Cyclic Voltammetric Stripping

Daily routine for best performance

Metrohm

Content

1 Introduction

The analysis of organic additives in electroplating baths by cyclic voltammetric stripping (CVS) is a robust method and widely used in the electroplating industry. To ensure that continuously reliable results are obtained, standardized daily operation procedures are of the highest importance. They all contribute to keeping the measuring system at best performance.

This document acts as a guideline throughout 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. Further, general recommendations and procedures, which do not have to be carried out on a daily basis, are described.

The recommendations and descriptions in the following refer to the analysis of acid copper plating baths. For the analysis of other plating baths, e.g. tin, tin/lead or electroless copper plating baths, some recommendations may not apply.

Figure 1: Fully automated plating bath analysis with the 894 Professional CVS and the 858 Professional Sample Processor

2 Start-up – Procedures at the beginning of a working day

The steps mentioned in this section should be carried out when starting up the system at the beginning of a working day. They ensure that highly reliable and reproducible results are obtained already with the first determination.

2.1 Preparation of the 807 Dosing Units

Figure 2: 807 Dosing Units included in standard fully automated Professional CVS setups

Actions

Prepare each 807 Dosing Unit twice with the respective solution. Use a waste beaker instead of the measuring vessel. Then rinse the electrodes and tubings thoroughly with deionized water, before reinstalling the measuring vessel.

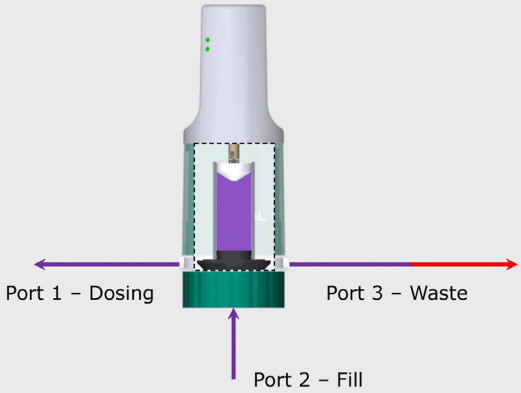
Comments

- The preparation should be done with a waste beaker instead of the measuring vessel below the measuring head. Preparing concentrated solutions such as suppressor concentrate directly into the measuring vessel can lead to carryover and influence the following determination. If the preparation is done within a viva method in an automated setup the measuring vessel cannot be exchanged for a waste beaker. In this case it has to be ensured that the measuring vessel is rinsed sufficiently after the preparation.

- The preparation should be done via port 3 (see chapter 5.6) for waste. This makes the preparation faster and additionally less solution is prepared into the measuring vessel, which could lead to carryover effects. This second benefit is especially important, if the 807 Dosing Unit is prepared in a fully automated viva method with the measuring vessel installed.

Info: *What is Dosino preparation and why is it important?*

The dosing system, consisting of an aspiration tube (port 2), the 807 Dosing Unit and a dosing capillary (port 1), has to be filled homogeneously with the respective solution.



When the same 807 Dosing Unit is used for different solutions with different compounds and concentrations, the old solution has to be replaced in all parts of the dosing system by the new solution. Preparation means that all of these parts are subsequently filled with the new solution and the old solution is directed to the waste. Two repetitions of the preparation procedure have proven to be sufficient. One preparation cycle is usually not sufficient.

2.2 Replacing the bridge electrolyte

Figure 3: Bridge electrolyte vessel 6.1245.010

Info: *What is the bridge electrolyte vessel and what is it used for?*

The bridge electrolyte is used to separate the reference electrode from the measuring solution. By using a bridge electrolyte the measuring solution cannot enter the reference system, where it could change the reference potential or damage the reference system. In CVS the chloride concentration in the measuring vessel has an influence on the analysis. To avoid that chloride from the reference system leaks into the measuring solution, KNO_3 solution is used as the bridge electrolyte. The bridge electrolyte ($c(KNO_3)$ = 1 mol/L) is available from Metrohm, e.g. 6.2310.010.

Actions

Replace the bridge electrolyte in the electrolyte vessel ($c(KNO_3)$ = 1 mol/L) every day. Make sure that no air bubbles are present at the bottom of the electrolyte vessel to avoid contact problems.

Comments

- More information on how to handle the reference electrodes in voltammetry can be found in our multimedia guide «Electrodes in Voltammetry» (A.717.0003), also available online in the product help center (Metrohm.com ► Support & Service ► Product Help Center ► Cyclic Voltammetric Stripping).

2.3 Working electrode – WE (Pt RDE)

Figure 4: Pt RDEs: 1 mm (6.1204.190), 2 mm (6.1204.610) and 3 mm (6.1204.170), from left to right

Actions

Daily electrochemical cleaning by conditioning in VMS is the best measure to guarantee reproducible results. Before the first analysis is started on a working day, the working electrode should be conditioned. More details can be found in chapter 2.3.1.

Comments

- In case of accidental excessive Cu plating, the WE can be dipped in concentrated nitric acid for a few seconds to dissolve the copper. Then the electrode is rinsed extensively with deionized water and conditioning is carried out again.
- Mechanical treatment of the working electrode must not be done. It is neither recommended nor necessary. On the contrary, it can damage it irreversibly. Mechanical treatment not only includes polishing, but also sonication with ultrasound.
- More information on how to handle the rotating disk electrodes in voltammetry can be found in our multimedia guide «Electrodes in Voltammetry» (A.717.0003), also available online in the product help center (Metrohm.com ► Support & Service ► Product Help Center ► Cyclic Voltammetric Stripping).

2.3.1 Conditioning of the WE

It is recommended to run the conditioning in VMS at least once per day after all electrodes are installed and the 807 Dosing Units are prepared.

