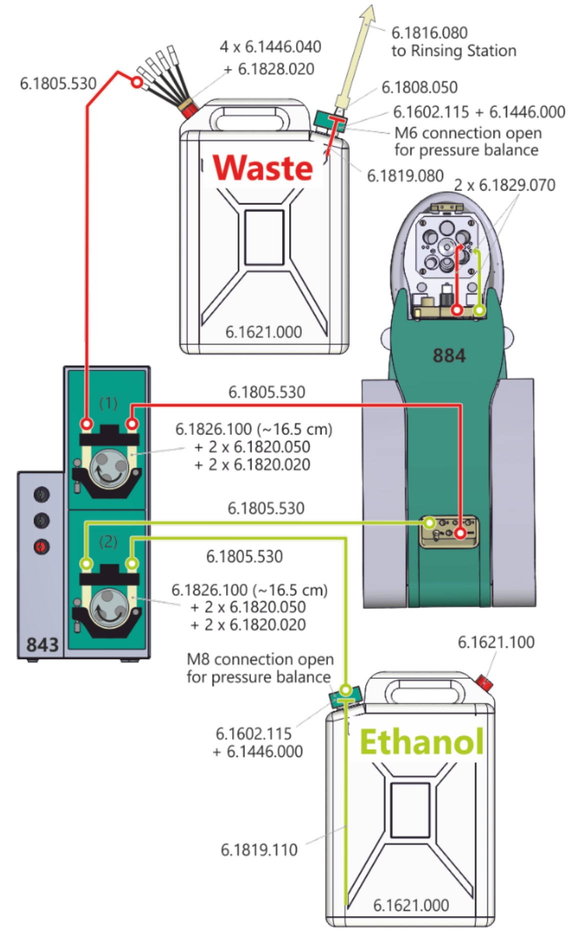


Figure 11. Overview of tubing connections for draining and rinsing.

For the installation of the pump tubing at the 843 Pump Station, please refer to *843 Manual* [**4**] chapter 3.2. The adapter 6.1820.020 must be used for the connection of the M6 thread of the FEP tubing (6.1805.530) to the tubing olives (6.1820.050).

As rinsing solution, «Ethanol for rinsing» should be used which is acidified with HNO_3 (see 1.3). Since the HNO_3 concentration does not need to be extremely precise, the rinsing solution can be prepared in the «Ethanol» container by mixing e.g., 0.5 mL HNO_3 (conc.) and 5 L ethanol.

To prevent evaporation of organic solvents, all unused openings of the containers except for one must be closed with stoppers.

Please note! One opening must remain unblocked for pressure balancing. Closing all openings can cause a malfunction in the draining and rinsing system.

The larger opening of the bottle attachment (6.1602.115) must be closed with the SGJ stopper (6.1446.000). The M8 connector (for the ethanol container) and the M6 connector (for the waste container) must remain open for pressure balancing. The remaining M6 connectors on the five-way tubing connector (6.1828.020) of the waste container must be closed with M6 thread stoppers (6.1446.040). To close the corresponding opening at the ethanol container, the cap 6.1621.100 should be used.

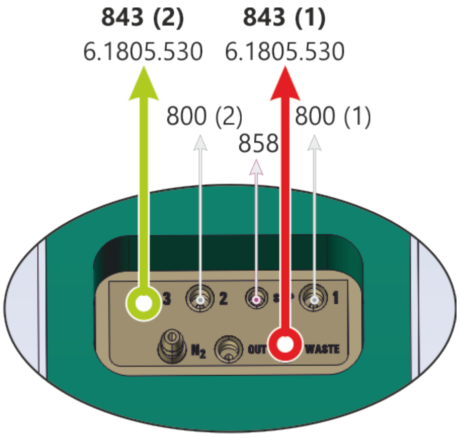


Figure 12. Details of the tubing connections for draining and rinsing on the tubing connector on the back of the measuring head arm.

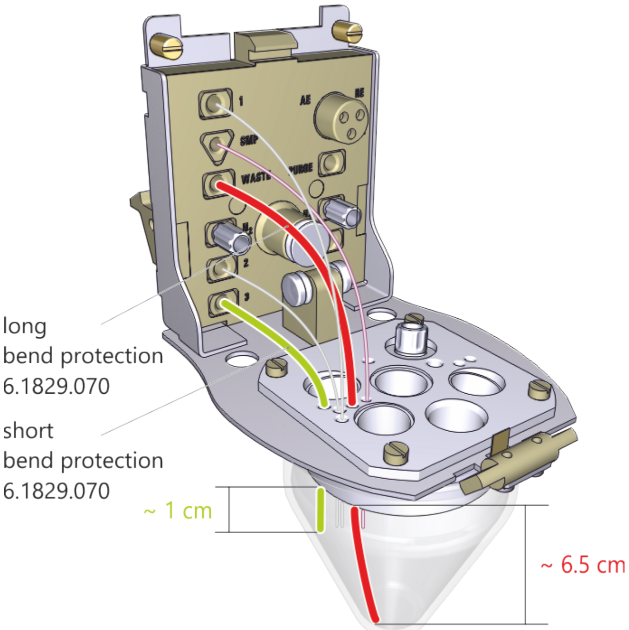


Figure 13. Details of the tubing connections for draining and rinsing in the measuring head.

The length of the two pieces of tubing (6.1829.070) in the measuring head must be adapted by means of the capillary cutter (6.2621.080). The tubing for the rinsing solution must be shortened to approx. 1 cm measured from the bottom edge of the measuring head insert. The tubing for draining must go to the bottom of the measuring vessel (see **Figure 13**).

2.4.2 Rinsing sample needle and transfer tube

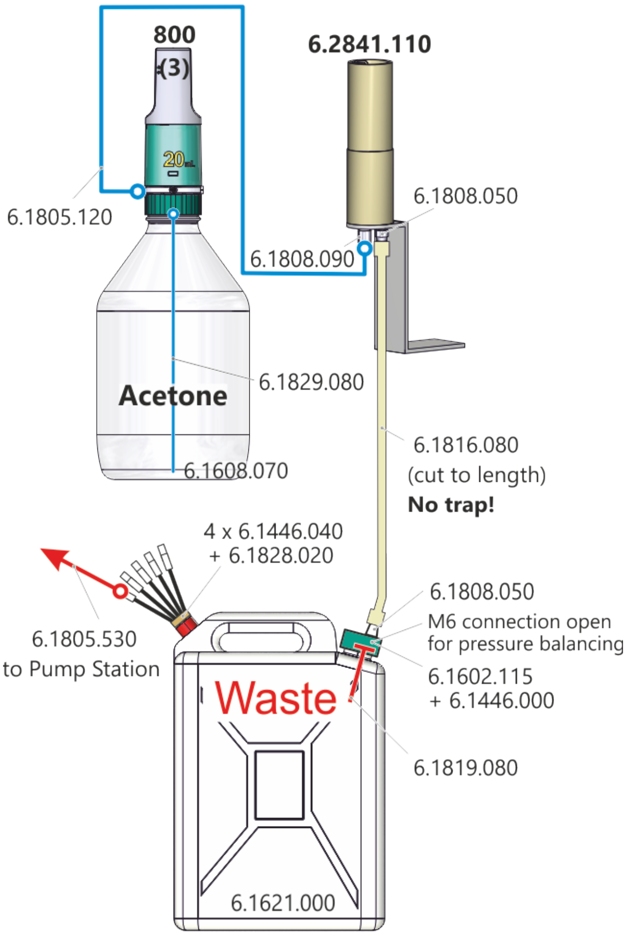


Figure 14. Details of the tubing connections at the rinsing station attached to the sample changer.

Setup of tubing connections for the rinsing station is shown in **Figure 14**. For the supply of rinsing solution, a FEP tubing must be connected between the M6 connector of the rinsing station and port 1 of the 807 Dosing Unit. The 2 L glass bottle should be filled with «Acetone for rinsing station» (see 1.3).

For draining the waste from the rinsing station, the silicone tubing (6.1816.080) must be connected between the olive tubing adapter (6.1808.050) on the rinsing station and the olive tubing adapter (6.1808.050) on the bottle attachment on the waste container. The tubing must be cut to length to ensure that no siphon forms which would hinder an unimpeded drainage.

