Determination of antioxidants in lubricants

Daily routine for best performance

Metrohm

Content

1 Introduction

The determination of antioxidants in lubricants in general is a straightforward determination. Nevertheless, there are some details which should be taken care of to guarantee repeatable and reliable results.

This document acts as a guideline through the working day. Procedures are described, which should be carried out when starting up the system, during the working day and when the system is shut down. In chapter 1 checklists with bullet points for the different phases can be found. In chapter 2 to 4 theses bullet points are described more in detail.

The most crucial point in this application is the condition of the electrodes. The application runs with an external calibration. For the calibration to be valid, it has to be ensured that the performance of the electrodes remains unchanged over the time the calibration is used. The best way of achieving this is to use standardized processes which incorporate cleaning and test procedures for the system.

Further general recommendations and procedures, which do not have to be carried out on a daily basis, are described in chapter 5. And chapter 6 has a checklist which should help with troubleshooting and give answers to the most frequently asked questions.

The recommendations and descriptions in the following mainly refer to the analysis with a fully automated system. For the analysis with a manual system some recommendations may not apply.

The following documents also contain useful information and are referred to in this document, where applicable.

Manual – 884 Professional VA (8.884.8003EN)

Manual – 858 Professional Sample Processor (8.858.8002EN)

Manual – 843 Pump Station with peristaltic pump (8.843.8003EN)

Manual – 807 Dosing Unit (8.807.8002EN)

Tutorial for VA trace analysis (8.103.8033EN)

viva Help – Access in the **viva** software by pressing «F1» on the keyboard

1.1 Checklist – Procedures at the beginning of the working day

The following steps should be carried out at the beginning of the working day before the first sample is determined.

	Procedures at the beginning of the working day
☐	Lock the snap-action lever of the tubing cartridge of the peristaltic pump on the sample changer → see 2.1 Peristaltic pump of the sample changer
☐	Close and fix the pressure clamps of the two peristaltic pumps of the Pump Station → see 2.2 Peristaltic pumps of the pump station
☐	Check the level of all solutions. Fill up electrolytes and rinsing solutions and empty the waste container if required.
☐	Fill all dosing units air bubble-free with electrolytes and rinsing solution → see 2.3 Dosing units
☐	Wipe the electrodes (working electrode, reference electrode, and auxiliary electrode) with a soft lint-free tissue moistened with some ethanol or isopropanol → see 2.4 Working electrode – WE (GC) and 2.5 Reference and auxiliary electrode – RE und AE (Pt rod).
☐	Run a test determination with a check standard → see 2.6 Test measurement

1.2 Checklist – Procedures during the working day

The following steps should be carried out before a sample series is started

	Procedures during the working day
☐	Make sure the system is in proper conditions → see 3.1 Cleaning electrode and 3.2 Check electrode condition
☐	Setup a sample table with all necessary sample information → see 3.3 Setup of a sample table
☐	Prepare the sample vials and make sure the sample size and the sample position on the rack is correctly specified in the sample table → see 3.4 Preparation of sample vial

1.3 Checklist – Procedures at the end of the working day

The following steps should be carried at the end of the working day

	Procedures at the end of the working day
☐	Fill all dosing units with water → see 4.1 Dosing units
☐	Release pressure from the pump tubing of the sample changer → see 4.2 Peristaltic pump of the sample changer
☐	Release pressure from the pump tubing of the peristaltic pumps of the pump station → 4.3 Peristaltic pumps of the pump station
☐	Store away the electrodes → see 4.4 Storing electrodes

2 Startup – Procedures at the beginning of the working day

2.1 Peristaltic pump of the sample changer

Actions

Fix the tubing cartridge so that the snap-action lever (1) snaps in. Adjust the contact pressure lever (2) that sample is transferred by the peristaltic pump.

Comments

- Do not tighten the contact pressure lever (2) too much. This could block the pump and will reduce the lifetime of the pump tubing.

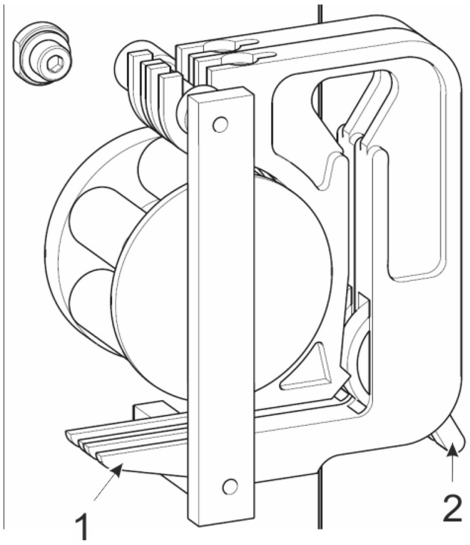


Figure 1 Tubing cartridge of the peristaltic pump of the 858 Professional Sample Processor

2.2 Peristaltic pumps of the pump station

Actions

For both peristaltic pumps:

Fix the pressure clamp (1) with the fixing lever (2). The flow of liquid can be regulated with the clamping screw on the lever. Make sure the pump tubing is secured by the two tube clamps (3).

Comments

- Attach a safety shield to each of the two pumps and make sure that it snaps in. Without the safety shield the pump will not run.

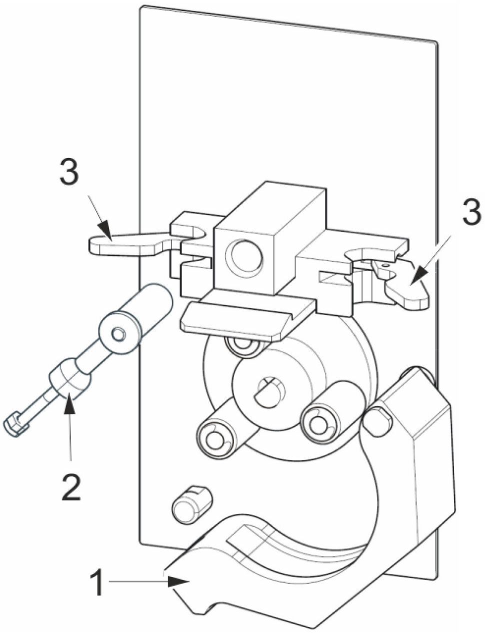


Figure 2 Peristaltic pump of the 843 Pump Station

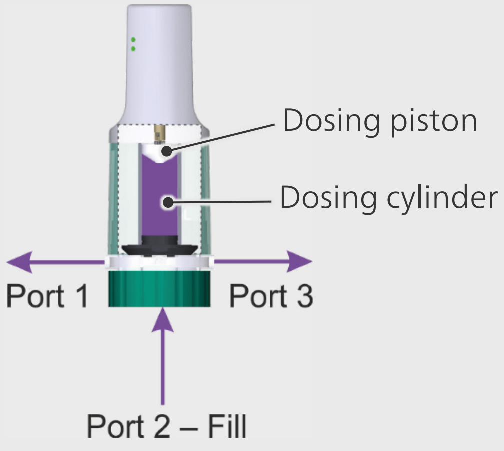
2.3 Dosing units

Figure 3 807 Dosing Unit with 800 Dosino and 2 L glass bottle

Actions

Each dosing unit has to be filled with the respective solution. After the preparation check that the dosing cylinder is free of air bubbles.

Info: *Why is the correct preparation of dosing unit(s) important?*



The dosing system consists of aspiration tube (port 2), dosing cylinder, dosing tube and capillaries (port 1 and 3). In order to correctly dose the volumes defined in the method all tubings and the dosing cylinder have to be completely filled air bubble free.

Comments

- **Dosing units can be prepared using the function «Manual» in the viva software**

Manual →

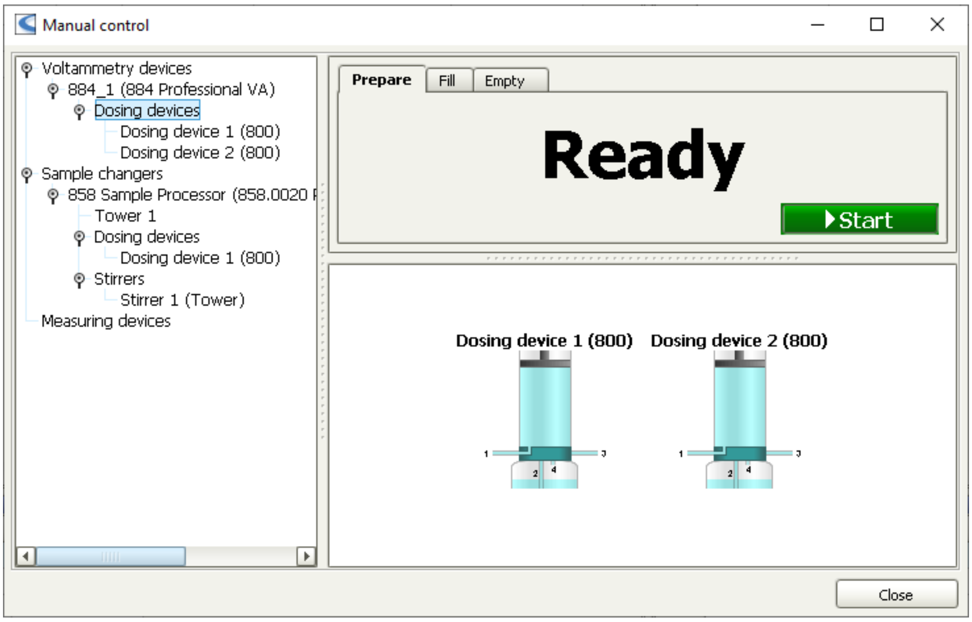


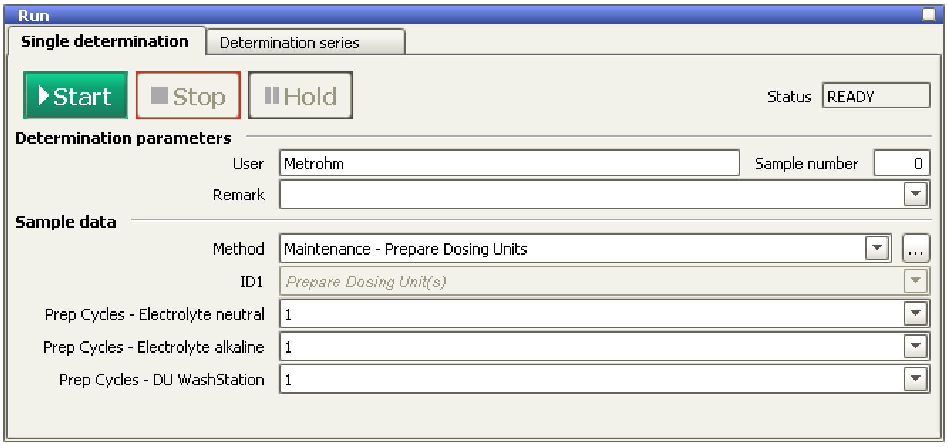
Figure 4 Manual control of Dosinos in the **viva** software