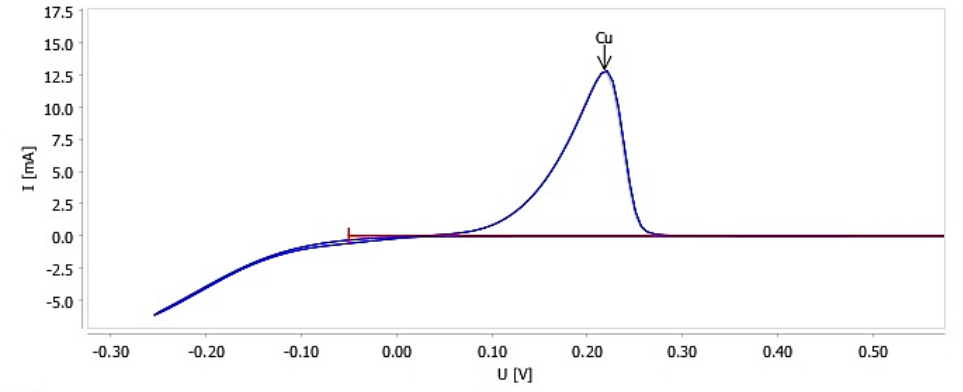
The Cu stripping peak area reflects the state of the system, provided that the same solutions and voltammetric parameters are used. If the peak area is smaller (or higher) than usual, it can be an indicator for leakage from an 807 Dosing Unit (especially suppressor concentrate), impurities, state of the RDE, wrong reference potential among others. The problem source has to be identified and fixed, before continuing work (see also chapter 6.2).

If conditioning takes too long because the area of the stripping peak does not stabilize, replace the VMS and restart the conditioning. If exchanging the VMS and repeating the conditioning does not solve the problem, please refer to the troubleshooting chapter 6.2.1: «Instable signal».

Info: *What is conditioning and why should it be done regularly?*

In CVS reproducible measuring curves are of highest importance to obtain reliable results. For this purpose the electrode has to be electrochemically conditioned. Thereby it is immersed in VMS and cyclic voltammograms are recorded until the measured curves are reproducible. During this conditioning procedure Cu is deposited and removed from the working electrode repetitively, until the amount of deposited Cu on the working electrode does not change anymore.

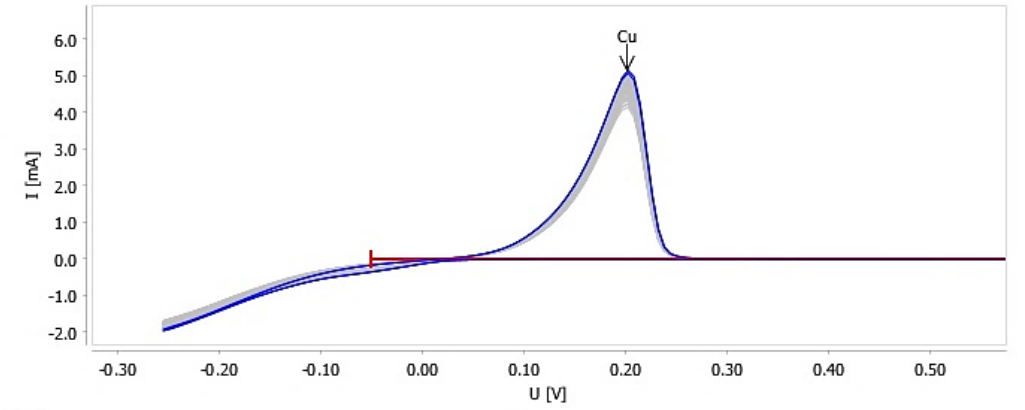
Carrying out this procedure regularly helps to keep the working electrode in good shape and to be ready for analysis quickly.



Cu

	CALL	Var	Rep	Baseline type	Start base point	End base point	Cu Area [mC]	Cu Area RSD
1	CALL COND{1}		1	Horizontal manually	0.800	-0.050	9.600	
2	CALL COND{1}		2	Horizontal manually	0.800	-0.050	9.653	
3	CALL COND{2}		1	Horizontal manually	0.800	-0.050	9.670	
4	CALL COND{2}		2	Horizontal manually	0.800	-0.050	9.697	0.4
5	CALL VA	1	1	Horizontal manually	0.800	-0.050		
6	CALL VA	1	2	Horizontal manually	0.800	-0.050		

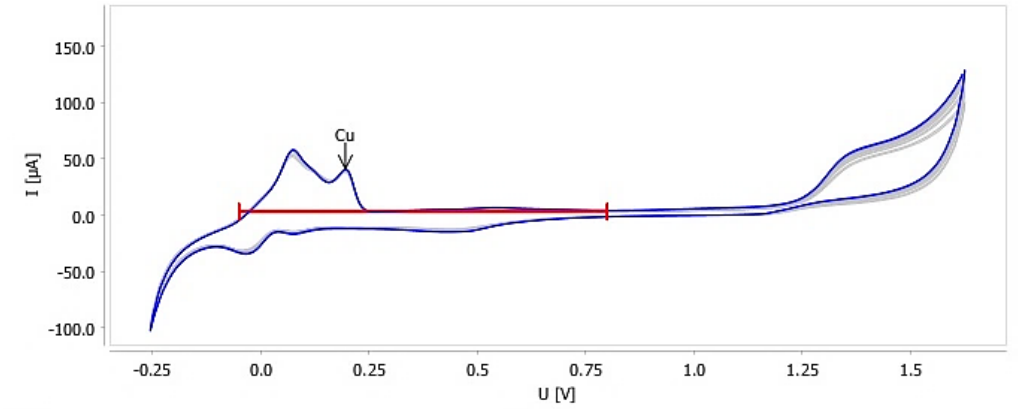
Figure 5: A well-conditioned working electrode gives highly reproducible measuring curves and stabilizes fast. (The more anodic part of the voltammogram is not shown for better visualization.)



Cu

	CALL	Var	Rep	Baseline type	Start base point	End base point	Cu Area [mC]
37	CALL COND{19}		1	Horizontal manually	0.800	-0.050	3.644
38	CALL COND{19}		2	Horizontal manually	0.800	-0.050	3.684
39	CALL COND{20}		1	Horizontal manually	0.800	-0.050	3.646
40	CALL COND{20}		2	Horizontal manually	0.800	-0.050	3.691
41	CALL VA	1	1	Horizontal manually	0.800	-0.050	
42	CALL VA	1	2	Horizontal manually	0.800	-0.050	

Figure 6: A working electrode in bad condition gives less reproducible measuring curves and takes long for stabilization. (The more anodic part of the voltammogram is not shown for better visualization.)



Cu

	CALL	Var	Rep	Baseline type	Start base point	End base point	Cu Area [µC]
7	CALL COND{4}		1	Horizontal manually	0.800	-0.050	86.071
8	CALL COND{4}		2	Horizontal manually	0.800	-0.050	86.761
9	CALL COND{5}		1	Horizontal manually	0.800	-0.050	86.187
10	CALL COND{5}		2	Horizontal manually	0.800	-0.050	85.735
11	CALL VA	1	1	Horizontal manually	0.800	-0.050	
12	CALL VA	1	2	Horizontal manually	0.800	-0.050	

Figure 7: Example measuring curves for conditioning with contamination in the measuring vessel. If a stripping area is obtained, which is much smaller than usual, it is a strong indicator for a contaminated measuring vessel or additives leaking from an 807 Dosing Unit.