2.5 Optional: tubing connections with two electrolytes for sample preparation

2.5.1 Overview

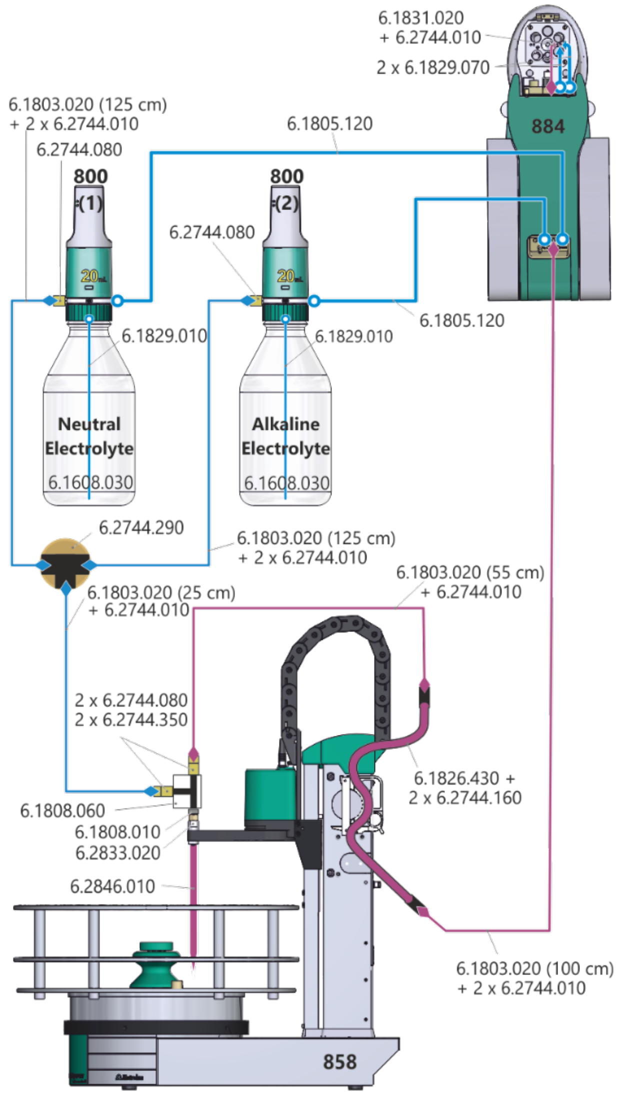


Figure 15. Overview of tubing connections with two electrolytes for sample preparation.

For the installation of the peristaltic pump, please refer to *858 Manual* [**5**] chapter 3.12. The coupling with security device (6.2744.160) should be used for the connection of the pump tubing (6.1826.430).

2.5.2 Details 858 Professional Sample Processor

The handling of two electrolytes requires two T connectors. One T connector (6.2744.290) must be attached to the front of the energy chain (see **Figure 16**), and the second one (6.1808.060) must be attached to the robotic arm of the 858 Professional Sample Processor (see **Figure 17**).

If the option for sample preparation with «Electrolyte alkaline» is not required, the system can be installed as described in 2.3 Tubing connections with one electrolyte for sample preparation.

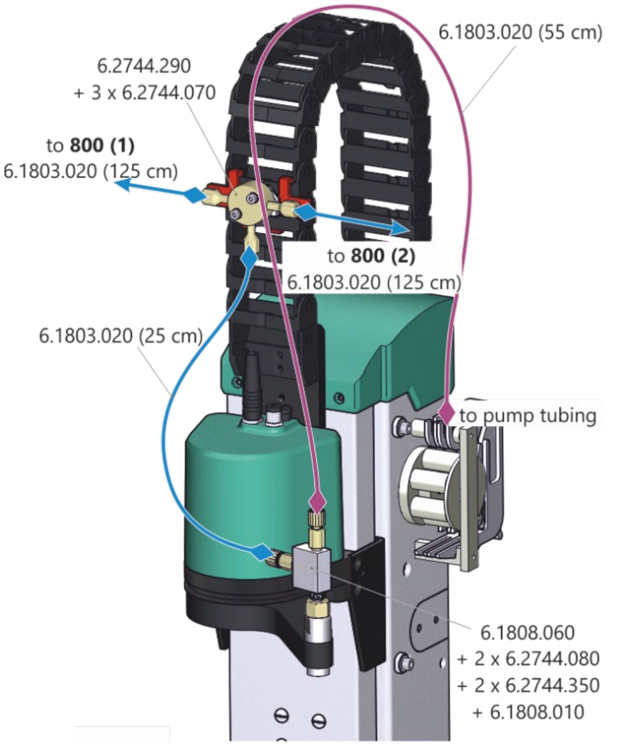


Figure 16. Details of the T connector 6.2744.290 for the connection of two electrolytes for sample preparation.

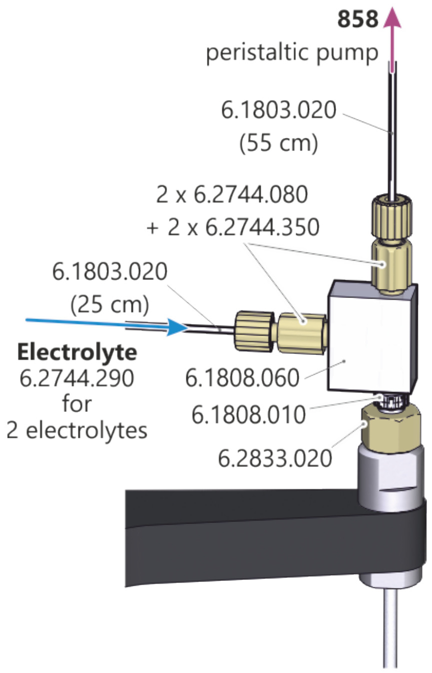


Figure 17. Details of the T connector 6.1808.060 on the swing arm with two electrolytes for sample preparation.

T connector 6.2744.290

The two electrolytes are connected to the opposite sides of the T connector, whereas the third junction is connected to the T connector 6.1808.060 attached to the robotic arm of the 858 Professional Sample Processor.

T connector 6.1808.060

One junction of the T connector is fixed to the needle holder (6.2833.020) on the robotic arm by means of the M6/M6 adapter (6.1808.010). The opposite side of the T connector is connected to the peristaltic pump of the 858 Professional Sample Processor for transferring the extracted sample from the sample vial to the measuring vessel of the 884 Professional VA.

The third junction is connected to the T connector 6.2744.290 for the optional addition of «Electrolyte neutral» or «Electrolyte alkaline» to the sample vial.

2.5.3 Details 884 Professional VA

See 2.3.3 Details 884 Professional VA.

2.5.4 Details 807 Dosing Unit 20 mL for electrolyte

See 2.3.4 Details 807 Dosing Unit 20 mL for electrolyte.

Both 807 Dosing Units are set up as shown in **Figure 10a**. Only the 807 Dosing Unit for the «Electrolyte alkaline» must be additionally equipped with the adsorber tube as shown in **Figure 10b**.

3 viva «Configuration»

In addition to this Application Bulletin, it is recommended to have the following document available.

8.103.8033xx	**viva** VA Tutorial (trace analysis) [**7**] In the following chapters it will be referred to as *Tutorial*.

3.1 Devices – 884 Professional VA

The 884 Professional VA is automatically recognized by the viva software. When an instrument is connected for the first time it needs to be entered in the **viva** «Configuration». The corresponding dialog will pop up automatically. Device name should be kept as used in the **viva** example methods provided with this Application Bulletin.

Device name	884_1

For a step-by-step description, please see the *Tutorial* [**7**] chapter «4.1.1 Configuring the instrument».

3.2 Devices – 858 Professional Sample Processor

The 858 Professional Sample Processor is automatically recognized by the **viva** software. When an instrument is connected for the first time it needs to be entered in the **viva** «Configuration». The corresponding dialog will pop up automatically. Device name should be kept as used in the **viva** example methods provided with this Application Bulletin.

Device name	858 Sample Processor

For a step-by-step description, please see the *Tutorial* [**7**] chapter «6.1.1 Configuring the instrument».

3.2.1 Tower

Tower parameters

Max. stroke path	160	mm
Min. beaker radius	off	
Lift rate	25	mm/s
Axial distance	166.0	mm

Swing Head

Swing position	0	mm
Rinse position	0	mm

External Position	Angle	Work position
1	116.7°	115 mm
2	109.5°	35 mm

3.2.2 Rack

Rack name	6.2041.340	
Shift rate	20	°/s

3.2.3 Rack data

Rack parameters

Beaker radius samples	off	
Beaker sensor	off	
Rack offset	0	°

Lift positions – Tower 1

Work position	147*	mm
Rinse position	160	mm
Shift position	0	mm
Special position	120	mm

* The volume of extraction solution of the reference oil or the in-service oil transferred into the measuring vessel will depend on this setting. In order to avoid aspiration of sand into the sample needle, there should be a gap of at least 1 cm between the sample needle tip and the sand at the bottom of the vial. On the other hand, the transferred volume must be sufficient for the electrodes to be immersed in the solution.

Lift positions – Tower 2

Work position	Not available
Rinse position	Not available
Shift position	Not available
Special position	Not available

Special beakers

Not used	

3.3 Sensors/Electrodes

Along with the software, a set of electrodes is preinstalled in the **viva** «Configuration». The following three electrodes must be present if the measuring command is used as specified in the **viva** example methods provided with this Application Bulletin.

Sensor name	Sensor type
Auxiliary electrode	Auxiliary electrode
RDE	RDE/SSE
Reference electrode	Reference electrode

3.4 807 Dosing Unit

An 807 Dosing Unit attached to an 800 Dosino (which is connected to the 884 Professional VA or 858 Professional Sample Processor) is automatically recognized by the **viva** software. When the 807 Dosing Unit is connected for the first time, it needs to be entered in the **viva** «Configuration». The corresponding dialog will pop up automatically. For a step-by-step description, please see the *Tutorial* [**7**] chapter «5.1.3 Configuring dosing units». The length of the tubing used in the measuring head arm of the 884 Professional VA can be found in *884 Manual* [**6**] chapter 8.1.