Please take care that:

- The transfer needle of the sample changer is in the waste position of the rinsing station during preparation of the dosing units.
- Dosing units are prepared in sequence and not in parallel if the two dosing units are connected to the transfer needle of the sample changer via a T connector.

For details on the different functions in the «Manual control» window see «**viva** Help – Manual control / Manual control - Functions».

- The preparation of the dosing units can be simplified if a method is used for the preparation, e.g. «Maintenance - Prepare dosing units». In this method only the preparation cycles (Prep Cycles) for each dosing unit need to be defined in the «Run» subwindow. If a dosing unit should not be prepared with solution the value «0» has to be entered. (more information regarding this method see chapter 5.6.2 Preparation of dosing units with a viva method)



Status: READY

Determination parameters

User: Metrohm

Sample number: 0

Remark:

Sample data

Method: Maintenance - Prepare Dosing Units

ID1: *Prepare Dosing Unit(s)*

Prep Cycles - Electrolyte neutral: 1

Prep Cycles - Electrolyte alkaline: 1

Prep Cycles - DU WashStation: 1

Figure 5 Example for the «Run» subwindow with the method for the preparation of dosing units

- In order to fill all tubings connected to the dosing unit automatically the length and the diameter of the tube have to be defined correctly in the configuration of the respective dosing unit (see 5.6.1 Configuration – Dosing units).
- A small air bubble can always remain at the piston, even after preparation of the dosing unit. This will not affect the accuracy of the dosing. Problems can only occur when the air bubble gets bigger and surrounds the dosing piston.

2.4 Working electrode – WE (GC)

Actions

Before the first determination of the day wipe the working electrode with a soft, lint-free tissue (e.g. Kimtech® Science precision wipes) which is moistened with a solvent (e.g. isopropanol or ethanol).

Figure 6 Glassy carbon (GC) working electrode 6.1204.600

Comments

- For more information on the cleaning of the electrode see chapter 5.4 Working electrode – WE (GC).

2.5 Reference and auxiliary electrode – RE und AE (Pt rod)

Actions

The two platinum rod electrodes do not need special maintenance. Nevertheless, it is recommended to wipe the electrodes with a soft, lint-free tissue (e.g. Kimtech® Science precision wipes) which is moistened with a solvent (e.g. isopropanol or ethanol).

Figure 7 Separate Pt rod electrode 6.0343.100

Comments

- When cleaning the electrodes care has to be taken that the platinum rod is not turned within the electrode shaft. Otherwise, an internal connection can break, and the electrode needs to be replaced.

2.6 Test measurement

Actions

To make sure that the electrodes and the complete system are in proper condition carry out the determination of a check standard at the beginning of the working day. Details on the test measurement can be found in chapter 5.3 Test measurement with a check standard.

Comments

- As check standard a fresh oil is used which had been used for calibration before. The determination is carried out similar to the determination of a used oil.
- If nothing else is specified, the result of the test determination should be between 90% and 100%.
- If the result is outside the specifications, follow the recommendations in chapter 5.3.2 Test measurement outside specifications.

3 Procedures during the working day

3.1 Cleaning electrode

3.1.1 Wipe electrodes clean

Actions

At the end of a single determination or a sample series, wipe all three 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).

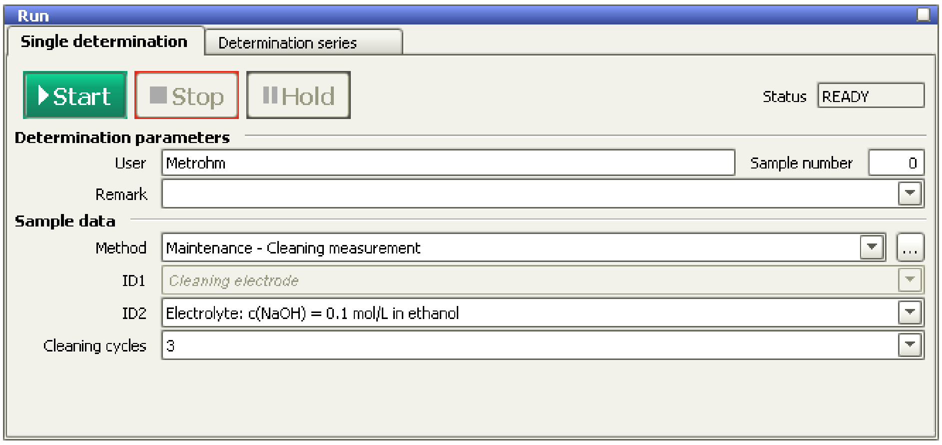
Comments

- When cleaning the platinum rod electrodes (reference and auxiliary electrode) care has to be taken that the platinum rod is not turned within the electrode shaft. Otherwise, an internal connection can break, and the electrode needs to be replaced.

3.1.2 Electrochemical cleaning of electrodes

Actions

For bigger sample series a mechanical cleaning in between determinations by wiping the electrodes clean is not possible. Instead, an electrochemical cleaning should be carried out in regular intervals. For the electrochemical cleaning a method like e.g., «Maintenance - Cleaning measurement» is used. The parameter «Cleaning cycles» in the «Run» window (see Figure 8) defines the number of repetitions of the cleaning measurement. Usually 3-5 «Cleaning cycles» are sufficient. This method can also be integrated into a sample series (see Figure 9).



Status: READY

Determination parameters

User: Metrohm

Sample number: 0

Remark:

Sample data

Method: Maintenance - Cleaning measurement

ID1: *Cleaning electrode*

ID2: Electrolyte: c(NaOH) = 0.1 mol/L in ethanol

Cleaning cycles: 3

Figure 8 Example for the «Run» window with the method for electrochemical electrode cleaning

Comments

- The frequency of the electrochemical cleaning depends on the samples to be analyzed and the expected accuracy of the results. Usually, an electrochemical cleaning after every 5th to 10th sample is sufficient. For very sticky samples the cleaning can also be carried out after every determination.
- Details on the method for the electrochemical cleaning in alkaline electrolyte can be found in chapter 5.4.2 Electrochemical cleaning of the electrode

> **Info**: *Why is it necessary to clean the electrodes mechanically or electrochemically?*
>
> Oil samples do not always completely dissolve in the electrolyte. For this reason, sample, but also residues of the electrochemical reaction, can deposit on the surface of the electrodes. Over the time this decreases the sensitivity of the determination. A reduced sensitivity means a smaller peak. Using an external calibration curve, a smaller peak means a lower result. To minimize this problem the electrodes and measuring vessel are rinsed with ethanol after every determination. Nevertheless, for some samples rinsing alone is not sufficient. In these cases, the electrode has to be cleaned either mechanically or electrochemically to remove such contaminations.

3.2 Check electrode condition

Actions

To ensure reproducible results over a longer period of time, it is recommended to check the electrode condition from time to time. For this purpose, the determination of a check standard is carried out. For details see chapter 5.3 Test measurement with a check standard.

Comments

- The electrode conditions should be checked when the system has not been used for a couple of hours, e.g., at the beginning of the working day.
- The electrode conditions should be checked frequently when many different sample types are analyzed in series.

Info: *Why should the electrode condition be checked in regular intervals?*

The condition of the glassy carbon working electrode changes with every determination, because of the deposition of sample and residues from the electrochemical reaction. These contaminations can affect the sensitivity of the determination. A different sensitivity means a different peak size. If the sensitivity is different between calibration and sample determination, this means a wrong result. How fast the electrode condition changes depends on the sample and the measuring conditions. For some samples nearly no effect can be observed, for other samples the electrode conditions can change within a few determinations. An influence of the electrode condition on the result can only be recognized when the result is known, which is only the case when a check standard is measured from time to time.