2.4 Auxiliary electrode – AE (Pt rod)

Figure 8: Separate Pt rod electrode 6.0343.100

Actions

The auxiliary electrode does not require regular maintenance.

Comments

- Mechanical treatment is usually not necessary. If it is done nevertheless, it should be carried out carefully with a soft tissue. Care should be taken that the Pt rod is not twisted. Otherwise the contact wire may be torn off.
- In case of accidental excessive Cu plating, the AE can be dipped in concentrated nitric acid for a few seconds to dissolve the copper. Then the electrode is rinsed extensively with deionized water and conditioning is carried out as described in chapter 2.3.1.

2.5 Check standard for system validation

A check standard is an artificial sample with known concentrations of organic additives diluted in VMS. It does not contain contaminations or breakdown products, which are normally present in a real sample.

Actions

Check standards should be determined regularly to verify, if the system is running properly.

Comments

- A check standard solution should be prepared freshly before the analysis. Especially some brighteners are not stable for a longer period of time in dilute solutions.
- The validity of DT calibration curves, intercept values, electrolyte values and response curves can be evaluated with a check standard measurement.
- The recovery for a suppressor determination should be (100 ± 10)%.
- The recovery for a brightener or leveler determination should be (100 ± 20)%.

3 Procedures during the working day

The following points should be considered throughout the working day.

3.1 Preparation of the 807 Dosing Units

Actions

Prepare each 807 Dosing Unit twice if a new solution is used. Use a waste beaker instead of the measuring vessel. Then rinse the electrodes and tubings thoroughly with deionized water, before reinstalling the measuring vessel.

Comments

- When an 807 Dosing Unit has to be filled with a different solution, e.g. a sample for the suppressor determination, a different VMS or another additive concentrate, the 807 Dosing Unit has to be thoroughly rinsed with the new solution.
- The preparation should be done with a waste beaker instead of the measuring vessel below the measuring head. Preparing concentrated solutions such as suppressor concentrate directly into the measuring vessel can lead to carryover and influence the following determination. If the preparation is done within a viva method in an automated setup the measuring vessel cannot be exchanged for a waste beaker. In this case it has to be ensured that the measuring vessel is rinsed sufficiently after the preparation.
- The preparation should be done via port 3 (see chapter 5.6) for waste. This makes the preparation faster and additionally less solution is prepared into the measuring vessel, which could lead to carryover effects. This second benefit is especially important, if the 807 Dosing Unit is prepared in a fully automated viva method with the measuring vessel installed.

3.2 Ensure temperature stability

Actions

Make sure to maintain a stable temperature of the system throughout the working day and during determinations. Plating baths are often operated at an elevated temperature, e.g. 50 °C. Therefore, samples have to be left to cool down prior to the analysis, especially when high volumes are used.

Comments

- Letting a fresh plating bath sample cool down is especially important for determinations, where a high sample amount with respect to the total volume of the measuring solution is used. This is usually the case for brightener determinations by LAT or MLAT, or some leveler applications.
- For determinations using a separate calibration or a value from a different determination (calibration for DT, intercept for LAT, electrolyte value or response curve for RC), it is important that the temperature of the measuring solution during the calibration or recording of a separate value (intercept or electrolyte) does not significantly differ (<5 °C) from the temperature during the sample determination.
- The measuring system should not be exposed to direct sunlight or placed below an air conditioner.
- Measuring vessels with a thermostat jacket (6.1418.220 / 6.1418.250) can be used in combination with a water bath circulator to ensure a stable temperature of the measuring solution.
- A temperature sensor (6.1110.120) can be connected to the instrument and used in viva methods to wait until a specified temperature has been reached.

Figure 9: Ensuring a correct temperature with dedicated equipment (left: measuring vessel with thermostat jacket, right: temperature sensor).

Info: *What is the effect of the temperature on CVS measurements?*

The amount of Cu deposited on the working electrode during a CVS sweep depends on the temperature. This has a direct influence on the result. If for example in a brightener determination the sample has a higher temperature than the intercept solution, too high results are obtained. The condition for the measurement of the intercept value and the sample is not the same. The intercept value would be higher if measured at the same temperature as the sample. As a consequence a too small intercept value is subtracted, and consequently the calculated result is too high.

The temperature dependency of CVS measurements is also documented in the blog post «A thermal rollercoaster: Unraveling temperature dependence in CVS determinations». As an example from the blog post the temperature dependency of the recovery of a brightener determination is shown in the table below. The recovery rates of a check standard solution determined by CVS-MLAT are given depending on the temperature and the proportion of the sample in the measuring solution. The temperature of the intercept solution was always 20 °C, whereas the temperature of the sample was varied. This is especially pronounced if the sample volume is high compared to the intercept volume.

Intercept solution		Sample		Recovery rate		
Volume [mL]	Proportion [%]	Volume [mL]	Proportion [%]	Sample temperature		
				20 °C	30 °C	40 °C
16.6	39.9	25	60.1	99%	118%	126%
21.6	51.9	20	48.1	101.%	113%	117%
26.6	63.9	15	36.1	101%	109%	110%
31.6	76.0	10	24.0	101%	101%	104%
36.6	88.0	5	12.0	99%	100%	99%

3.3 Solution addition

Actions

Electrodes are initially conditioned in each CVS method. After this step, the electrodes must not be removed from the measuring solution anymore. Manual additions, which are done after the initial conditioning in a method, have to be done via the pipetting opening. The measuring head must not be lifted during a determination.