The following 807 Dosing Unit names correspond to the names used in the **viva** example methods provided with this Application Bulletin. However, 807 Dosing Unit names can be chosen freely, independent of instrument and MSB port the Dosino is physically connected to.

3.4.1 807 Dosing Unit for «Electrolyte neutral»

Hardware

Name	Electrolyte neutral

Parameters for preparation

Dosing port Prep/Empty	**Dosing port 2**	
Dosing rate Dosing port 1	**10**	mL/min
Dosing rate Dosing port 2	maximum	mL/min
Dosing rate Fill port	maximum	mL/min
Dosing rate Special port	maximum	mL/min

Tubing parameters

	Port	Length	Diameter
Dosing port 1	Port 1	170 cm	1 mm
Dosing port 2	Port 3	135 cm	2 mm
Fill port	Port 2	25 cm	2 mm
Special port	Port 4	0 cm	2 mm

Valve disk

Rotation direction	automatic

3.4.2 807 Dosing Unit for «Electrolyte alkaline»

Hardware

Name	Electrolyte alkaline

Parameters for preparation

Dosing port Prep/Empty	**Dosing port 2**	
Dosing rate Dosing port 1	**10**	mL/min
Dosing rate Dosing port 2	maximum	mL/min
Dosing rate Fill port	maximum	mL/min
Dosing rate Special port	maximum	mL/min

Tubing parameters

	Port	Length	Diameter
Dosing port 1	Port 1	0/170 cm*	1 mm
Dosing port 2	Port 3	135 cm	2 mm
Fill port	Port 2	25 cm	2 mm
Special port	Port 4	0 cm	2 mm

* Depends on the hardware setup: 0 cm for option with 1 electrolyte (2.3), 170 cm for option with 2 electrolytes (2.5).

Valve disk

Rotation direction	automatic

3.4.3 807 Dosing Unit for rinsing station

Hardware

Name	WashStation

Parameters for preparation

Dosing port Prep/Empty	Dosing port 1	
Dosing rate Dosing port 1	maximum	mL/min
Dosing rate Dosing port 2	maximum	mL/min
Dosing rate Fill port	maximum	mL/min
Dosing rate Special port	maximum	mL/min

Tubing parameters

	Port	Length	Diameter
Dosing port 1	Port 1	100 cm	2 mm
Dosing port 2	Port 3	0 cm	2 mm
Fill port	Port 2	35 cm	2 mm
Special port	Port 4	0 cm	2 mm

Valve disk

Rotation direction	automatic

3.5 Solutions

Solutions that should be added automatically must be defined in the **viva** «Configuration» and need to be assigned to the 807 Dosing Unit which is used for the addition. For a step-by-step description, please see the *Tutorial* [7] chapter «5.1.4 Defining solutions».

Table 1 lists the solution names and corresponding 807 Dosing Units as used in the **viva** example methods.

Table 1. 807 Dosing Units and solutions.

Solution name	**Type***	**807 Dosing Unit**
Electrolyte neutral	A	Electrolyte neutral
Electrolyte alkaline	A	Electrolyte alkaline

*Solution type: A – auxiliary solution

4 viva «Method»

This Application Bulletin comes with four example methods using the described hardware setup:

- AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol
- AB445 – ASTM D6810 – Phenol
- AB445 – Maintenance - Electrochemical cleaning
- AB445 – Maintenance - Prepare dosing units

The methods already establish the basic sequences for the applications, the use of 800 Dosinos for automatic addition, the application of a sample changer and pumps to process a sample series, as well as the calculation of the results. However, certain commands and settings must be adapted to the used hardware and the requirements of the specific application.

Please note! Method «AB445 – ASTM D6810 – Phenol» requires the hardware setup described in 2.5. All other methods can be used with the setup for one or two electrolyte(s) for sample preparation.

For details about method parameters, please also refer to the **viva** – Online help. To access the help menu, press [F1] in the **viva** software, or select in the menu Help ▶ viva Help.

4.1 Method run

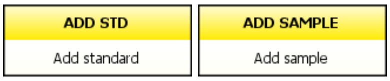
The following commands must be adapted:

Please note! Not all of these commands are present in all example methods.

4.1.1 Measuring commands

- If the name of the 884 Professional VA differs from the specifications in 3.1, assign the correct instrument name.
- If the application differs from the standard procedure for the determination of antioxidants, adapt the measuring parameters on the tabs «Pre-treatment», «Sweep», «Post-treatment», and «Potentiostat» according to the requirements. These parameters are then found in separate application documentation.

4.1.2 Dosing commands



- It is necessary in the method to include the volume of reference oil (**ADD STD**) or in-service oil (**ADD SAMPLE**) into the volume bookkeeping. Both commands use the volume specified in the workplace for «Sample amount».
- No changes are required.

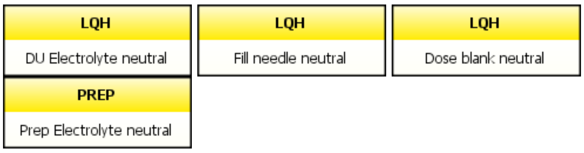
Solution «Electrolyte neutral»

- Command for the addition of «Electrolyte neutral» when the volume must be included in the volume bookkeeping.
- If the name of the solution differs from the specifications in 3.5, select the correct solution name from the drop-down list «Solution».

Solution «Electrolyte alkaline»

- Commands for the addition of «Electrolyte alkaline» when the volume must be included in the volume bookkeeping.
- If the name of the solution differs from the specifications in 3.5, select the correct solution name from the drop-down list «Solution».

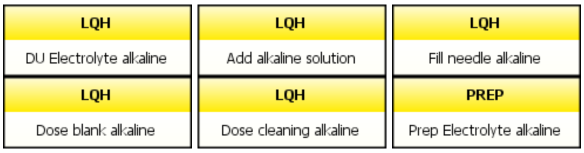
807 Dosing Unit «Electrolyte neutral»



- Commands for additional liquid handling operations with «Electrolyte neutral» when the volume should not be included in the volume bookkeeping.

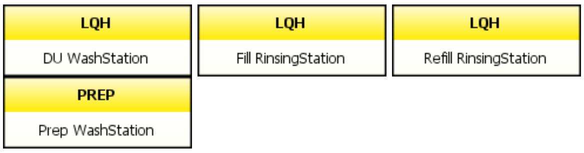
- If the name of the 807 Dosing Unit differs from the specifications in 3.4.1, select the correct name from the drop-down list «Name of dosing unit».

807 Dosing Unit «Electrolyte alkaline»



- Commands for additional liquid handling operations with «Electrolyte alkaline» when the volume should not be included in the volume bookkeeping.
- If the name of the 807 Dosing Unit differs from the specifications in 3.4.2, select the correct name from the drop-down list «Name of dosing unit».

807 Dosing Unit «WashStation»



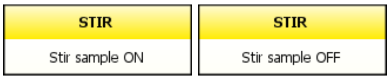
- Commands for liquid handling operations with the 807 Dosing Unit «WashStation». The volume is not included in the volume bookkeeping.
- If the name of the 807 Dosing Unit differs from the specifications in 3.4.3, select the correct name from the drop-down list «Name of dosing unit».

4.1.3 Automation commands

Stirrer of the 884 Professional VA

- Commands to control the stirrer in the 884 Professional VA.
- If the name of the instrument differs from the specifications in 3.1, select the correct name from the drop-down list «Device name».

741 Stirrer



- Commands to control the 741 Stirrer connected to the 858 Professional Sample Processor.

  Please note! The 741 Stirrer itself does not appear in the configuration. Instead, the 858 Professional Sample Processor to which it is connected must be selected in the command.

- If the name of the 858 Professional Sample Processor differs from the specifications in 3.2, select the correct name from the drop-down list «Device name».

858 Professional Sample Processor

- Commands to control the 858 Professional Sample Processor.
- If the name of the instrument differs from the specifications in 3.2, select the correct name from the drop-down list «Device name».

- Commands to control the peristaltic pump are built-in to the 858 Professional Sample Processor as well as the two peristaltic pumps of the 843 Pump Station.

  Please note! The 843 Pump Station itself does not appear in the configuration. Instead, the sample changer to which it is connected must be selected in the command.

- If the name of the 858 Professional Sample Processor differs from the specifications in 3.2, select the correct name from the drop-down list «Device name».

4.1.4 Preparing reference or in-service oil sample

The track shown in **Figure 18** is used in the methods «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol» and «AB445 – ASTM D6810 – Phenol».

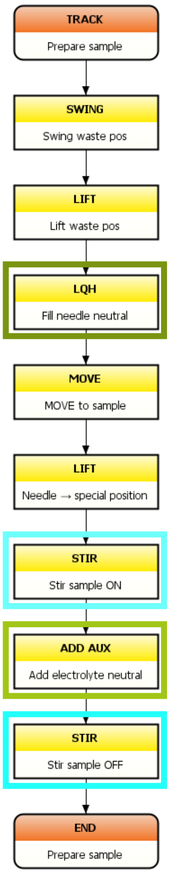


Figure 18. Method snippet – TRACK controlling the preparation of the reference oil or in-service oil sample on the rack of the 858 Professional Sample Processor.