3.3 Setup of a sample table

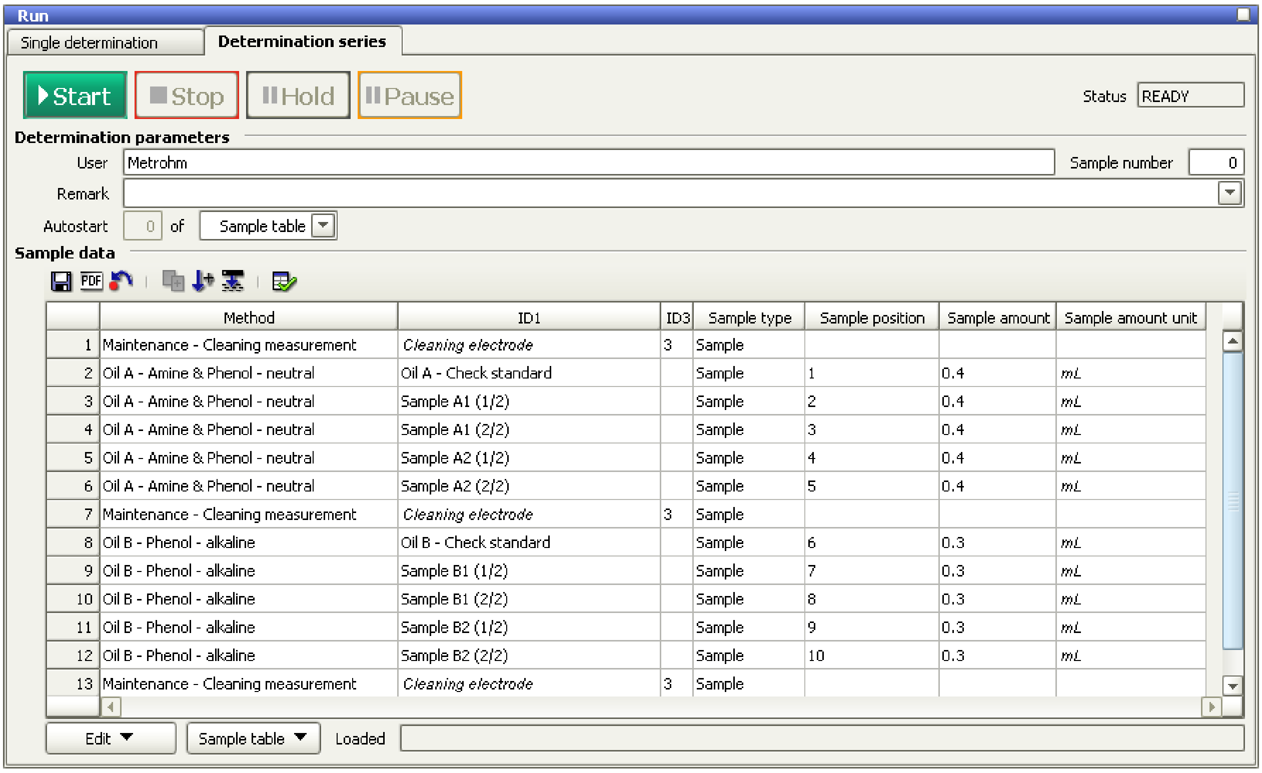
For an automated system all determinations to be carried out have to be listed in a sample table. The sample table is found in the «Run» window on the tab «Determination series». The information for an individual determination, e.g. when working with a manual system, can also be specified on the tab «Single determination».

The following information are mandatory for a calibration or determination:

- Method
- Sample type
- Sample position (not required for a manual system)
- Sample amount

If an electrochemical cleaning, as described in chapter 5.4.2 Electrochemical cleaning of the electrode, should be carried out in between determinations, also this cleaning measurement has to be specified in the sample table.

Figure 9 shows an example for a sample table, with two different methods for sample determination and an integrated electrochemical cleaning after every fifth sample.



Status READY

Determination parameters

User Metrohm

Sample number 0

Remark

Autostart 0 of Sample table

Sample data

	Method	ID1	ID3	Sample type	Sample position	Sample amount	Sample amount unit
1	Maintenance - Cleaning measurement	*Cleaning electrode*	3	Sample			
2	Oil A - Amine & Phenol - neutral	Oil A - Check standard		Sample	1	0.4	*mL*
3	Oil A - Amine & Phenol - neutral	Sample A1 (1/2)		Sample	2	0.4	*mL*
4	Oil A - Amine & Phenol - neutral	Sample A1 (2/2)		Sample	3	0.4	*mL*
5	Oil A - Amine & Phenol - neutral	Sample A2 (1/2)		Sample	4	0.4	*mL*
6	Oil A - Amine & Phenol - neutral	Sample A2 (2/2)		Sample	5	0.4	*mL*
7	Maintenance - Cleaning measurement	*Cleaning electrode*	3	Sample			
8	Oil B - Phenol - alkaline	Oil B - Check standard		Sample	6	0.3	*mL*
9	Oil B - Phenol - alkaline	Sample B1 (1/2)		Sample	7	0.3	*mL*
10	Oil B - Phenol - alkaline	Sample B1 (2/2)		Sample	8	0.3	*mL*
11	Oil B - Phenol - alkaline	Sample B2 (1/2)		Sample	9	0.3	*mL*
12	Oil B - Phenol - alkaline	Sample B2 (2/2)		Sample	10	0.3	*mL*
13	Maintenance - Cleaning measurement	*Cleaning electrode*	3	Sample			

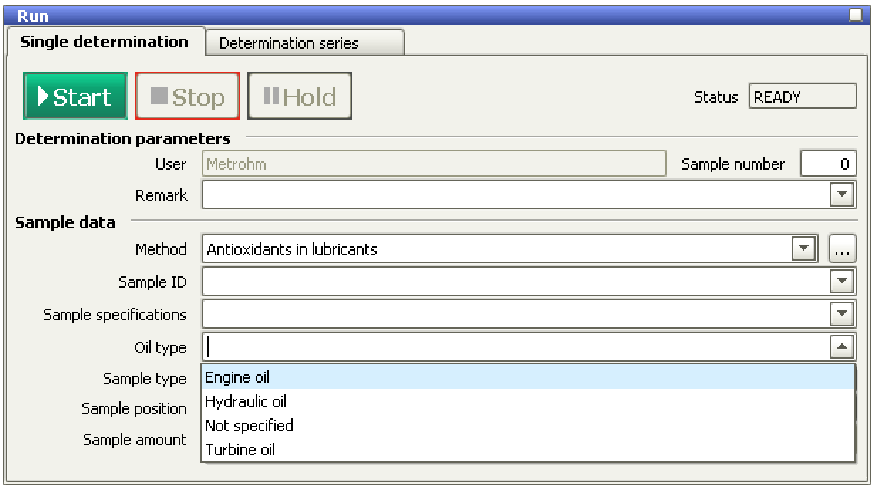
Loaded

Figure 9 Example for a sample table in the «Run» window

Comments

- The «Method» contains information about the sequence of the determination, as well as the evaluation of the curves and the calculation of the final result. It is recommended to have a separate method for each oil type. This allows to store an individual calibration for each oil type.
- To determine the remaining antioxidant content of a used oil a calibration with a fresh oil of the same type is required. Both, the calibration with the fresh oil and the determination of the used oil, have to be carried out with a method with the same method name, since the calibration is linked to the method name. For details and recommendations on the recording of a calibration curve see chapter 5.1 Calibration.
- The calibration can be used for a longer period of time, but it is recommended to validate the calibration in regular intervals, using a check standard as described in chapter 5.3 Test measurement with a check standard.
- The «Sample type» defines whether a calibration or a determination is carried out. To record a calibration curve the sample type «Standard» has to be selected. To carry out the determination of a sample or check standard the sample type «Sample» has to be selected.
- The «Sample position» defines the position of standard or sample on the rack of the sample changer. For measurements for which no solution has to be placed on the rack, e.g. electrochemical cleaning, no sample position needs to be defined.

- The «Sample amount» is the volume of standard or sample measured into the sample vial which is placed on the sample changer rack. The sample amount has to be specified accurately since it has a direct effect on the result.
- Determinations are carried out in the order in which they are listed in the sample table. Individual samples can be excluded from the series, without deleting the line, using the function «Set lines inexecutable».
- To increase the confidence level of the result it is recommended to run at least a double determination for each sample.
- By default, the text fields ID1 to ID3 are available to identify samples in the database and enter additional sample information. If necessary, additional fields can be activated in the method. For more information see chapter 5.7.1 Modify and create sample data variables.
- Sample tables can be saved and loaded. For details see «**viva** Help – Support / How to proceed? / Sample tables»
- Reoccurring entries for sample data variables can be stored as text templates. This allows to simply select the entry for a certain ID instead of typing it in.



Status READY

User Metrohm

Sample number 0

Method Antioxidants in lubricants

Engine oil
Hydraulic oil
Not specified
Turbine oil

Figure 10 «Run» window with text templates for a sample data variable

For details, how to create text templates see chapter 5.7.2 Text templates.

- For additional information on sample tables in **viva** also see «**viva** Help – Workplace / Sample tables» and «**viva** Help – Support / How to proceed? / Sample tables»

3.4 Preparation of sample vial

Actions

- For sample preparation use a 50 mL screw cap vial made of PP with a conical bottom.
- Measure 1 g quartz sand (0.2 – 0.3 ± 0.1 mm) into the vial.

- Accurately measure the sample amount into the vial using a positive displacement pipette. The sample size to be used depends on the sample. Usually between 0.2 mL and 0.6 mL are used.
- Enter the effectively added sample amount in the respective field in the software.
- Cover the vial as shown in Figure 11.
    - Place the 50 mL vial (2) (e.g. 6.2747.020) in a 75 mL glass sample beaker (1) (e.g. 6.1432.210) and push the vial down to the bottom.
    - Put on a sheet of aluminum foil (3) (e.g. 6.2820.000) to cover the opening and firmly press the foil to the edges of the vial to fix the foil.

Figure 11 Sample vial for automated system

- Place the vial on the rack of the sample changer and enter the sample position in the sample table in the software.

Info: *Why should a positive displacement pipette be used to measure the sample amount?*

The sample amount used for the determination has to 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 and 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» has to 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 has to 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.