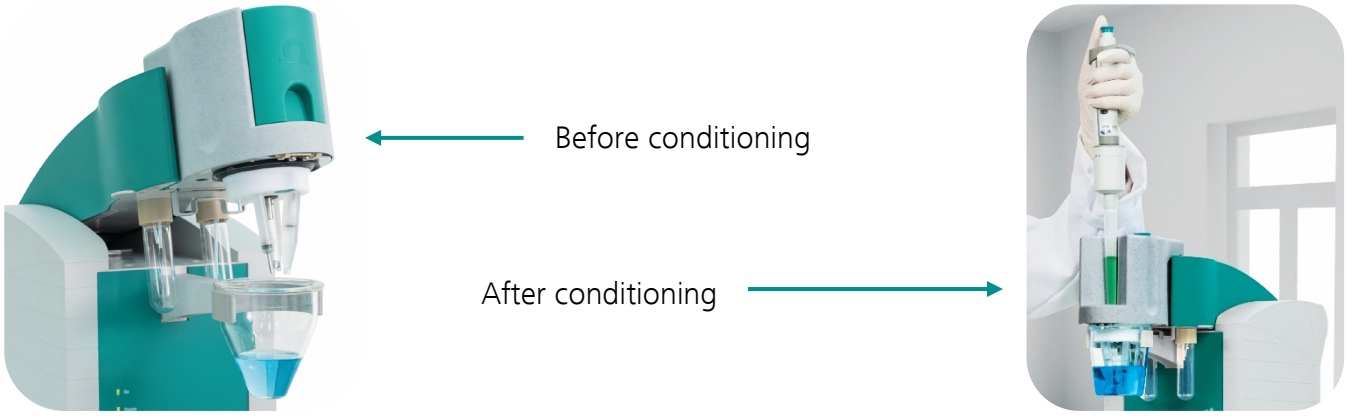


Figure 10: Manual solution addition

Comments

- Keeping the electrodes immersed in the solution throughout a determination is important to maintain their conditioned state and to obtain reproducible and stable measuring curves.
- At the very beginning of a determination the solutions can be added with opened measuring head. At this time the electrodes are not conditioned yet for the respective application.

Info: *Why is it important to keep the electrodes immersed in the measuring solution during a determination?*

At the beginning of a determination the working electrode is conditioned in the respective solution, e.g. in VMS in a suppressor determination or in the intercept solution in a brightener determination. The conditioning has the aim to get the working electrode in a state, where reproducible measuring curves are obtained. This requires that the working electrode stays immersed in the solution. When the working electrode is removed from the solution its state is changed again.

4 Shut-down – Procedures at the end of a working day

The following procedures should be carried out when the system is not used for a longer period of time, e.g. overnight.

4.1 Refilling of the reference electrode

Figure 11: Reference electrode 6.0728.130

Info: *Why is the reference potential so important for CVS?*

In CVS the first vertex potential is a key parameter to a well-working and robust method. The amount of Cu deposited on the working electrode is in direct relation to the first vertex potential. Since all potentials are applied relative to the potential of the reference electrode, a stable and reproducible reference potential is crucial.

The reference electrode used in CVS is Ag|AgCl|c(KCl) = 3 mol/L. It is a reference electrode of the second kind, which means that the reference potential depends on the solubility of a sparingly soluble compound. This compound is AgCl, whose solubility only depends on the chloride activity. The reference electrolyte (c(KCl) = 3 mol/L) is available from Metrohm, e.g. 6.2308.020.

Actions

Replace the electrolyte in the reference electrode every second or third day. This should be done at the end of a working day, when shutting down the instrument to allow for sufficient time for equilibration of the reference potential.

Comments

- After replacing the electrolyte, allow at least 4 hours for the reference potential to equilibrate. Refilling the reference electrode at the end of the working day gives the electrode potential sufficient time for equilibration.
- Care should be taken, that no air bubbles are present at the diaphragm or around the AgCl cartridge to avoid contact problems.
- More information on how to handle the reference electrodes in voltammetry can be found in our multimedia guide «Electrodes in Voltammetry» (A.717.0003), also available online in the product help center (Metrohm.com ► Support & Service ► Product Help Center ► Cyclic Voltammetric Stripping).
- If the maintenance-free reference electrode 6.0730.100 is used, no actions are necessary.

4.2 Electrode storage

If the electrodes are not used for a short time, e.g. a few hours, they can be left in the measuring vessel, immersed in deionized water.

If the system is not used overnight or for a longer time, then the reference electrodes have to be stored separately. The working electrode and the auxiliary electrode can be stored dry.

Figure 12: Electrode storage: a few hours in deionized water (left) or RE removed from measuring head, if not used overnight or longer (right)

Info: *Why is it important to store the electrodes appropriately?*

To have the measuring system ready for operation fast and to ensure a long lifetime of the electrodes they should be stored appropriately, when not in use. The most critical electrode in this regard is the reference electrode. Wrong storage can cause the reference potential to shift or even lead to irreversible damage of the reference electrode.

Storage in the wrong solution is especially a problem for gel-filled reference electrodes. The chloride concentration in the gel decreases with time if the electrode is not stored in c(KCl) = 3 mol/L. This leads to diffusion potentials within the reference electrode, which lead to a shift of the reference potential.

If the gel in a gel-filled reference electrode 6.0730.100 dries out, the reference electrode has to be replaced by a new one. Dried out gel cannot be regenerated.

If the LL-Ag/AgCl reference electrode without gel filling (6.0728.130) dries out, it can be regenerated. More information on how to revive dried out reference electrodes can be found in our multimedia guide «Electrodes in Voltammetry» (A.717.0003), also available online in the product help center (Metrohm.com ▶ Support & Service ▶ Product Help Center ▶ Cyclic Voltammetric Stripping).

4.2.1 LL-Ag/AgCl reference electrode 6.0728.130

Actions

The reference electrode, assembled with the bridge electrolyte vessel, is stored in a separate vessel (e.g. 6.2008.040 or 6.2743.057). The bridge electrolyte vessel should be filled with a solution of $c(KNO_3)$ = 1 mol/L to the mark prior to storage. The storage vessel has to be filled with deionized water or $c(KNO_3)$ = 1 mol/L.

Comments

- More important than the used storage solution for the reference electrode is that the reference electrode does not run dry. A storage vessel has to be used, where the solution cannot evaporate.
- In a fully automated system it is not possible to store the electrodes individually at the end of a determination series without human interaction. In this case the measuring vessel has to be filled with deionized water after the last determination. The measuring vessel must not be emptied after a determination series because the reference electrode would dry out after a while. The reference electrode should furthermore not be stored in VMS or in the measuring solution.