Before the preparation of the sample, the sample needle must be filled with the intended electrolyte. For this purpose, the swing head is moved to the waste position (see **Figure 5**) of the rinsing station. A small volume of electrolyte is added to waste using the command **LQH – Fill needle neutral**, in case of method «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol», or **LQH – Fill needle alkaline**, in case of method «AB445 – ASTM D6810 – Phenol». 10 mL of the same electrolyte is then added to the sample vial in the command **ADD AUX – Add electrolyte neutral** or **ADD AUX – Add electrolyte alkaline**, respectively.

Before the addition of the electrolyte, the 741 stirrer is switched on with the command **STIR – Stir sample ON**. After the addition of the electrolyte, the stirring continues for another 20 seconds, controlled in the command **STIR – Stir sample OFF**. The «Stirring rate» is also defined in these two commands. If the stirrer bar bounces around in the sample vial during the mixing, the stirring rate must be reduced, provided that the stirrer was properly positioned (see 2.2.2).

4.1.5 Transferring aliquot of extraction solution

The tracks shown in **Figure 19** are used in the methods «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol» and «AB445 – ASTM D6810 – Phenol».

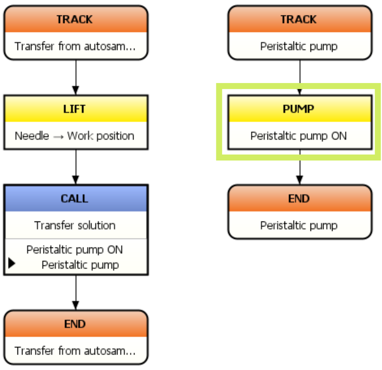


Figure 19. Method snippet – TRACKs controlling the transfer of the extraction solution.

An aliquot of the extraction solution of the reference oil or the in-service oil sample is transferred from the vial on the rack to the measuring vessel by means of the built-in peristaltic pump of the 858 Professional Sample Processor.

To avoid the aspiration of sand into the sample needle, the sample is only partly transferred. The transferred volume will depend on the «Work position» defined in 3.2.3.

The peristaltic pump for the transfer is controlled by the command **PUMP – Peristaltic pump ON**. The time for the transfer of the extraction solution is specified in the parameter «Duration». The time should be set in a way that the transfer tubing from the 858 Professional Sample Processor to the measuring vessel of the 884 Professional VA is empty at the end of the transfer. The predefined time of 300 s is more on the safe side. Besides the volume of the extraction solution to be transferred, other factors like the inner diameter of the pump tubing, the adjustment of the contact pressure of the tubing cartridge, and the pump rate, affect the transfer time. Therefore, the parameter «Duration» should be adapted to the specific hardware setup.

4.1.6 Addition of alkaline solution in the combined method

The tracks shown in **Figure 20** are used in the method «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol».

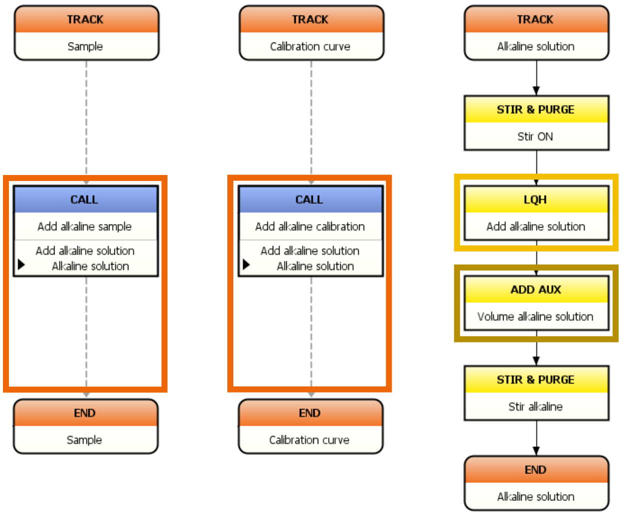


Figure 20. Method snippet – TRACKs controlling the addition of alkaline solution in the method combining ASTM D6971 and ASTM D6810.

In the method «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol» the sample is extracted with «Electrolyte neutral». After the determination of the amine type antioxidants in this solution, phenol type antioxidants are determined under alkaline conditions. The addition of 2 mL «Electrolyte alkaline» via port 3 of the 807 Dosing Unit is defined in the command **LQH – Add alkaline solution**. The command **ADD AUX – Volume alkaline solution** is necessary to include the added volume into the volume bookkeeping. If modifications of the addition volume are necessary, they must be done in the **LQH** command. The volume is automatically adapted in the **ADD AUX** command.

The command **CALL – Add alkaline sample** and all following commands in the **TRACK - Sample** as well as **CALL – Add alkaline calibration** and all following commands in the **TRACK – Calibration curve** can be deleted if only amine type antioxidants should be determined. In this case the **TRACK – Alkaline solution** is also obsolete.

4.1.7 Rinsing sample needle and transfer tubing

The tracks shown in **Figure 21** are used in the methods «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol» and «AB445 – ASTM D6810 – Phenol».

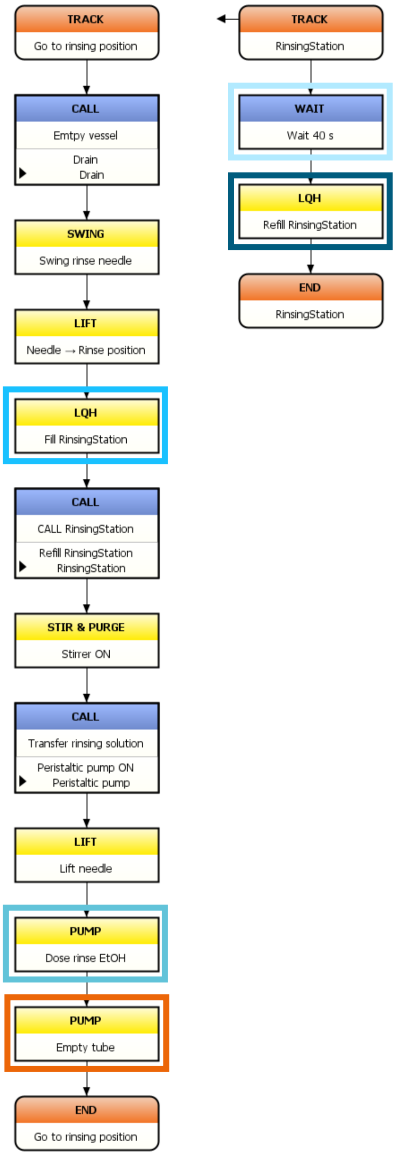


Figure 21. Method snippet – TRACKs controlling flushing of the sample needle and the rinsing of the transfer tubing.

After each sample, the sample needle and the transfer tubing from the 858 Professional Sample Processor to the measuring vessel of the 884 Professional VA need to be rinsed with acetone. This is controlled from the **TRACK – Go to rinsing position**. The rinsing solution is supplied from the rinsing position of the rinsing station (see **Figure 5**). The transfer time for the rinsing solution corresponds to the time for transfer of extraction solution as defined in the command **PUMP – Peristaltic pump ON** (see 4.1.5).

In a first step, the sample needle is flushed from the outside. For this purpose, the sample needle is moved into the rinsing position of the rinsing station and the inner tube of the rinsing station is filled with 7 mL rinsing solution using the command **LQH – Fill RinsingStation**. This volume is larger than the capacity of the inner tube. The excess solution drains into waste. The remaining solution in the rinsing station is used to rinse the sample needle and the transfer tube from the inside. When the rinsing solution in the inner tube is almost used up, after the waiting time defined in the command WAIT – Wait 40 s, another 3 mL of fresh rinsing solution are provided using the command LQH – Refill RinsingStation. The dosing rate in this command correlates approximately with the pumping rate of the peristaltic pump with the described setup. If a different pump tubing with a different inner diameter is installed or the pump rate defined in the command PUMP – Peristaltic pump ON is modified, the time in the command WAIT – Wait 40 s and the dosing rate in the command LQH – Refill RinsingStation may need to be adapted.

The command PUMP – Empty tube ensures that the transfer tube is empty at the end of the rinsing process.

Please note! The command PUMP – Dose rinse EtOH addresses the rinsing pump of the 843 Pump Station and supplies «Ethanol for rinsing» to the measuring vessel.

4.1.8 Rinsing measuring vessel

The tracks shown in **Figure 22** are used in the methods «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol», «AB445 – ASTM D6810 – Phenol», and «AB445 – Maintenance - Electrochemical cleaning».

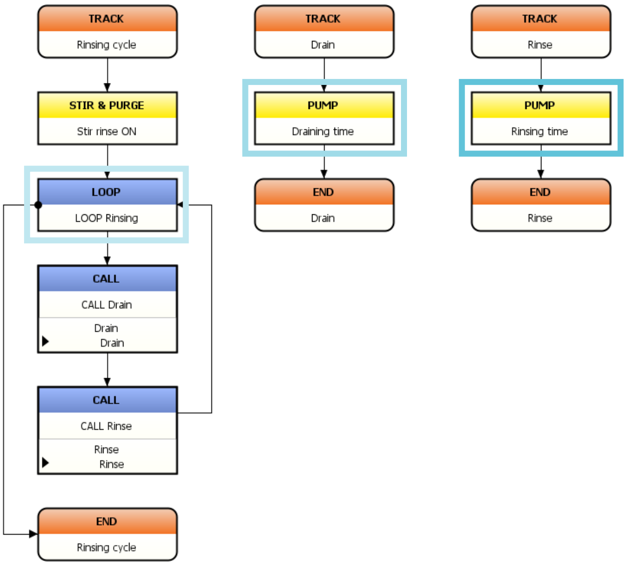


Figure 22. Method snippet – TRACKs controlling the rinsing of the measuring vessel.