Comments

- Before the determination can be carried out the antioxidants in the sample need to be extracted into the electrolyte used for the determination. Since the sample is not always completely soluble in the electrolyte quartz sand is added to adsorb the remaining insoluble sample matrix.
- An error of ±10% for the amount of quartz sand is acceptable. Therefore, the sand can either be weighed or measured by volume using a spoon of suitable size. 1 g quartz sand of the given particle size corresponds to approx. 0.5 mL.
- Carry out the following steps after the addition of the sample, if the sample preparation is not carried out automatically by the system:
    - Accurately dose 10 mL of the electrolyte into the vial.
    - Close the screw cap vial with the associated cap.
    - Thoroughly mix the sample with the sand and the electrolyte. Make sure that always the same time and intensity is used for the mixing. It can either be done manually by shaking or more conveniently be means of a vortex mixer.
    - Let the sand settle before an aliquot of the extraction solution is taken for analysis. Make sure that there is always the same time interval between the extraction of the sample and the determination.

4 Shut down system – Procedures at the end of the working day

4.1 Dosing units

Actions

At the end of the working day the dosing units should be rinsed and filled with deionized water. This can either be done using the «Prepare» function in viva «Manual control» (see Figure 4) or a **viva** method (see Figure 5 and chapter 5.6.2 Preparation of dosing units with a viva method)

Comments

- When preparing the dosing units manually, please take care that:
    - The transfer needle of the sample changer is in the waste position of the rinsing station during preparation of the dosing units.
    - Dosing units are prepared in sequence and not in parallel if the two dosing units are connected to the transfer needle of the sample changer via a T connector.
- Storing the dosing unit with water will increase the lifetime of the dosing cylinder, since especially the alkaline electrolyte corrodes the glass cylinder.
- Storing the dosing unit with water prevents blockage of the valve and the formation of crystals inside the dosing cylinder.
- Emptying the dosing cylinder for overnight storage will favor the formation of crystals. When the dosing unit is only emptied, a small amount of electrolyte will remain in the dosing cylinder and in the tubings. In this way the solvents can evaporate more easily, thus facilitating the formation of crystals.
- If the dosing unit should not be used for a longer period of time (more than one week) it is recommended to disassemble and clean it. After drying, the dosing unit can be reassembled and stored dry. Greasing the valve disk is not recommended since the solvents used in the application will wash down the grease in short time. Information on the cleaning of dosing units can be found in chapter 5.6.3 Maintenance of dosing units.

Info: *Why should a dosing unit be rinsed with water?*

Between valve disk and distributor disk as well as between piston and glass cylinder a thin film of solution is found. If the dosing unit in not used for some time this film dries out. On the one hand, this will cause the valve and the distributor disk to stick together. Often the disks do not easily separate, which makes the dosing unit unusable. On the other hand, the evaporation of the solvent leads to crystal formation. Especially the solvents ethanol and acetone used in the determination of antioxidants easily evaporate. What remains are the conducting salts from the electrolyte. The tiny crystals can scratch the contact areas between valve and distributor disc as well as between piston and glass cylinder. Both can lead to a leakage of the dosing unit.

4.2 Peristaltic pump of the sample changer

Actions

When the peristaltic pump for sample transfer is not used for a longer time, e.g., over the weekend, it is recommended to release the pressure from the pump tubing by unlocking the snap-action lever (1).

Comments

- It is recommended to leave the contact pressure lever (2), which is used for the adjustment of the flow rate in position. In this way the peristaltic pump can easily be set back to work by fastening the snap-action lever.

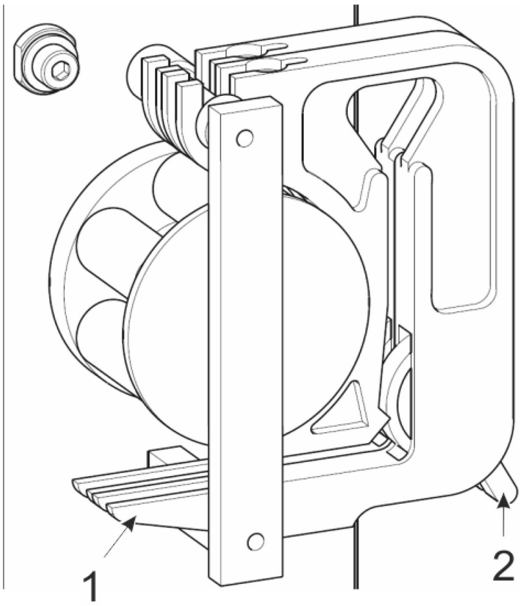


Figure 12 Tubing cartridge of the peristaltic pump of 858 Professional Sample Processor

4.3 Peristaltic pumps of the pump station

Actions

When the peristaltic pumps for draining and rinsing the measuring vessel are not used for a longer time, e.g., over the weekend, it is recommended to release the pressure from the pump tubing by unlocking the pressure clamp (1) and one of the two tube clamps (3).

Comments

- The position of the clamping screw of the fixing lever (2) should not be changed. In this way the peristaltic pump can easily be set back to work by fastening the tube clamp and the pressure clamp.

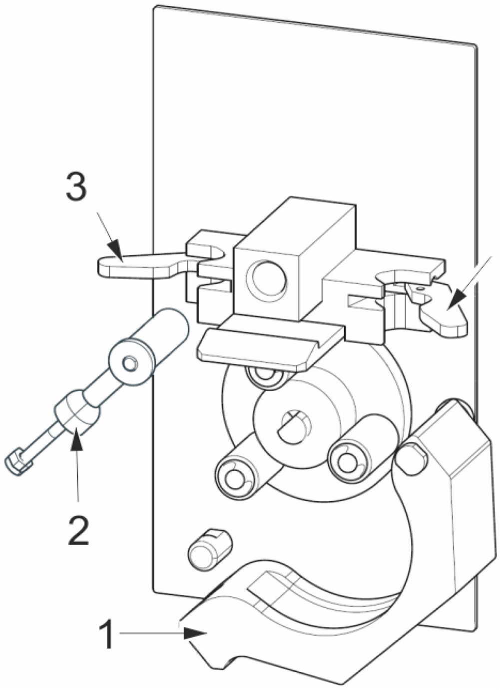


Figure 13 Peristaltic pump of the 843 Pump Station

Info: *Why should the pressure be released from the pump tubing?*

By releasing the pressure when the pump tube is not in use the lifetime of the tube can be increased. When the pump tubing stays clamped while it is not in use it can deform. This does not only affect the efficiency of the pump but can also fatigue the material which makes it crack more easily. Furthermore, the use of organic solvents in the electrolytes increases the risk that the inside of the pump tubing sticks together, which makes the tube unusable.

4.4 Storing electrodes

4.4.1 Short time storage

Actions

When the electrodes are not used for a few hours, e.g., over night, they can be kept immersed in the rinsing solution, usually ethanol.

4.4.2 Long time storage

Actions

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) and afterwards store the electrodes dry. The electrodes can remain in the measuring head.

5 General tips and information

5.1 Calibration

Special care has to be taken for the recording of the calibration curve. If the calibration is not done correctly, it will affect the accuracy of all results obtained from determinations with this calibration.

- For calibration an unused oil of the same oil type as the sample has to be used. Preferably the fresh oil used as standard is from the same batch as the used oil sample.
- The same sample size should be used for calibration and for sample.
- It is strongly recommended to create a method with a different method name for each oil type. Only in this way it is possible to store calibration data specifically for one oil type, which makes it possible to reuse the calibration data over a long time.
- Instead of recording a new calibration it is recommended to validate the calibration data from time to time with the determination of a check standard (see 5.3 Test measurement with a check standard). The validation of the calibration is strongly recommended when:
    - One of the electrodes is replaced, especially the working electrode.
    - Reagents for the preparation of the electrolyte change, e.g., different supplier.

5.1.1 Recommended procedure for the recording of the calibration curve

- Make sure the measuring system is in proper condition.
- Electrochemical cleaning of the electrodes (see 5.4.2 Electrochemical cleaning of the electrode)
- Recording calibration curve
- Repeat recording of calibration curve
- Validate the calibration curve with the determination of a check standard (see 5.3 Test measurement with a check standard)

Info *Why should the calibration curve be recorded two times?*

According to experience the first determination after a cleaning measurement shows a slightly different sensitivity than the following determinations. For security reasons it is recommended to record a second calibration curve, since the calibration measurment is not only a single determination but affects the result of all determinations it used for.

5.1.2 Calibration method «External calibration» in viva

- To record a calibration curve, the sample type «Standard» has to be selected. To run the determination of a sample or check standard the sample type «Sample» has to be selected.
- The calibration measurement is stored in the database. In addition, the calibration data are stored in the calibration data pool, which can be found in the **viva** program part «Configuration» in the sub-window «Calibration data». The calibration data are identified by the method name.
- The calibration data in the **viva** program part «Configuration» are used for the determination of a sample carried out with a method with the same name. Since the calibration data are identified by the method name, the name of the method used for the calibration and the determination of sample have to be identical.
- When a new calibration is recorded with a method for which a calibration already exists, the calibration data in the configuration are overwritten and used for the then following determinations. In the database the old calibration data remain unchanged and a new entry with the new data is created. In this way a recalculation of new data with an older calibration is always possible.
- Existing determinations can be recalculated with other calibration curves (older or newer) provided that the method names of calibration and sample are identical. To recalculate a determination with a different calibration curve:
    - Go to the determination overview, mark the determination(s) to be recalculated and the calibration to be used for recalculation.
    - Select the function «Determinations / Reprocess …» from the menu bar
    - The window «Reprocessing» opens, containing the selected determinations. When a calibration curve is among the selection the button [Recalculate] is automatically active. Press the button [Recalculate].
    - Check the results of the recalculation and press the button [OK] to take over the recalculated data into the database. Press the button [Cancel] to keep the old data.

5.2 Curve evaluation

In general curves are automatically evaluated by the software. Since the curve shape can differ significantly between different sample types, certain parameters in the software allow the adaptation of the evaluation to the specifics of a curve. The optimization of these parameters is part of the application development and does not need to be revised on a daily basis. Nevertheless, certain circumstances can make it necessary to adjust the evaluation parameters for individual determinations, e.g. when peaks shift on the potential axis. Following is a description of the most important evaluation parameters and their effect on the automatic evaluation.