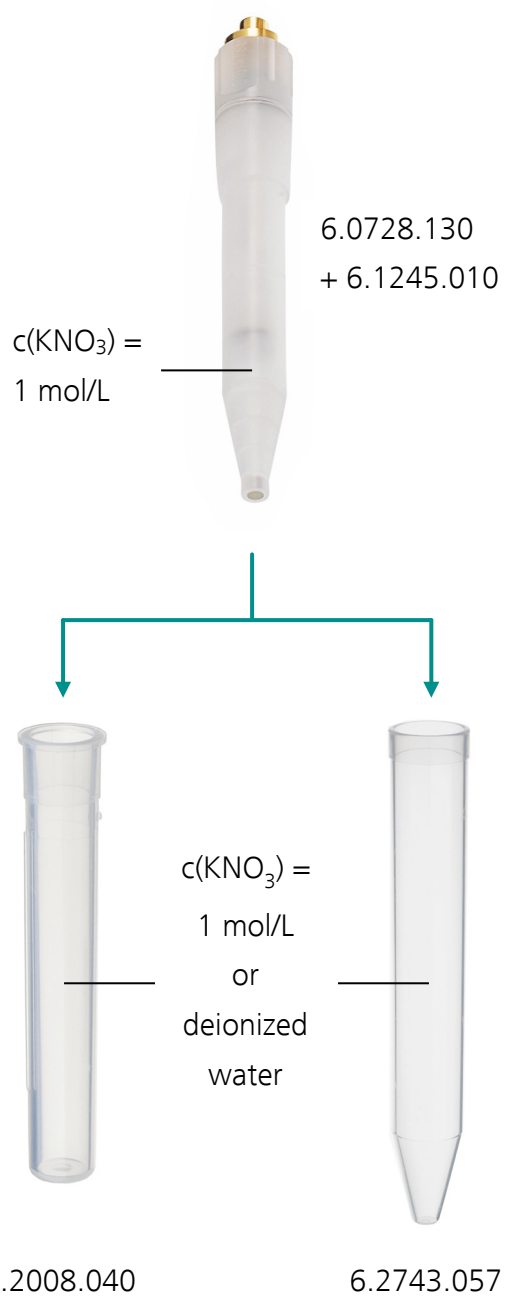


Figure 13: Storage of the LL-Ag/AgCl reference electrode.

4.2.2 Maintenance-free reference electrode 6.0730.100

Actions

The maintenance-free reference electrode does not need special storage conditions, if it is constantly used. It can be left in the measuring vessel, filled with deionized water. It only needs to be prevented from drying out.
However, from time to time (e.g. once per week), the reference electrode should be stored in 3 mol/L KCl overnight. For this purpose it is put in a separate vessel (e.g. the transport vessel, with which it is delivered, 6.2008.040 or 6.2743.057). The storage vessel has to be filled with c(KCl) = 3 mol/L.

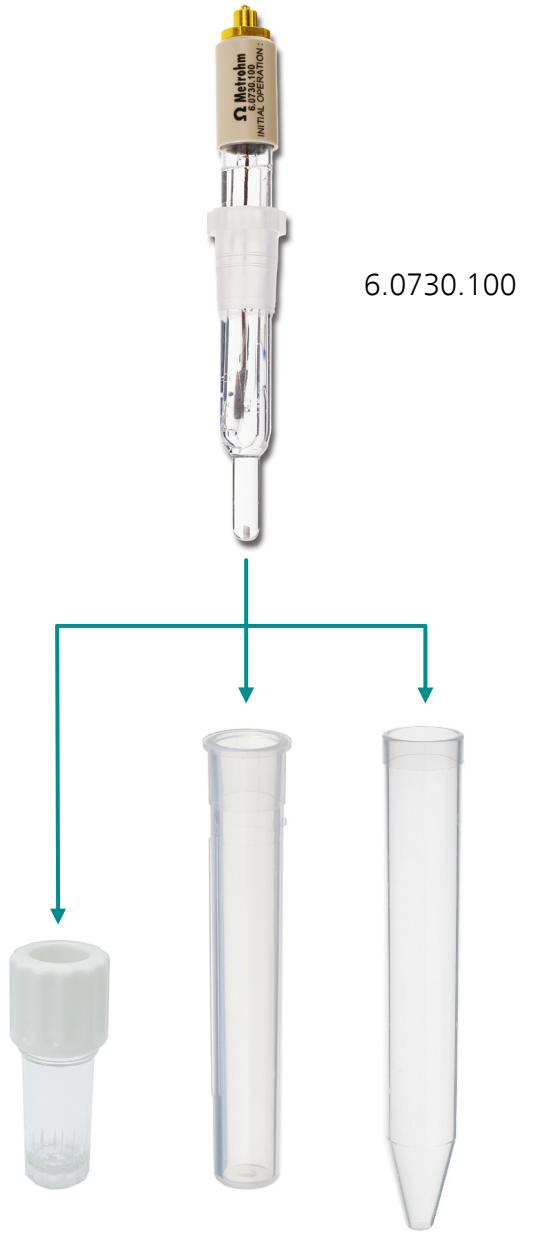


Figure 14: Regular storage of the maintenance-free reference electrode.

Comments

- The gel of the maintenance-free reference electrode cannot be refilled, but the KCl in it is lost over time by diffusion into the measuring solution or deionized water. To compensate for the loss, the maintenance-free reference electrode has to be stored in c(KCl) = 3 mol/L from time to time.
- In a fully automated system it has to be ensured that the measuring vessel is filled at the end of the last determination. The maintenance-free reference electrode should furthermore not be stored in VMS or in the measuring solution.
- If the maintenance-free reference electrode is not used for a longer time it has to be stored in a tight vessel in a solution of 3 mol/L KCl. For this purpose preferably the transport vessel is used, with which the reference electrode is delivered.
- Under no circumstances may this reference electrode dry out as this will destroy it irreparably.

4.3 Storage of the 807 Dosing Units

Actions

Prepare the 807 Dosing Units with deionized water at the end of the working day and leave them filled.

Comments

- Preparing the 807 Dosing Units with deionized water prevents blockage due to crystallization.
- If the 807 Dosing Units are not used for a longer time (e.g. a week or longer) they should be disassembled, rinsed and left to dry. After drying they are reassembled, greased and stored dry. See also chapter 5.3 of this document and «Manual 807 Dosing Unit», 8.807.8002, chapter 5.

Figure 15: Preparation of the 807 Dosing Units with deionized water.

5 General tips

5.1 Solutions

The solutions used for CVS should be stored appropriately to address their individual stability.

5.1.1 VMS

There is no special requirement for the storage of the virgin make-up solution (VMS).

The VMS consists of $CuSO_4$, H_2SO_4 and chloride in case of acid Cu baths. This solution is very stable.

5.1.2 Additives

Store the organic additives in a gas-tight vessel in a dark, cool place, e.g. a cupboard.

The organic additives, especially brighteners, are sensitive to light, high temperature and oxygen.