After each sample, the measuring vessel needs to be rinsed with «Ethanol for rinsing». The rinsing and draining times are defined in the command PUMP – Rinsing time and PUMP – Draining time. The number of rinsing cycles is defined in the command LOOP – LOOP Rinsing.

Times for rinsing and draining depend on the total volume used in the determination and the setup of the 843 Pump Station, e.g., pressure applied to the pump tubing by means of the pressure clamp and fixing lever. **Table 2** gives a reference point, but the exact times should be verified with the respective system setup.

Table 2. Example values for draining and rinsing settings.

Cell volume	10 mL
Number of rinsing cycles	2
Draining time	15 s
Rinsing time	4 s

4.2 Evaluation

Settings regarding evaluation and documentation of the determination are located in the «Evaluation» part of the method. The example methods «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol» and «AB445 – ASTM D6810 – Phenol» already contain all necessary settings to determine and calculate the remaining amine and phenol content of a sample. If modifications are necessary, the next subchapters point out where important parameters are found.

For more information on the evaluation part of the **viva** method, also refer to *Tutorial* [**7**] chapter «4.2.1.4 Defining the evaluation».

4.2.1 Substances

In the «Substances» part the substance name, settings for peak recognition, and baseline parameters are defined.

4.2.2 Standards

Under «Standards», the concentration of the used standard solution is defined.

In these applications, the actual concentration of antioxidant in the standard is often unknown and set arbitrarily to 100%. The result for the sample is calculated as % remaining antioxidant, which is a dimensionless quantity. For the calculation, a concentration of 1000 mL/L is specified for the standard. This represents an undiluted reference oil, independent of the actual concentration of the antioxidant in the oil.

If the concentration of antioxidant in the reference oil (in #g/L, #mol/L or #mL/L) is known, the correct concentration and concentration unit can be entered here. In this case the automatically calculated results will show the actual concentration of antioxidant in the sample. The user-defined results will still show the relative concentration of «Remaining Amine» and/or «Remaining Phenol» in the in-service oil sample. For the calculation of the user-defined results, see 4.2.4.

Please note! The name of the standard solution shown as header of the column must be spelled exactly as the name of the standard solution in the command **ADD STD – ADD STANDARD**. In case of inconsistent spelling, no calibration curve can be calculated.

4.2.3 Calibration

The calibration technique is defined under «Calibration». In the methods «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol» and «AB445 – ASTM D6810 – Phenol», «External calibration» with «Linear regression through 0» must be selected.

4.2.4 Results

On the «Results» tab, the assignment of the automatically calculated result to a result variable is defined. If the standard concentration is unknown and therefore chosen arbitrarily under 4.2.2, the «Assignment» should be «none». If the standard concentration is defined correctly, a result variable «RSxx» can be selected under which the result will be displayed in the «Determination overview» of the database.

The remaining antioxidant content is calculated with «User-defined results». The following formulas are used for the calculation:

Remaining amine:

```
'RS.Sweep neutral.Amine.CONC'  /
'ED.Standards.Standard.Amine.CONC'  * 100
```

and / or

Remaining phenol:

```
'RS.Sweep alkaline.Phenol.CONC'  /
'ED.Standards.Standard.Phenol.CONC'  * 100
```

The formulas need to be adapted if the name of the command **DP – SWEEP NEUTRAL** or **DP – SWEEP ALKALINE** (see 4.1.1), the name of the standard solution (see 4.2.2), or the name of the substances (see 4.2.1) is changed.

5 Operation

5.1 Initial preparation

- The 10 L container «Ethanol» for rinsing of the measuring vessel (see **Figure 11**) must be filled with «Ethanol for rinsing». See also 2.4.1 Rinsing measuring vessel.
- The 10 L container «Waste» must be emptied (see **Figure 11**).
- Contact pressure for the peristaltic pumps of the 858 Professional Sample Processor and the 843 Pump Station must be adjusted.
- The 2 L glass bottle must be filled with «Acetone for rinsing station» (see **Figure 12**).
- The 1 L glass bottles must be filled with «Electrolyte neutral» and «Electrolyte alkaline», respectively (see **Figure 6** and **Figure 15**).
- The 807 Dosing Units «Electrolyte neutral», «Electrolyte alkaline», and « WashStation» must be prepared with the respective solutions. For Preparation of 807 Dosing Units, see 5.2.

5.2 Preparation of 807 Dosing Units

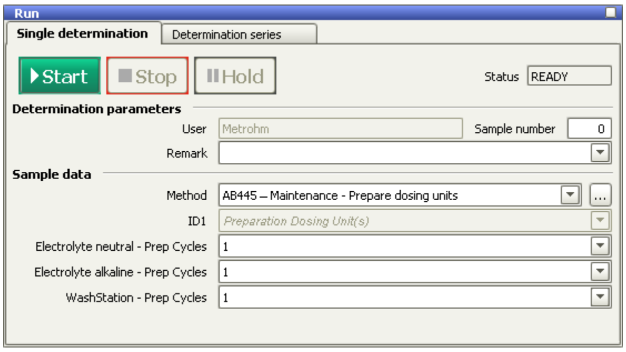
5.2.1 Manual operation

For startup or shutdown of the system, the preparation of 807 Dosing Units can be done from the viva «Manual control». In this case, care must be taken that:

- The sample needle is moved to the waste position of the rinsing station (see **Figure 5**) before 807 Dosing Units «Electrolyte neutral» and/or «Electrolyte alkaline» are prepared.
- 807 Dosing Units «Electrolyte neutral» and «Electrolyte alkaline» are not prepared simultaneously.
- The measuring vessel is replaced by a waste beaker or the pump for draining the measuring vessel is switched on when 807 Dosing Units «Electrolyte neutral» and/or «Electrolyte alkaline» should be prepared.

5.2.2 Workplace

More conveniently, the 807 Dosing Units can be prepared using the method «AB445 – Maintenance - Prepare dosing units», which is provided with this Application Bulletin. The method allows to specify the number of preparation cycles individually for each 807 Dosing Unit on the workplace as shown in **Figure 23**.



Status READY
User Metrohm
Sample number 0
Remark
Method AB445 – Maintenance - Prepare dosing units
ID1 *Preparation Dosing Unit(s)*
Electrolyte neutral - Prep Cycles 1
Electrolyte alkaline - Prep Cycles 1
WashStation - Prep Cycles 1

Figure 23. Example for the settings in the «Run» window to prepare the 807 Dosing Units using the method «AB445 – Maintenance - Prepare dosing units»

Features of the method:

- The preparation of the 807 Dosing Unit is repeated as many times as specified in the workplace, 1 = once, 2 = twice, etc.
- With «Prep cycles» = 0, the respective 807 Dosing Unit is not prepared.
- The sample needle is moved to the waste position of the rinsing station (see **Figure 5**) before 807 Dosing Units «Electrolyte neutral» and/or «Electrolyte alkaline» are prepared.
- 807 Dosing Units «Electrolyte neutral» and «Electrolyte alkaline» are prepared sequentially. 807 Dosing Unit «WashStation» is prepared in parallel with «Electrolyte neutral» or «Electrolyte alkaline».
- The measuring vessel is continuously drained when 807 Dosing Units «Electrolyte neutral» and/or «Electrolyte alkaline» are prepared.

Please note! When the method «AB445 – Maintenance - Prepare dosing units» should be used in a sample series, make sure that ID1 to ID4 are activated for the tab «Determination series» under «Properties run window» on the «Display» tab.

5.3 Electrochemical cleaning of electrodes

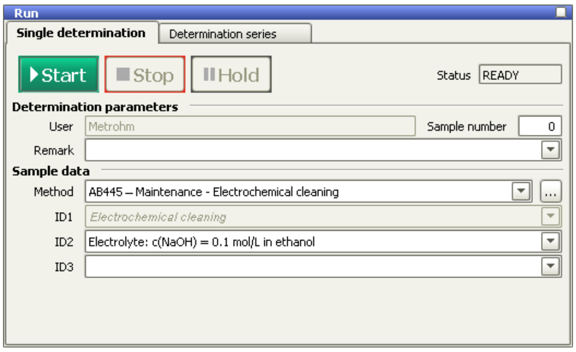
In an automated system it is not possible to wipe the electrode clean after each determination. Instead, the measuring cell is rinsed with «Ethanol for rinsing». Over time, rinsing alone is not sufficient to maintain the sensitivity of the determination. Therefore, the electrodes are cleaned electrochemically using the method «AB445 – Maintenance – Electrochemical cleaning». For recommendations regarding frequency of electrochemical cleaning and cleaning of electrodes in general, please refer to chapter 7.3 Cleaning of electrodes in this Application Bulletin.