For a step-by-step description on how to reprocess data in **viva**, please check the «Tutorial for VA trace analysis » chapter 7.3 Reprocessing determinations.

5.2.1 Characteristic potential

Evaluation – Substances – Recognition

Purpose

By means of the characteristic potential a peak is assigned to a substance.

Adjustment

If a peak is not evaluated, or the wrong peak is evaluated. Change the characteristic potential closer to the peak maximum of the peak which is supposed to be evaluated.

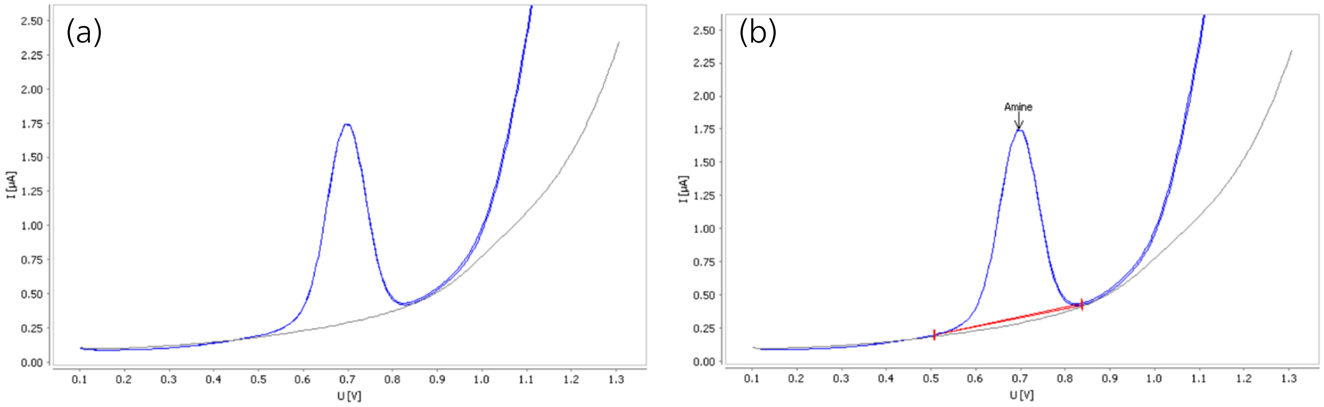


Figure 14 Automatic peak evaluation with characteristic potential 0.4 V (a) and 0.7 V (b).

5.2.2 Smoothing

Evaluation – General – Data processing

Purpose

The smoothing reduces the noise of the measured curve and evens bumps in the curve.

Adjustment

For the determination of antioxidants, the value for the smoothing is usually between 1 and 10. In rare cases it can be increased to 15. Higher values should not be used since that will downsize the peak.

If a peak has a shoulder, and the position of the basepoints differs between the replications, change the value for the smoothing.

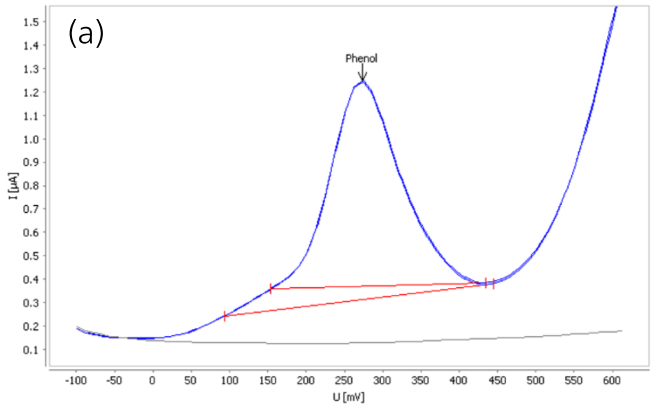


Figure 15 Automatic peak evaluation for a peak with a shoulder with smoothing 1 (a) and 5 (b).

If neighboring peaks are not evaluated reproducibly, the value for the smoothing can direct the way the baselines are drawn. The two options are the evaluation as individual peaks with valley-to-valley baselines (Figure 16 (a)) or overlapping peaks with a perpendicular separation of the peaks (Figure 16 (b)). Smaller values for smoothing will favor a valley-to-valley evaluation. A higher value will favor evaluation as overlapping double peaks. A very high value will merge a double peak into a single broad peak.

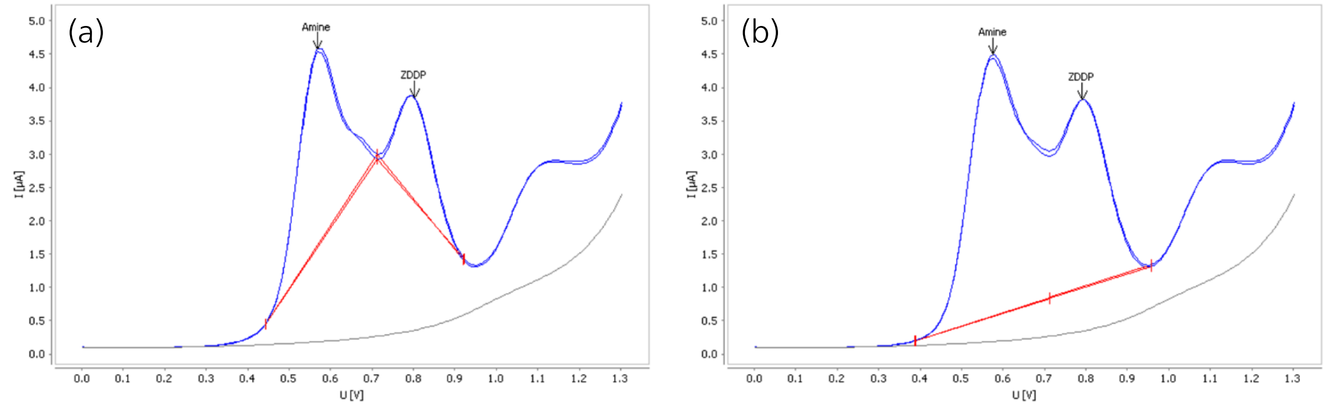


Figure 16 Automatic peak evaluation for two neighboring peaks with smoothing 5 (a) and 6 (b).

5.2.3 Min. measured quantity

Evaluation – Substances – Recognition

Purpose

The «Min. measured quantity» is the threshold which defines the minimum height of a signal to be accepted as a substance peak. It suppresses the evaluation of noise.

Adjustment

For the determination of antioxidants, the value is usually around 10 nA.

Increase the value to suppress the evaluation of unexpected, unknown signals. Decrease the value if a peak of interest is not evaluated.

5.2.4 Max. width

Evaluation – Substances – Recognition

Purpose

The «Max. width» is the threshold which defines how broad a signal can be to be accepted as a substance peak.

Adjustment

Decrease the value if the evaluation of a hump in the background should be suppressed. Increase the value if a broad peak is not evaluated.

5.2.5 Manual adjustment of base points

A manual adjustment of the baseline should only be the very last option when the adjustments to the automatic evaluation does not show a satisfying result. For details, please refer to «Tutorial for VA trace analysis » chapter «7.3.3 Changing baselines and base points in the method» and chapter «7.3.4 Adjusting baselines and base points for individual curves».

5.3 Test measurement with a 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. Since it is the same oil which is used for calibration and as sample the result can be expected to be 100%.

5.3.1 Execution of the check standard determination

- Select an oil type with an existing calibration and load the corresponding method.
- Run the fresh oil used as standard for that calibration as sample. Use the same sample size for the determination as for the calibration. The setting for sample type has to be «Sample».
- 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 100%.
- If the result for the check standard is outside the specifications, see the recommendations in chapter 5.3.2 Test measurement outside specifications.

5.3.2 Test measurement outside specifications

If the result of the check standard is outside the specified range the following steps should be carried out:

1) Thoroughly wipe all 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). Take care not to turn the platinum rod electrodes (reference and auxiliary electrode) within the electrode shaft. Repeat the test measurement.
2) If wiping the electrodes clean is not sufficient, the electrodes should be electrochemically cleaned. For details on the electrochemical cleaning see chapter 5.4.2 Electrochemical cleaning of the electrode. Repeat the test measurement.
3) If wiping the electrode clean and electrochemical cleaning are not sufficient, the working electrode should be polished with aluminum oxide. For details of the polishing of the working electrode see chapter 5.4.1 Mechanical cleaning of the electrode. Also, the platinum rod of the reference and auxiliary electrode can be polished with aluminum oxide. But for these two electrodes special care has to be taken that the platinum rod is not turned in the electrode shaft.
   After polishing the electrodes everything needs to be thoroughly rinsed, first with water, then with ethanol. Then the electrodes are electrochemically electrochemical cleaned as described in chapter 5.4.2 Electrochemical cleaning of the electrode. Finally, the test measurement is repeated.
4) If none of the previous measures shows acceptable results, a new calibration has to be recorded.
5) If the new calibration does not show a sufficient sensitivity the working electrode has to be replaced.

5.4 Working electrode – WE (GC)

5.4.1 Mechanical cleaning of the electrode

- Do **not** clean the electrode in an ultrasonic bath.
- The electrode can be mechanically cleaned by wiping it with a soft, lint-free tissue (e.g. Kimtech® Science precision wipes) which is moistened with a solvent (e.g. isopropanol or ethanol). Especially the glassy carbon surface should be thoroughly cleaned.
- The electrode can be mechanically cleaned by polishing with aluminum oxide. After polishing the electrode has to be thoroughly rinsed, first with water, then with ethanol. Afterwards the electrode should be electrochemically cleaned as described in chapter 5.4.2 Electrochemical cleaning of the electrode using 5 conditioning cycles. Finally, it is

recommended to check the electrode performance it as described in chapter 5.3 Test measurement with a check standard.