5.1.3 Calibration and check standard solutions

Prepare calibration standards and check standard solutions freshly before they are used.

These solutions have limited stability. Especially diluted brightener solutions should not be used longer than one day. The stability in VMS can change between different brighteners. For some brighteners it might also be necessary to prepare a new check standard solution after a few hours.

5.2 Calibration curves, intercept and electrolyte values

Values which are used for multiple determinations, such as the calibration factor for a suppressor determination, the intercept value for a brightener determination by LAT, or the electrolyte value or the response curve for a leveler determination, should be recorded regularly. Exact numbers cannot be given since the measurement interval strongly depends on the additive system.

The validity of these values can be checked by the determination of a check standard solution.

- The recovery for a suppressor determination should be (100 ± 10)%.
- The recovery for a brightener or leveler determination should be (100 ± 20)%.

5.3 Maintenance of 807 Dosing Units

Actions

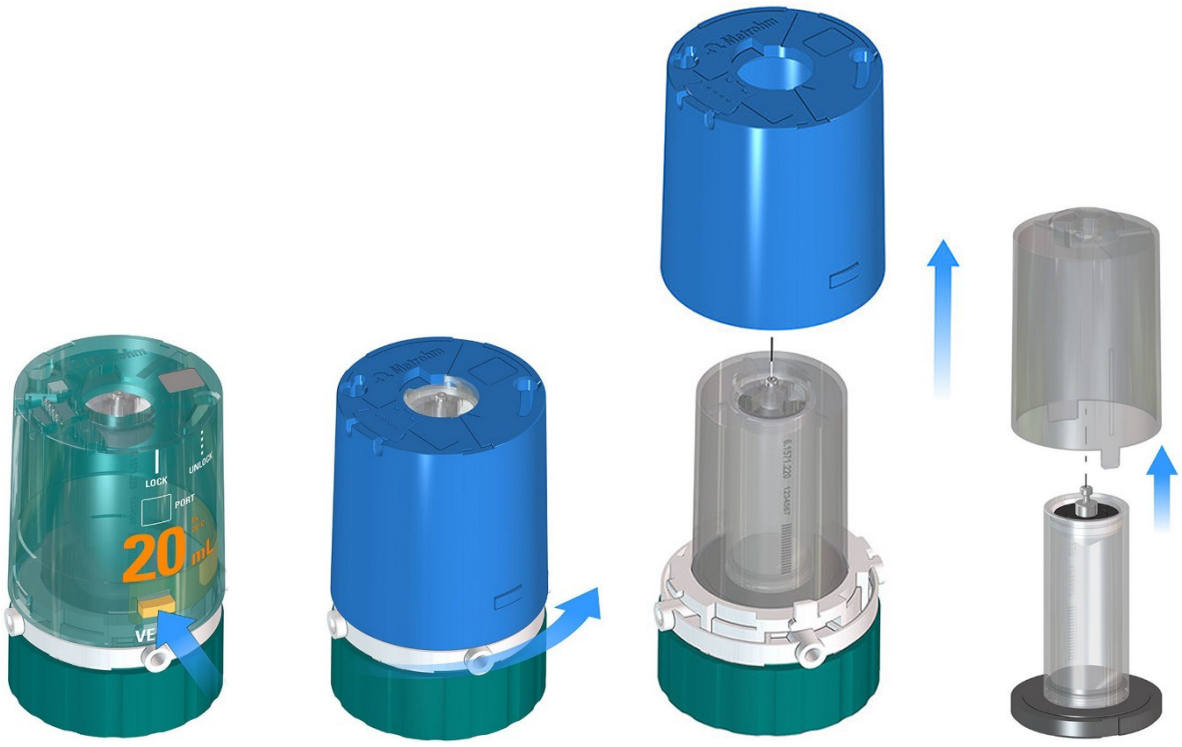
Carry out regular maintenance of the 807 Dosing Units, e.g. every 2-4 weeks.

Comments

- The 807 Dosing Units are useful devices which allow highly precise automatic addition of solutions, even down to very small volumes such as 10 µL. This high precision requires proper handling and upkeep of the 807 Dosing Units.
- The solutions used in CVS are often highly concentrated solutions of $CuSO_4$ or organic substances, which can crystallize out and block the 807 Dosing Unit. To avoid this, we recommend regular maintenance.
- In this procedure they are thoroughly cleaned. After complete drying the necessary parts are greased and the 807 Dosing Units are reassembled.
- When greasing the parts indicated below, only very little grease should be used to avoid that excess grease is transported into the measuring solution, where it can interfere with the measurement.

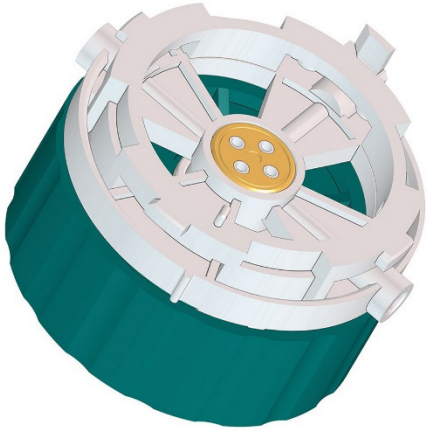
5.3.1 Procedure

- The 807 Dosing Unit is emptied and disassembled (see also «Manual 807 Dosing Unit», 8.807.8002, chapter 5.2).



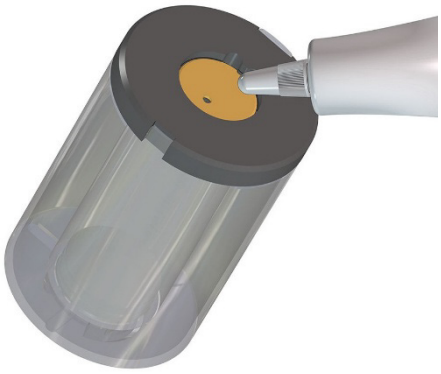
- Important: The glass cylinder must <u>not be</u> removed from the cylinder base, and the piston has to remain in the glass cylinder. Otherwise the 807 Dosing Unit may become untight and leakage can occur. The piston, glass cylinder and cylinder base must always remain assembled together.