5.3.1 Manual operation

- 807 Dosing Unit «Electrolyte alkaline» must be prepared with the solution «Electrolyte alkaline».
- 843 Pump Station for draining and rinsing must be operational.

5.3.2 Workplace

- The method can be carried out as «Single determination» but also within a «Determination series».
- The method does not require solution from the rack of the sample changer nor a sample, therefore no entry fields for «Sample type», «Sample position», «Sample amount», or «Sample amount unit» are available.



Status READY
User Metrohm
Sample number 0
Remark
Method AB445 – Maintenance - Electrochemical cleaning
ID1 *Electrochemical cleaning*
ID2 Electrolyte: c(NaOH) = 0.1 mol/L in ethanol
ID3

Figure 24. Example for the «Run» window when the method «AB445 – Maintenance - Electrochemical cleaning» is loaded for a «Single determination».

5.3.3 Course of events

The cleaning of the electrodes is controlled by the 884 Professional VA and **viva**.

1. The measuring vessel is emptied using the 843 Pump Station.
2. 5 mL «Electrolyte alkaline» are added to the measuring vessel from the 807 Dosing Unit «Electrolyte alkaline».
3. The «Sweep DP» is repeated until the relative standard deviation of the current at 900 mV is less than 3%, or for 10 runs, whichever is reached first.
4. At the end of the electrochemical cleaning, the measuring vessel is emptied and rinsed using the 843 Pump Station.

5.4 Calibration and determination

5.4.1 Manual operation

- 807 Dosing Units «Electrolyte neutral», «Electrolyte alkaline», and «WashStation» must be prepared with the respective solutions.
- The peristaltic pump of the 858 Professional Sample Processor must be operational.
- The 843 Pump Station for draining and rinsing must be operational.

5.4.2 Preparation of sample vials

Add

- 1 g quartz sand
- 1 stirring bar (12 mm, 6.1903.010)
- 0.05–0.6* mL reference oil or in-service oil sample

into a 50 mL sample vial (6.2747.020).

*The sample volume to be used for the determination depends on the application. For recommendations regarding the selection of the sample volume, please refer to chapter 7.1 Selection of sample volume in this Application Bulletin.

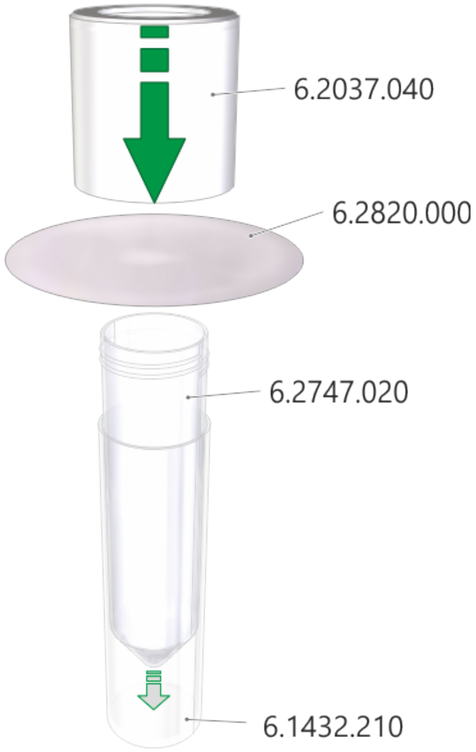


Figure 25. Preparation of a sample vial.

Place the 50 mL sample vial in the 75 mL glass sample beaker (6.1432.210). Make sure the plastic vial is pushed down to the bottom.

Use a sheet of aluminum foil (6.2820.000) to cover the sample vial. By hand, the aluminum foil must be pressed firmly around the thread of the plastic vial. The foil holder (6.2037.040) can be used as a tool to push down the foil along the side of the glass beaker first.

The prepared sample vials are placed on the rack of the sample changer.

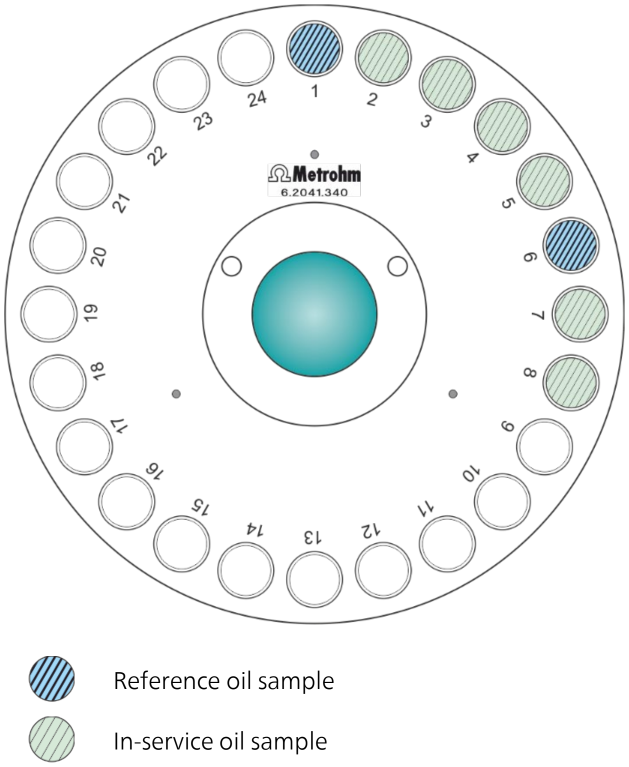
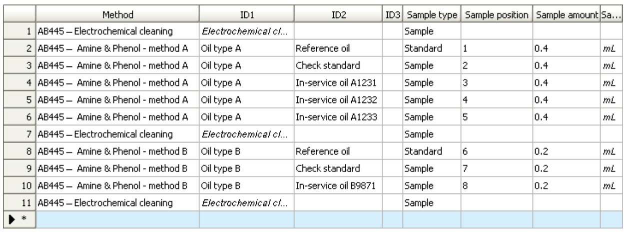


Figure 26. Example for positions of solutions on the rack 6.2041.340.

Please note! It is not necessary to reserve sample positions on the rack for the electrochemical cleaning as described in chapter 5.3.

5.4.3 Workplace

- Create a sample table in the «Run» window on the «Determination series» tab:



	Method	ID1	ID2	ID3	Sample type	Sample position	Sample amount	Sa...
1	AB445 – Electrochemical cleaning	*Electrochemical cl...*			Sample			
2	AB445 – Amine & Phenol - method A	Oil type A	Reference oil		Standard	1	0.4	*mL*
3	AB445 – Amine & Phenol - method A	Oil type A	Check standard		Sample	2	0.4	*mL*
4	AB445 – Amine & Phenol - method A	Oil type A	In-service oil A1231		Sample	3	0.4	*mL*
5	AB445 – Amine & Phenol - method A	Oil type A	In-service oil A1232		Sample	4	0.4	*mL*
6	AB445 – Amine & Phenol - method A	Oil type A	In-service oil A1233		Sample	5	0.4	*mL*
7	AB445 – Electrochemical cleaning	*Electrochemical cl...*			Sample			
8	AB445 – Amine & Phenol - method B	Oil type B	Reference oil		Standard	6	0.2	*mL*
9	AB445 – Amine & Phenol - method B	Oil type B	Check standard		Sample	7	0.2	*mL*
10	AB445 – Amine & Phenol - method B	Oil type B	In-service oil B9871		Sample	8	0.2	*mL*
11	AB445 – Electrochemical cleaning	*Electrochemical cl...*			Sample			
▶ *								

Figure 27. Example for a sample table with calibration and determinations for two different oil types. Solutions are positioned as shown in **Figure 26**.

- For a calibration with reference oil:
  - Select the sample type «Standard».
  - The volume of reference oil pipetted into the sample vial must be entered as «Sample amount» in milliliters.

  Please note! Make sure that the volume is correct. A later recalculation with a different volume will not be possible.

  - The position of the reference oil on the rack must be entered under «Rack position».
- For a determination of an in-service oil sample:
  - Select the sample type «Sample».
  - The volume of in-service oil pipetted into the sample vial must be entered as «Sample amount» in milliliters.
  - The position of the in-service oil on the rack must be entered under «Rack position».

  Please note! The determination must be carried out with the same method as the calibration since the method name is the identifier to select the correct calibration curve.

5.4.4 Course of events – determination of aromatic amine & hindered phenol

The preparation of reference oil or in-service oil sample and the execution of calibration or determination using a 1-point calibration is controlled by the 884 Professional VA and **viva**. The following steps are carried out when using the method «AB445 – ASTM D6971 & ASTM D6810 - Amine & Phenol».

1. A small volume of electrolyte from 807 Dosing Unit «Electrolyte neutral» is ejected to waste to fill the sample needle with the correct electrolyte.
2. 10 mL «Electrolyte neutral» are added to the reference oil or in-service oil in the sample vial on the rack of the 858 Professional Sample Processor.
3. The 741 Stirrer connected to the 858 Professional Sample Processor is used to agitate the mixture of sand, electrolyte and reference oil or in-service oil sample. The stirring starts before the addition of electrolyte and continuous another 20 s after the addition is finished. This makes a total of 80 s mixing time.
4. The measuring vessel attached to the 884 Professional VA is emptied using the 843 Pump Station.