- Information on the polishing of the glassy carbon electrode can be found in the Multimedia Guide «Electrodes in Voltammetry» (CD A.717.0003 or online http://va-electrodes.metrohm.com) or on the Metrohm website www.metrohm.com in the section Support and Service > Voltammetry > Maintenance – Rotating Disk Electrode > FAQs – How can I polish my glassy carbon electrode?

5.4.2 Electrochemical cleaning of the electrode

For the electrochemical cleaning it is recommended to use an alkaline electrolyte, such as c(KOH) = 0.06 mol/L in ethanol or c(NaOH) = 0.1 mol/L in ethanol.

For cleaning the electrode, repeated sweeps with the differential pulse measuring technique (DP) are carried out in the potential range between -0.1 V and 1.0 V, as e.g., in the method «Maintenance – Cleaning measurement». In this method the number of cleaning cycles can be defined in the «Run» window on the workplace (see Figure 9). Usually, 3-5 cleaning cycles are sufficient as shown in Figure 17.

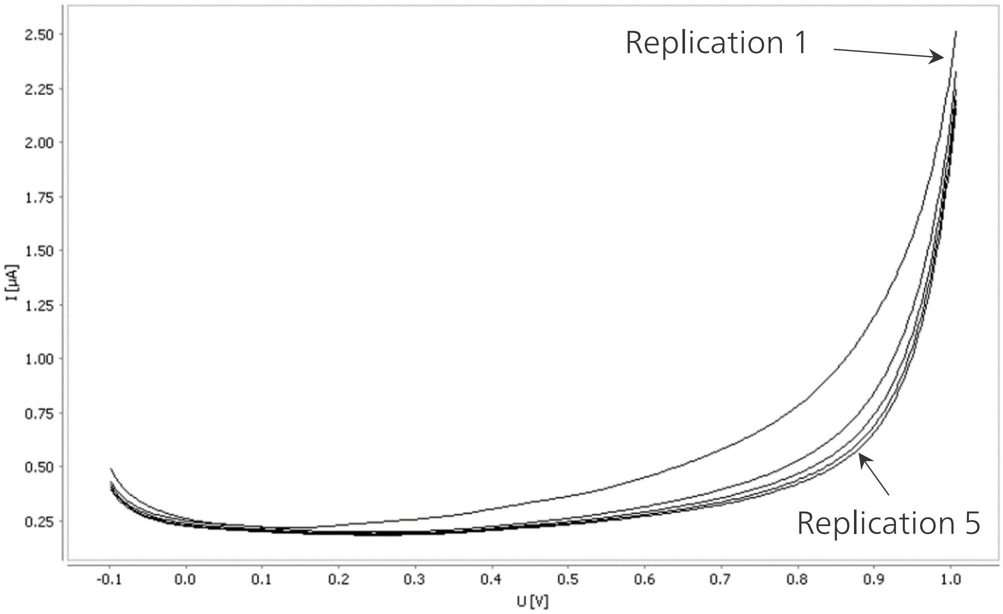


Figure 17 Example for a cleaning measurement with 5 «Cleaning cycles»

Criteria for the assessment of the electrochemical cleaning

The aim of the electrochemical cleaning is to obtain a background current as low as possible which is stable from one replication to the other. Figure 17 shows an example for a cleaning measurement in an alkaline electrolyte (c(NaOH) = 0.1 mol/L in ethanol) with 5 cycles. In this example there is a big difference in the background current between first and second replication. Between third and fifth replication no significant differences can be observed anymore. As a rule of thumb, for the last two replications the relative standard deviation of the current at 0.9 V should be less than 3%. In the above example it is 2.3%.

If the background current is not stable after the 5th replication it is recommended to replace the cleaning electrolyte and repeat the cleaning measurement.

5.5 Reference and auxiliary electrode – RE and AE (Pt rod)

The two platinum rod electrodes do not need special maintenance. Nevertheless, 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) from time to time.

Comments

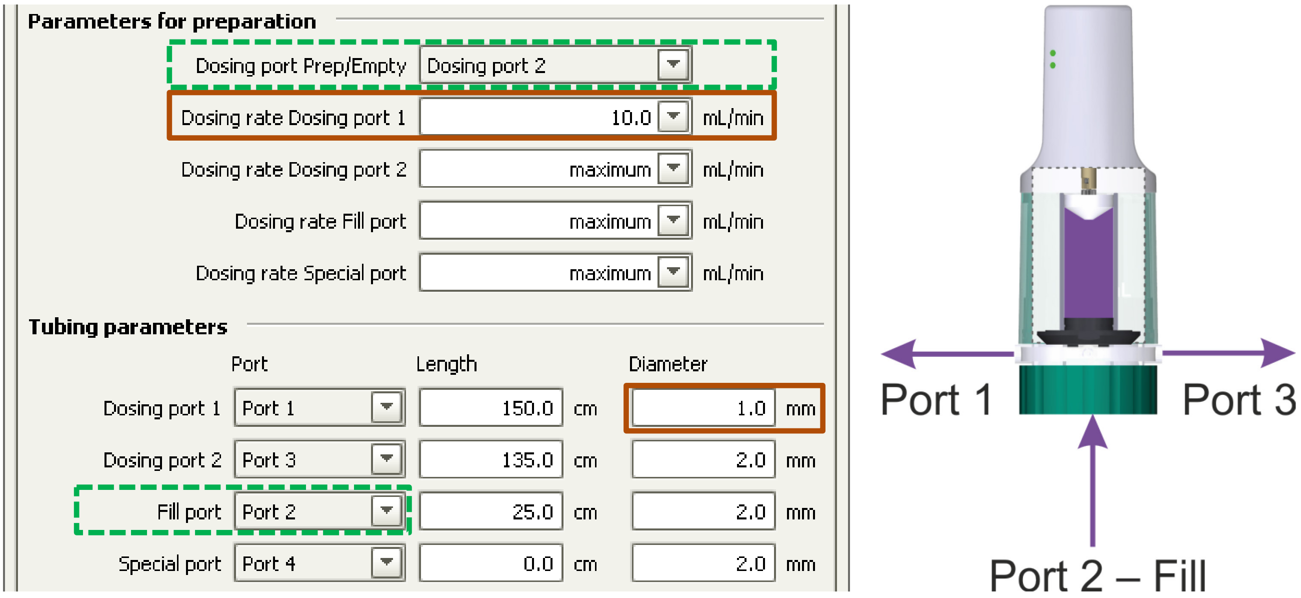
- When wiping the electrode, care has to be taken that the platinum rod is not turned within the electrode shaft. Otherwise, an internal connection can break, which makes the electrode unusable
- If the electrode is contaminated, the platinum rod can also be polished with aluminum oxide. Similar as when wiping the electrode, care has to be taken that the platinum rod is not turned within the electrode shaft. Because of the higher friction between the polishing cloth with aluminum aluminum oxide and the platinum rod this can more easily happen when polishing.

5.6 Dosing units

5.6.1 Configuration – Dosing units

Three dosing units are used in a fully automated system for the determination of antioxidants in lubricants. One dosing unit is used to feed the rinsing station attached to the sample changer with rinsing solution. The other two dosing units hold the neutral and basic electrolytes which are required for the respective application.

For the two dosing units containing the electrolytes both dosing ports (Port 1 and Port 3 on the dosing unit) are used to dose solution. It is important to note that the tube connected to port 1 is a capillary with an inner diameter of 0.97 mm. Because of the smaller inner diameter of the attached tube the maximum dosing rate at dosing port 1 should not exceed 10 mL/min independent of the volume of the dosing cylinder. Both parameters are framed in red (solid line) in Figure 18. For the filling via port 2, as well as dosing to port 3 the maximum rate can be used. Because of the higher dosing rate prep and empty of the dosing unit should be done via physical port 3 which corresponds to «Dosing port 2» (green, dashed frames in Figure 18).



Parameters for preparation

Dosing port Prep/Empty: Dosing port 2

Dosing rate Dosing port 1: 10.0 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	150.0	cm	1.0	mm
Dosing port 2	Port 3	135.0	cm	2.0	mm
Fill port	Port 2	25.0	cm	2.0	mm
Special port	Port 4	0.0	cm	2.0	mm

Figure 18 Settings in the properties of the dosing unit and connections at the dosing unit

In order to dose the correct volume, corresponding to the settings in the method, the dosing cylinder and all tubings have to be completely filled with solution. Preparation can be done automatically, when the dimensions of the connected tubings are known. The length and the diameter of the respective tubing need to be specified in the **viva** software, program part «Configuration» – «Dosing units». The settings shown in Figure 18 correspond to the setup specified in «AW VA CH4-0606-022021».

5.6.2 Preparation of dosing units with a viva method

The preparation of the dosing units can be simplified if a method is used for the preparation, e.g. «Maintenance - Prepare dosing units». In this method only the number of preparation cycles (Prep Cycles) for each dosing unit needs to be specified in the «Run» window (see Figure 5). If a dosing unit should not be prepared with solution, the value «0» has to be entered.