- All parts are rinsed with plenty of deionized water.
- The valve and distributor disk are cleaned with ethanol



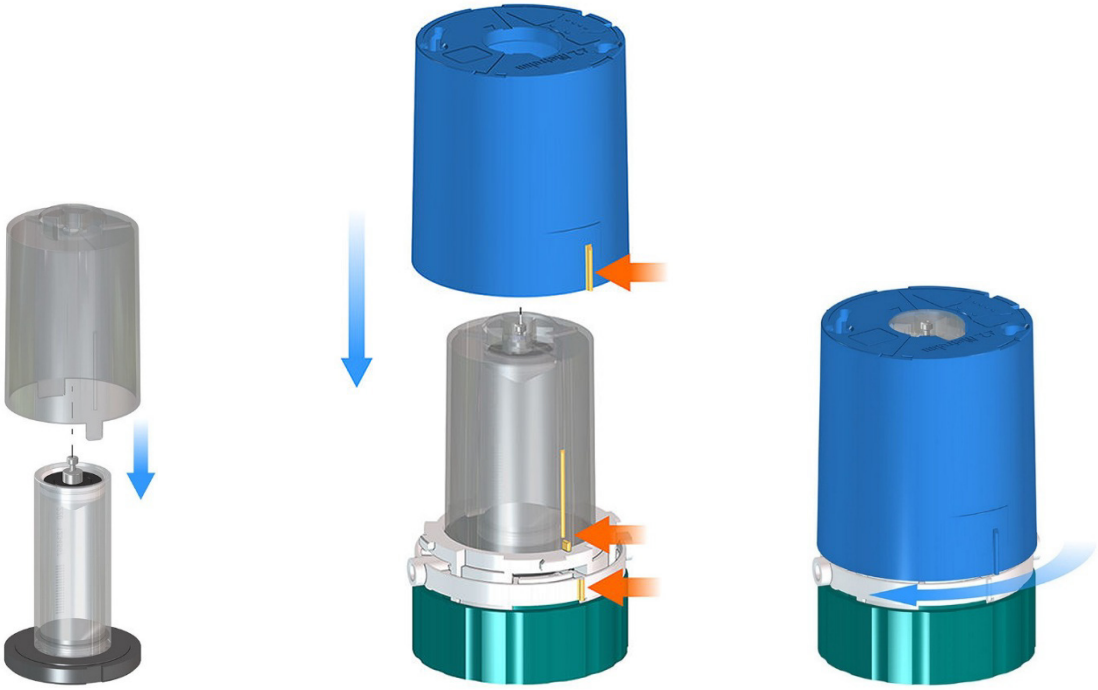
- All parts are left to dry completely.
- The centering tube is greased as indicated.

- Those parts that are in contact with solution should only be greased slightly. Use very little grease on the valve disk and remove excess with a soft tissue. Excess grease would be introduced into the dosing channel and is transported into the measuring vessel with time, which has to be avoided.



Especially the 807 Dosing Units containing sulfuric acid (VMS / Standard or sample) can get blocked sometimes between the distributor disk and the valve disk. If this happens repeatedly a special PTFE paste may be used to grease the valve disk.

- The 807 Dosing Unit is reassembled (see also «Manual 807 Dosing Unit», 8.807.8002, chapter 5.6).



5.4 Working electrode – WE (Pt RDE)

The standard and recommended platinum working electrode is 6.1204.610 with an electrode disk of 2 mm diameter in a glass shaft. Some of the advantages of this electrode are:

- Very good chemical resistance, since only the inert materials platinum and glass get in contact with the measuring solution.
- Longer lifetime compared to a platinum electrode with a PEEK shaft, since no glue is used at the intersection between glass and platinum. Glue slowly decomposes when in contact with aggressive media.
- Faster conditioning and more reproducible measurements compared to a platinum electrode with a PEEK shaft, due to an ideal intersection platinum – glass.
- Applications can smoothly be transferred from a 3 mm PEEK electrode to the 2 mm glass electrode.

The working electrode is a consumable. Even with proper handling as described before it will only last for a certain time. To assess the performance of the electrode it is recommended to monitor the peak area obtained during conditioning of the electrode (5.4.1) and, in case of doubts, run a cyclic voltammetric test (5.4.2).

5.4.1 Monitoring the peak area of electrode conditioning

As a measure for the performance of the electrode the peak area obtained during conditioning should be monitored over time (see chapter 2.3.1 Conditioning of the WE). A variation in the peak area in the range of ±20% is acceptable. If suddenly the area increases or decreases drastically, and electrode maintenance does not help, then it can be an indication that the end of the lifetime has been reached.

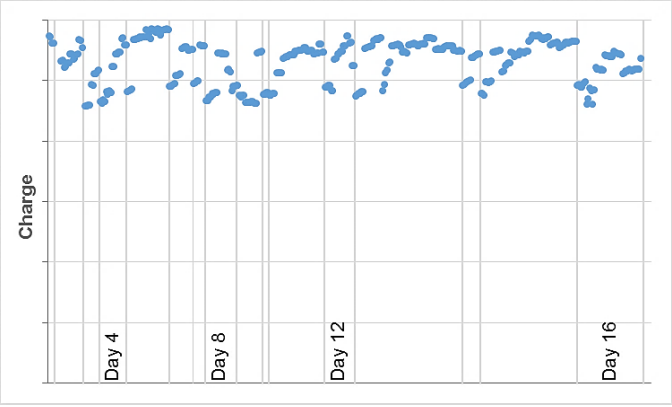


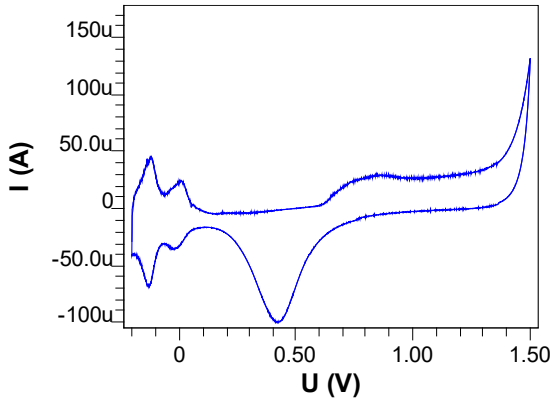
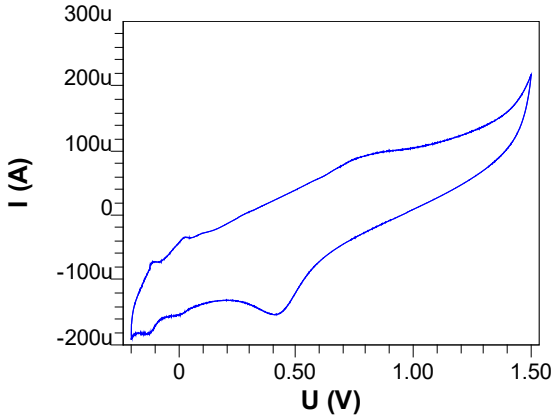
Figure 16: Example for the peak area (charge) obtained during conditioning over a period of 16 days