5. 5 mL «Electrolyte neutral» are added into the measuring vessel.

6. The blank current in the «Electrolyte neutral» is recorded.

7. The measuring vessel is emptied using the 843 Pump Station.

8. An aliquot of the extraction solution of reference oil or in-service oil sample is transferred from the sample rack to the measuring vessel of the 884 Professional VA by means of the built-in peristaltic pump of the 858 Professional Sample Processor.

9. Using the parameters in the measuring command **DP – SWEEP NEUTRAL**, one sweep is recorded to condition the electrodes. This curve is not used for result calculation.

10. Using the parameters in the measuring command **DP – SWEEP NEUTRAL**, two replications are measured in the extraction solution of reference oil or in-service oil sample. These curves are evaluated for aromatic amine.

11. 2 mL «Electrolyte alkaline» are added from the 807 Dosing Unit «Electrolyte alkaline» on top of the neutral extraction solution in the measuring vessel.

12. Using the parameters in the measuring command **DP – SWEEP ALKALINE**, one sweep is recorded to condition the electrodes. This curve is not used for result calculation.

13. Using the parameters in the measuring command **DP – SWEEP ALKALINE**, two replicates are measured in the mixture of extraction solution of reference oil or in-service oil sample and «Electrolyte alkaline». These curves are evaluated for hindered phenol.

14. The measuring vessel is emptied using the 843 Pump Station.

15. The sample needle and transfer tubing from the sample changer to the measuring vessel are rinsed with acetone from the rinsing station.

16. At the end of the determination, the measuring vessel is drained and rinsed with «Ethanol for rinsing» using the 843 Pump Station.

17. The dosing units «Electrolyte neutral», «Electrolyte alkaline», and «WashStation» are filled.

18. The calibration curve or the remaining antioxidant content is calculated.
    a. In case of sample type «Standard», the calibration curves for aromatic amine and hindered phenol are calculated. In addition to the database, the calibrations are also stored in the configuration to be used with samples which are carried out with the method with the same name.
    b. In case of sample type «Sample», the remaining antioxidant content is calculated. For the calculation, the calibration curve with the same method name and substance stored in the configuration is used.

The next sample starts again from step 1.

5.4.5 Course of events – determination of hindered phenol only

The preparation of reference oil or in-service oil sample and the execution of calibration or determination using a 1-point calibration is controlled by the 884 Professional VA and **viva**. The following steps are carried out when using the method «AB445 –ASTM D6810 - Phenol».

Please note! The setup described in chapter 2.5 is required for the execution of this method.

1. A small volume of electrolyte from 807 Dosing Unit «Electrolyte alkaline» is ejected to waste to fill the sample needle with the correct electrolyte.

2. 10 mL «Electrolyte alkaline» are added to the reference oil or in-service oil in the sample vial on the rack of the 858 Professional Sample Processor.

3. The 741 Stirrer connected to the 858 Professional Sample Processor is used to agitate the mixture of sand, electrolyte, and reference oil or in-service oil sample. The stirring starts before the addition of electrolyte and continues another 20 s after the addition is finished. This makes a total of 80 s mixing time.

4. The measuring vessel attached to the 884 Professional VA is emptied using the 843 Pump Station.

5. 5 mL «Electrolyte alkaline» are added into the measuring vessel.

6. The blank current in the «Electrolyte alkaline» is recorded.

7. The measuring vessel is emptied using the 843 Pump Station.

8. An aliquot of the extraction solution of reference oil or in-service oil sample is transferred from the sample rack to the measuring vessel of the 884 Professional

VA by means of the built-in peristaltic pump of the 858 Professional Sample Processor.

9. Using the parameters in the measuring command **DP – SWEEP ALKALINE**, one sweep is recorded to condition the electrodes. This curve is not used for result calculation.

10. Using the parameters in the measuring command **DP – SWEEP ALKALINE**, two replicates are measured in the extraction solution of reference oil or in-service oil sample and «Electrolyte alkaline». These curves are evaluated for hindered phenol.

11. The measuring vessel is emptied using the 843 Pump Station.

12. The sample needle and transfer tubing from the sample changer to the measuring vessel are rinsed with acetone from the rinsing station.

13. At the end of the determination, the measuring vessel is drained and rinsed with «Ethanol for rinsing» using the 843 Pump Station.

14. The dosing units «Electrolyte alkaline» and «WashStation» are filled.

15. The calibration curve or the remaining antioxidant content is calculated.
    a. In case of sample type «Standard», the calibration curve for hindered phenol is calculated. In addition to the database, the calibration is also stored in the configuration to be used with samples which are carried out with the method with the same name.
    b. In case of sample type «Sample», the remaining antioxidant content is calculated. For the calculation, the calibration curve with the same method name and substance stored in the configuration is used.

The next sample starts again from step 1.

6 Examples

6.1 Electrochemical cleaning

6.1.1 Measuring solution

5 mL Electrolyte alkaline

6.1.2 Curves

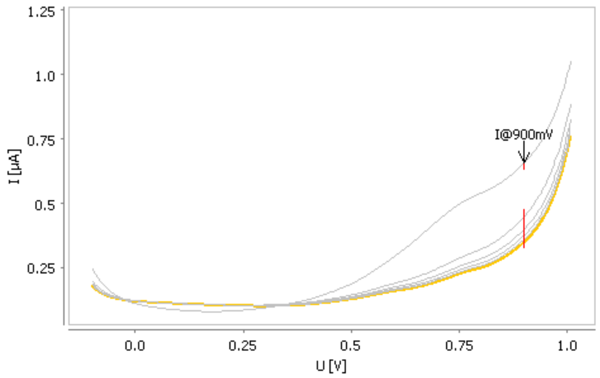


Figure 28. Example for the curves obtained with the method «AB445 – Maintenance - Electrochemical cleaning».

6.1.3 Results

Cleaning measurement	
Current at 900 mV	0.35 µA

6.2 Determination of remaining aromatic amine and hindered phenol content

6.2.1 Measuring solution

Extraction solution

0.2 mL in-service oil

10 mL Electrolyte neutral

Determination of aromatic amine

~5.5 mL extraction solution

Determination of hindered phenol

~5.5 mL extraction solution

+ 2 mL Electrolyte alkaline

6.2.2 Curves

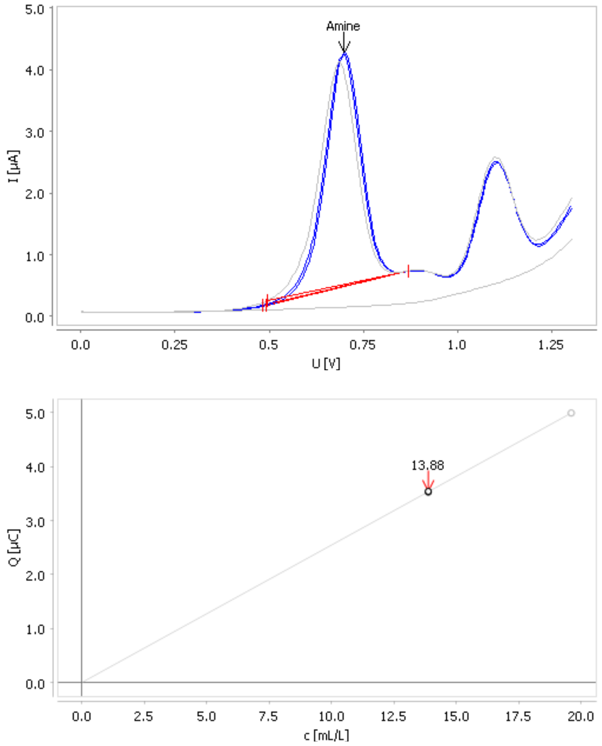


Figure 29. Voltammograms and calibration curve obtained for the determination of aromatic amine in an in-service oil in the neutral extraction solution.

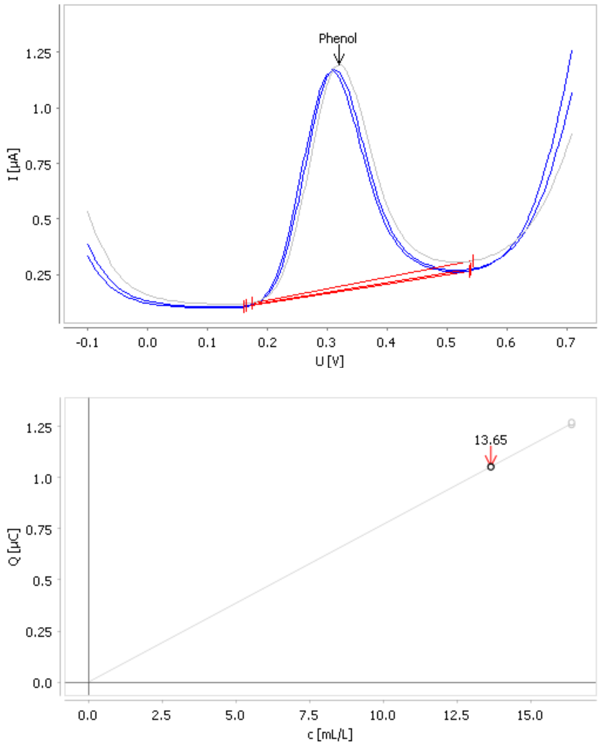


Figure 30. Voltammograms and calibration curve obtained for the determination of hindered phenol in an in-service oil after addition of «Electrolyte alkaline» to the neutral extraction solution.