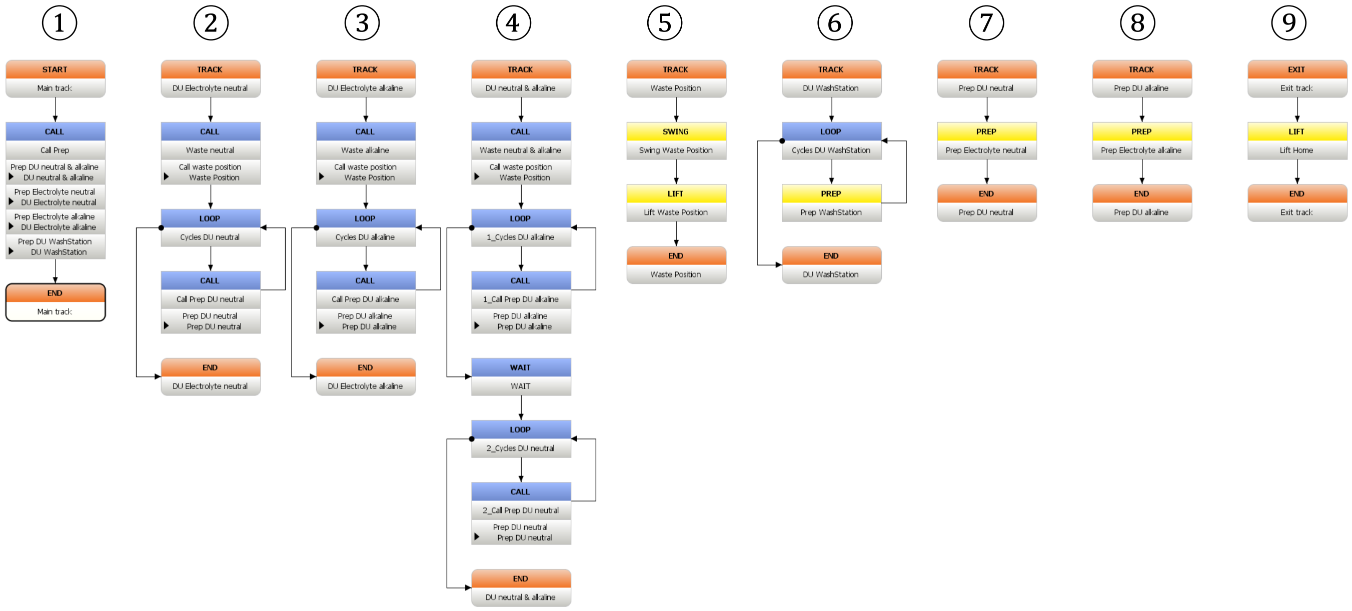


Figure 19 viva method sequence for the preparation of dosing units

The method ««Maintenance - Prepare dosing units» contains 4 tracks (②, ③, ④, and ⑥) for the preparation of dosing units. Each of the tracks ② (neutral electrolyte), ③ (alkaline electrolyte), and ⑥ (rinsing station at the sample changer) control the preparation of one dosing unit including a LOOP command which allows multiple preparations of the respective dosing unit. The number of preparation cycles corresponds to the value of the respective sample data variable «Prep Cycles – xxx» specified in the «Run» window on the workplace.

Track ④ takes care of the situation when both dosing units connected to the needle of the sample changer should be prepared at the same time. In this case the dosing units are prepared in sequence. Furthermore, each of the tracks ② to ④ calls for the transfer needle, attached to the sample changer, to be positioned in the waste position of the rinsing station, before the preparation starts.

A track is only called up under the condition that the respective sample data variable for the «Prep Cycles – xxx» is >0. The exact conditions under which a track is called are specified in track ①.

5.6.3 Maintenance of dosing units

Actions

Apart from rinsing with water, which is always recommended at the end of the working day (see 4.1 Dosing units), the dosing units should be checked and maintained in regular intervals (approx. once per month).

- For further information on handling and maintenance of the dosing unit also check the Manual – 807 Dosing Unit , e.g. chapter «3.7 – Disassembling the dosing unit», «3.8 – Assembling the dosing unit», or «4 – Handling and maintenance»
- A video tutorial how to clean a dosing unit can be found online on the Metrohm website www.metrohm.com in the section Support and Service > Titration > How to operate – clean the dosing unit

Unlocking the dosing unit

- To disassemble the dosing unit, keep the locking button pressed and rotate the housing about 1 cm counterclockwise. Once the housing is unlocked it can be removed.

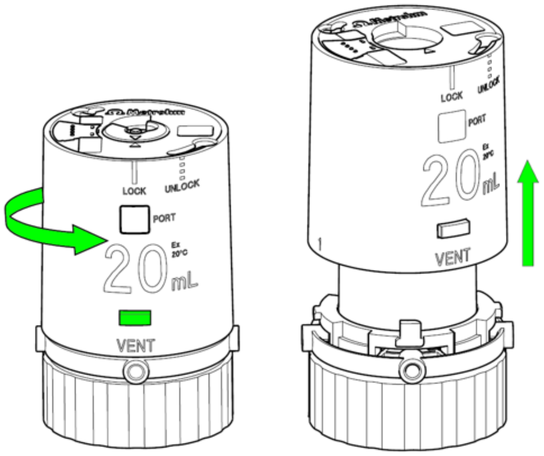


Figure 20 Unlocking the housing of the dosing unit

Valve disk and distributor disk

> **Note!** *Do not use force to separate valve and distributor disk.*
>
> If the two disks stick together run hot water from the water-tap over the two parts (for about 30 s). Use the centering tube to carefully twist the dosing cylinder against the distributor. If the disks still do not separate, place the distributor with the dosing cylinder in bowl of hot water, until they separate (about 30 min).

- Thoroughly rinse valve disk and distributor disk with water to remove all kind of contaminations. Also check and remove blockages of the valve opening or the outlet ports.
- Check the valve disk for scratches, especially concentrical circles, which can be an indication for an imminent leakage.
- Before reassembling make sure valve disk and distributor disk are completely dry.
- The valve disk does not need to be greased, since the solvents used in the application will wash down the grease in short time.

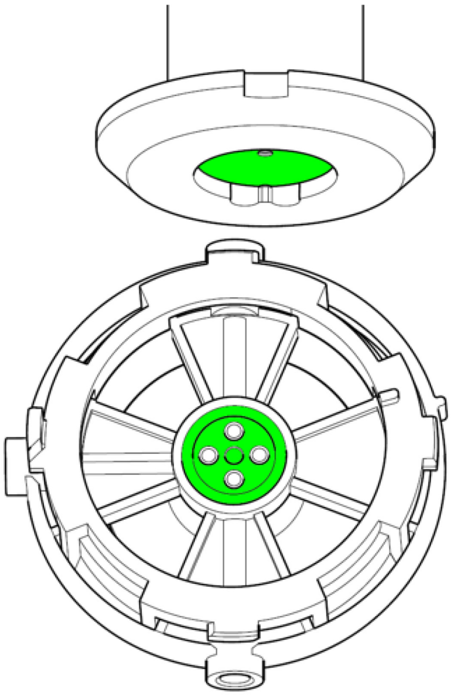


Figure 21 Cylinder base with valve disk and distributor with distributor disk

Dosing cylinder and dosing piston

> **Note!** Always keep the glass cylinder assembled with the cylinder base.

- Check the piston for deformations and damages, which can be an indication for an imminent leakage.
- If precipitations are visible in the dosing cylinder, it is recommended to remove the piston and clean both the dosing cylinder and the piston thoroughly with water. Also take care that the bore in the cylinder base is properly rinsed.
- If no precipitations are visible in the cylinder, no maintenance of the glass cylinder and the piston is required.

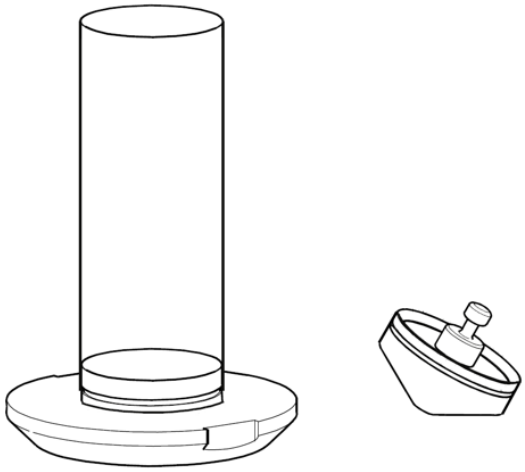


Figure 22 Dosing cylinder and dosing piston

Greasing housing and centering tube

- Grease the sliding surfaces on the interior edge of the housing and the upper side of the centering tube.

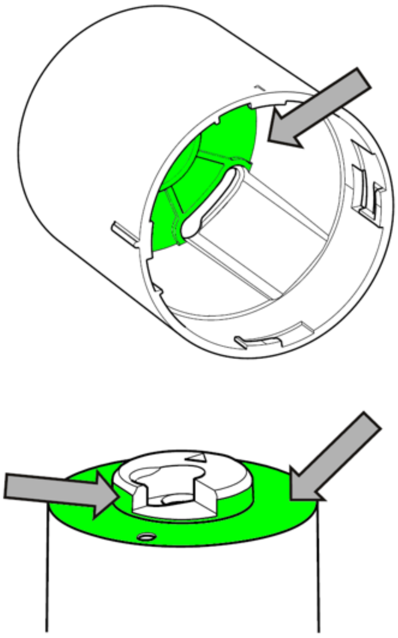


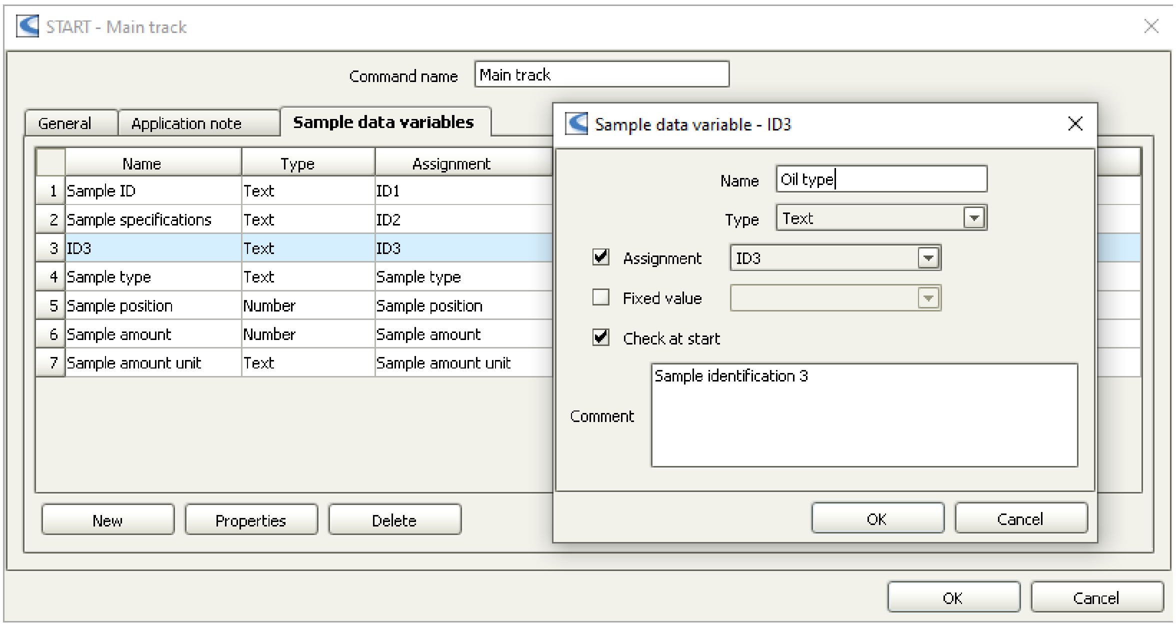
Figure 23 Housing and centering tube

5.7 Sample data variables

Sample data variables are variables which are not automatically created by the software but can be entered by the user in the «Run» subwindow on the workplace. They can be used to identify the sample and store sample information together with the determination. Up to 16 sample data variables can be defined per method.

5.7.1 Modify and create sample data variables

To the name of an existing variable or to activate a new field, load the method in the **viva** program part «Method» and open the properties window of the **START** command.



Command name: Main track

	Name	Type	Assignment
1	Sample ID	Text	ID1
2	Sample specifications	Text	ID2
3	ID3	Text	ID3
4	Sample type	Text	Sample type
5	Sample position	Number	Sample position
6	Sample amount	Number	Sample amount
7	Sample amount unit	Text	Sample amount unit

Name: Oil type
Type: Text
☑ Assignment: ID3
☐ Fixed value
☑ Check at start
Comment: Sample identification 3

Figure 24 Properties window of the **START** command with the dialog window to modify the properties of a sample data variable.

The button [Properties] opens the dialog window to adapt the properties of an existing sample data variable, like e.g. the name.

With the button [New], an additional field to be displayed in the «Run» subwindow on the workplace is created.

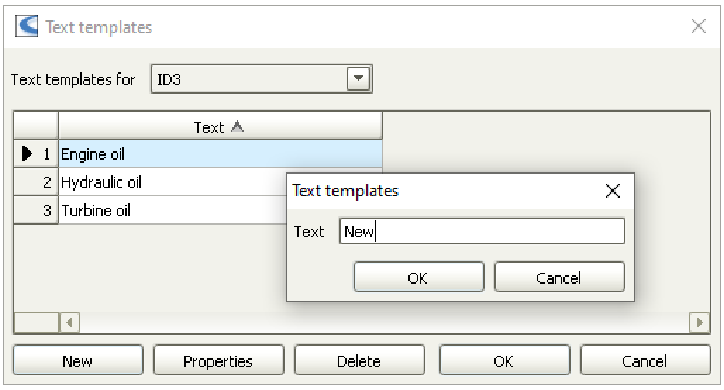
Comments

- It is recommended to give the variable a meaningful name, which will appear in the «Run» window on the workplace instead of an unspecific IDx.
- It is recommended to have the sample data variable always assigned to the same ID in all methods. This later on simplifies filtering and sorting in the database.

5.7.2 Text templates

Reccurring entries for sample data variables can be stored as text templates, which can then be selected in the «Run» subwindow on the workplace in a pull-down list (see Figure 10).

To create a text template, go to the program part «Workplace» and select «Text templates …» in the menu «Tools».



Text templates for: ID3

	Text
1	Engine oil
2	Hydraulic oil
3	Turbine oil

Text templates

Text: New

Figure 25 Window «Text templates» with the dialog window to enter the text for a new template.

In the window «Text templates» select the ID number for which a text template should be created, then press the button [New] to type in the intended text. Once everything is confirmed with ok the text for the respective ID will be available for single determinations as well as for sample series.

Comments

- The use of text templates is highly recommended. It simplifies filtering and sorting in the database, since the spelling of certain sample information is always identical.
- For details also see «**viva** Help – Workplace / Text templates».

6 Troubleshooting

6.1 Checklist

Please check the following points when problems occur (unusual measuring curves, no results, results outside the expected range, poor repeatability, etc.):

	Check	Action
☐	Have all electrode cables been connected correctly?	Connect all electrode cables correctly: Cable WE – Working electrode (GC RDE) Cable RE – Reference electrode (Pt rod) Cable AE – Auxiliary electrode (Pt rod)
☐	Have all tubings been connected and are all tubing connections tight?	Check all tubings and connections. If needed, use the wrench 6.2739.000 to tighten the tubing connections.
☐	Have all dosing units been filled air-bubble-free?	Repeat the preparation of the dosing units. If preparation of the dosing unit does not remove the air bubble, check all tubing connections for tightness and repeat the preparation. If all connections are tight, and the air bubble remains, do a maintenance on the dosing unit. If all measures do not solve the problem, replace the dosing unit.
☐	Have all dosing units been filled with the correct electrolyte?	Double-check the used electrolytes. In case of doubts prepare fresh electrolyte.
☐	Has the correct electrolyte been used for the application?	Check in the method that the correct electrolyte is used in the dosing command. Check in the configuration that the solution to be dosed is linked to the correct dosing unit. See «Tutorial for VA trace analysis » on the configuration of dosing units and solutions for automatic dosing.

☐	Is the contact pressure for all peristaltic pumps correctly adjusted?	Change the contact pressure and check whether that solves the problem.
☐	Are the pump tubings in proper condition?	Pump tubings are consumables. When alterations can be observed, e.g., cracks in the sidewalls or a hardening of the material, the pump tube should be replaced.
☐	Is the calibration still valid for the oil type to be determined?	Carry out a test determination as described in chapter 5.3 Test measurement with a check standard.
☐	When was the last time the working electrode has been cleaned?	Clean the electrode mechanically and electrochemically (see 5.4 Working electrode – WE (GC)).
☐	Is the peak correctly evaluated?	Check the measuring curves whether the correct peak is evaluated, and that the baseline is drawn correctly. If needed, adjust evaluation parameters, such as characteristic potential of the substance or the smoothing of the curve (see 5.2 Curve evaluation)
☐	Is the specified sample amount correct?	Make sure that the sample amount specified in the determination corresponds to the sample size dosed during the preparation of the sample vial (see 0 Preparation of sample vial)

6.2 FAQs

a) How often do I need to record a new calibration?

A new calibration curve should only be recorded if absolutely necessary. Instead, it is recommended to validate the existing calibration curve in regular intervals doing a test measurement as described in chapter 5.3 Test measurement with a check standard. Further information on the calibration curve can also be found in chapter 5.1 Calibration.

b) I would like to have more fields to enter sample information. Is that possible?

The text fields available for sample information are defined in the method. By default, ID1 to ID3 are available, but up to 16 IDs can be defined per method. For details see 5.7.1 Modify and create sample data variables.

c) When editing my sample table, I cannot see all sample information fields I have in the method. What can I do?

By default, only ID1 to ID3 are displayed in the sample table. To show more fields open the properties of the «Run» window for the «Determination series». On the tab «Display» in the section «Sample data» activate the IDs which should be displayed when editing entries in the sample table.

It is also recommended to adjust the IDs on the tab «Edit» in the section «Copy automatically into next line». These settings define which entries are automatically copied from the previous entry when a new line is created in the sample table.

For more information on the different functions in the sample table also see «**viva** Help – Workplace / Run subwindow / Determination series».

d) Is there a possibility to simplify the entry of recurring sample information?

The **viva** software offers the possibility to create text templates for sample IDs. These templates are then available in the «Run» window as a drop-down list for each sample ID (see Figure 10). For details on how to create text templates see 5.7.2 Text templates.

e) After a very short time there is a big gas bubble around the piston in the dosing unit. Is that normal? What can I do?

A small gas bubble at the piston is not unusual, even directly after the preparation of the dosing unit. A small gas bubble does not affect the correct dosing. When solutions with high vapor pressure, such as the organic solvent used in the application, are dosed it is also not unusual that the gas bubble increases over time. The size only gets critical when the gas bubble surrounds the piston. To prevent the formation of a gas bubble with a critical size, it is recommended to always prepare the dosing units at the beginning of the working day.

If a big gas bubble forms within a few determinations, it is an indication that either the dosing unit leaks or one of the connections is not tight. In this case first check all the tubing connections. You may use the wrench 6.2739.000 to fasten all tubing connectors.

If that does not help, do maintenance on the dosing unit as described in chapter 5.6.3 Maintenance of dosing units.

If also maintenance does not improve the situation, the dosing unit is worn out. In this case the dosing cylinder or the complete dosing unit has to be replaced.

f) I do not have a positive displacement pipette to measure the sample volume. What can I do to ensure that the sample size is precise anyhow?

Oil samples are too viscous to allow an accurate pipetting of the sample volume with an air displacement pipette, which is available in most chemical laboratories. If the sample amount is measured by volume, a positive displacement pipette should be used. If other pipettes are used it is recommended to weigh the sample and use the value of the weight instead of the volume as sample amount. The sample amount unit must remain «mL» no matter if volume or weight is used.

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Metrohm Ltd., CH-9100 Herisau, Switzerland.
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