6.2.3 Results

	Aromatic amine	**Hindered phenol**
Calibration		
Peak area	5.00 µC	1.27 µC
Determination		
Peak area	3.54 µC	1.05 µC
Remaining antioxidant	70.8%	83.3%

7 Comments

For more information and recommendations regarding application and maintenance, please refer to the document «Determination of antioxidants in lubricants – Daily routine for best performance» which can be downloaded from the Support & Service section of the Metrohm website.

7.1 Selection of sample volume

For a clear statement on the correct sample volume, it would be necessary to have information about the molar concentration of the antioxidants in the reference oil. Since this information is usually not available, an empirical approach must be chosen to select the sample volume for a certain oil type.

As a rule of thumb, the sample volume should be chosen in such a way that the peak with the reference oil has at least a height of 1 µA but does not exceed 6 µA. For the in-service oil sample, the same volume should be used as that for the reference oil.

If the oil type was previously analyzed with a different instrument, the sample volume used then is a good point to start from.

If a sample is completely unknown, some preliminary tests are recommended. Run the determination with 0.2 mL, 0.4 mL, and 0.6 mL sample volume. If the peak area with 0.6 mL is triple the area of 0.2 mL, then choose 0.6 mL. If this is not the case, check whether the peak area with 0.4 mL is double the area of 0.2 mL. In this case, choose 0.4 mL. If this is also not the case, then just use 0.2 mL. There are some rare cases where even 0.2 mL is too much sample, and the sample volume would need to be reduced to 0.1 mL or even 0.05 mL. Indications are that the peak height is still more than 6 µA, but also when the peak shows a strange shape or is not reproducible.

7.2 Pipetting of sample volume

The sample amount used for the determination must be accurately measured and specified in the software, since the amount of sample has a direct influence on the final result. Because of the viscosity of the oil samples, an air displacement pipette which is typically available in most laboratories is not suitable to measure the sample volume with sufficient accuracy. Instead, a positive displacement pipette should be used. This type of pipette uses a syringe-like disposable tip, consisting of a cylindrical tube and a piston, which allows accurate dispensing of viscous or volatile solutions.

If no positive displacement pipette is available, the dosed volume of sample should be weighed and the value of the weight in «g» must be entered as sample amount instead of the sample volume in «mL». Although the weight is used as sample amount, the sample amount unit in the software must remain «mL». The software could handle a sample mass, but it is not designed to use a standard with a mass instead of a volume.

7.3 Cleaning of electrodes

Generally, there are four levels of electrode cleaning:

1. Rinsing with «Ethanol for rinsing»
2. Electrochemical cleaning
3. Wiping the electrode with a soft lint-free tissue
4. Polishing

Please note! Do not clean the electrodes in an ultrasonic bath.

7.3.1 Rinsing with «Ethanol for rinsing»

After the determination, the electrodes and measuring vessel are automatically rinsed with «Ethanol for rinsing». This removes most parts of the oil and residues of the electrochemical reaction. Nevertheless, small remains can accumulate over time, causing a constant decrease in sensitivity which ultimately affects the accuracy of the results. To prevent such electrode fouling, it is recommended to carry out the electrochemical cleaning at regular intervals.

7.3.2 Electrochemical cleaning

For electrochemical cleaning, the method described in chapter 5.3 should be used. The procedure helps to restore and maintain the performance of the electrode. It can also be used within a sample series.

It is recommended to run the electrochemical cleaning procedure when the electrodes have not been used for a couple of hours, but also within a larger sample series. The frequency of the electrochemical cleaning depends on the samples to be analyzed and the expected accuracy of the results. Usually, an electrochemical cleaning at the beginning of the series and after every 5th to 10th sample is sufficient. For very sticky samples, the cleaning can also be carried out after every determination. Furthermore, it showed advantages when the electrodes were electrochemically cleaned before storage.

7.3.3 Wiping the electrodes with a soft tissue

For obvious reasons, mechanical cleaning of the electrodes is not possible in between determinations in a sample series. Nevertheless, it has proven to be helpful to wipe the electrodes from time to time, with a soft, lint-free tissue (e.g., Kimtech® Science precision wipes) which is moistened with a solvent (e.g., isopropanol or ethanol). This can be done for example at the end of a sample series and is not restricted to the glassy carbon working electrode. Also, the reference and auxiliary electrodes, as well as the inside of the measuring vessel, can be cleaned in this way.

Care must be taken when cleaning the platinum rod electrodes that the platinum rod is not turned within the electrode shaft. Otherwise, an internal connection can break, and the electrode will need to be replaced.

7.3.4 Polishing

The glassy carbon working electrode can be mechanically cleaned by polishing with aluminum oxide (6.2802.000 polishing set for solid-state electrodes). However, polishing is not necessary on a regular basis. Polishing is only recommended when the electrode performance cannot be recovered by rinsing, electrochemical cleaning, and wiping clean.

After polishing, the electrode must be thoroughly rinsed followed by electrochemical cleaning using the method described in chapter 5.3. At the end of this procedure, it is recommended to run a check standard (see 7.4) to validate the performance of the electrode.

7.4 Check standard

To check the proper function of the system, especially the performance of the electrodes, or to validate a calibration, it is recommended to run a determination with a sample of known concentration. Since no certified standards are available for this application, a fresh oil, which has previously been used for a calibration, is used as so-called check standard.

If everything is in order, the result can be expected to be around 100%. If nothing else is specified, the acceptable range for the result of the check standard is between 90% and 110%.

If the result of the check standard is outside the specified range, then clean the electrode as described in 7.3. If that does not improve the result, record a new calibration or replace the electrode.

7.5 Waste and ethanol container

Care must be taken that the containers for waste and ethanol are not closed completely. Keep at least one opening unsealed for pressure balancing. Overpressure may lead to a malfunction of the pumps.

7.6 Flammable liquids

The main components of the electrolytes and the rinsing solution are acetone and/or ethanol. Please inform yourself about safety guidelines and precautions when handling a flammable liquid.

7.7 Electrolyte alkaline

The «Electrolyte alkaline» is susceptible to the formation of poorly soluble sodium carbonate. The precipitations do not interfere with the application. Nevertheless, the formation should be prevented by using a CO_2 adsorber in the adsorber tube 6.1619.000.

Precipitations in the storage bottle can be rinsed off with water after decanting the electrolyte.

7.8 Storing electrodes

When the electrodes are not used for a few hours, e.g., during the night, all electrodes can be stored in the rinsing solution (ethanol).

When the electrodes are not used for a longer time, e.g., over the weekend, it is recommended to wipe the electrodes clean with a soft, lint-free tissue (e.g., Kimtech® Science precision wipes) which is moistened with a solvent (e.g., isopropanol or ethanol). After that, the electrodes are stored dry. They can stay in the measuring head with an empty measuring vessel underneath.

7.9 Storing 807 Dosing Units

When an 807 Dosing Unit is not used for a longer time (e.g., during the night, over the weekend) it should be rinsed with deionized water. For storage, the 807 Dosing Unit should not be emptied. Instead, it is kept with the dosing cylinder filled with deionized water.

Please also refer to *807 Manual* [**3**] for recommendations regarding maintenance and greasing of 807 Dosing Units. A difference from the recommendations in the manual is that it is not recommended to grease the valve disk since the organic solvents will wash away the grease quite easily.

7.10 Example methods

The methods provided with this Application Bulletin are compatible with **viva** 3.0.

7.11 References

[**1**] ASTM International - Subcommittee D02.09.0C. *ASTM D6971-09(2014) - Standard Test Method for Measurement of Hindered Phenolic and Aromatic Amine Antioxidant Content in Non-zinc Turbine Oils by Linear Sweep Voltammetry*. https://doi.org/10.1520/D6971-09R14 (accessed 2019-03-01).

[**2**] ASTM International - Subcommittee D02.09.0C. *ASTM D6810-21 - Standard Test Method for Measurement of Hindered Phenolic Antioxidant Content in Non-Zinc Turbine Oils by Linear Sweep Voltammetry*. https://doi.org/10.1520/D6810-21 (accessed 2021-08-13).

[**3**] Metrohm AG. *8.807.8002xx – 807 Dosing Unit*. https://www.metrohm.com/en/products/8/8078/88078002.html.

[**4**] Metrohm AG. *8.843.8003xx – 843 Pump Station with peristaltic pump*. https://www.metrohm.com/en/products/8/8438/88438003.html.

[**5**] Metrohm AG. *8.858.8002xx – 858 Professional Sample Processor*. https://www.metrohm.com/en/products/8/8588/88588002.html.

[**6**] Metrohm AG. *8.884.8003xx – 884 Professional VA*. https://www.metrohm.com/en/products/8/8848/88848003.html.

[**7**] Metrohm AG. *8.103.8033xx – VA tutorial (trace analysis)*. https://www.metrohm.com/en/products/8/1038/81038033.html.