5.4.2 Cyclic voltammetric test of platinum RDEs

In case of doubts about the state of the electrode a cyclic voltammetric test should be carried out to assess the wear of the electrode. This can be done by means of the preinstalled methods, which can be found in the installation directory of the viva software (%ProgramFiles(x86)%\Metrohm\viva\examples \methods\CVS\Cyclic voltammetric test on Pt-RDEs.vmet) or in the program data path of the 797 VA Computrace (Windows 7, 32 bit: %ProgramData%\Metrohm\797 VA Computrace\Method\CVS\Cyclic voltammetric test on Pt RDE.mth). The resulting cyclic voltammogram should look like the example below. Assessment criteria are:

- The difference between anodic and cathodic current at +0.1 V should be as small as possible.
- The overall progression of the voltammogram should be approximately horizontal.
- The hydrogen adsorption and desorption peaks between -0.2 V and +0.1 V should be clearly visible. Note that the absence of these peaks does not necessarily mean that the electrode is defective. The peaks can also disappear if the electrode is contaminated.

More details on the cyclovoltammetric test can be found in the Application Work AW VA CH4-0453-122006.

Example of a good electrode (2 mm Pt)	Example of a bad electrode (2 mm Pt)
	

5.5 Driving axle

Figure 17: Driving axle 6.1204.510 (left) and 6.1204.520 (right) assembled with a 2 mm Pt RDE tip 6.1204.610

The driving axles do not require maintenance. Keep in mind that this item is a consumable. The standard driving axle (6.1204.210/6.1204.510) has a lifetime of approx. 3 – 6 months. The driving axle with mercury contact (6.1204.220/6.1204.520) has a lifetime of approx. 1 year.

With both driving axles care has to be taken, that no solution enters the gaps between the driving axle and the RDE. Otherwise corrosion in the ball bearings inside the driving axle will be the result. For these reasons, only touch the driving axles with clean fingers/gloves and avoid overfilling of the measuring vessel (see next section).

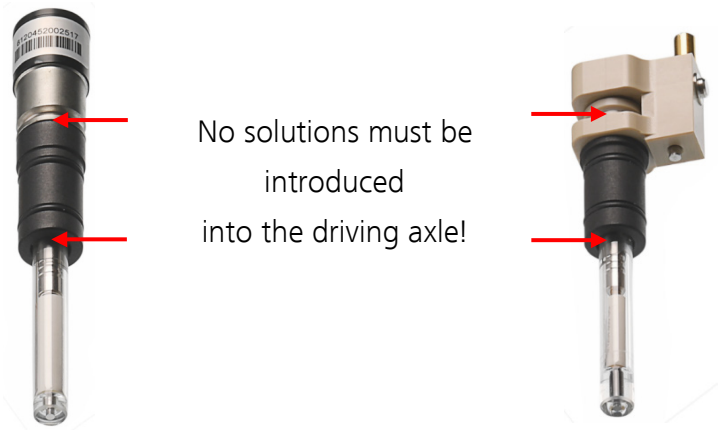


Figure 18: No solutions must enter the gaps in the driving axles!

5.5.1 Fill level in the measuring vessel

Actions

The fill level in the measuring vessel should be only so high that no solution can enter the gap between the RDE and the titanium axle. The maximum level should be kept approx. 1 cm below the gap between driving axle and RDE.

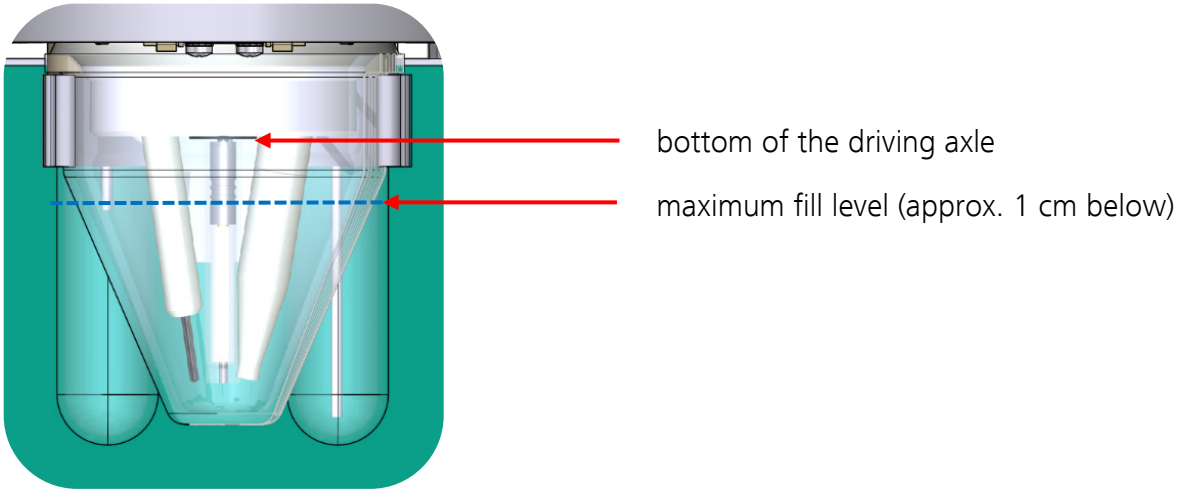


Figure 19: Maximum fill level in the measuring vessel

Comments

- This also has to be considered when the measuring vessel is rinsed.
- The rotating part of the driving axle is made of titanium and the black part of PTFE. Both parts have excellent chemical resistance. However, a ball bearing is used inside the driving axle which can corrode, when exposed to aggressive solutions. Therefore it must be avoided that measuring solution enters the gap between the titanium axle and the PTFE part. Besides corrosion of the ball bearings also crystallization can occur, which leads to mechanical abrasion of the PTFE. Both crystals and abrasion particles can lead to a blockage of the driving axle. In addition, the particles can fall into the measuring vessel.
- If the application requires a higher volume of the measuring solution, a bigger measuring vessel should be used. Various sizes are available from Metrohm.

5.6 Tubing configuration on the 807 Dosing Unit

For 807 Dosing Units it is recommended to use the following setup, where port 3 is used for the preparation.

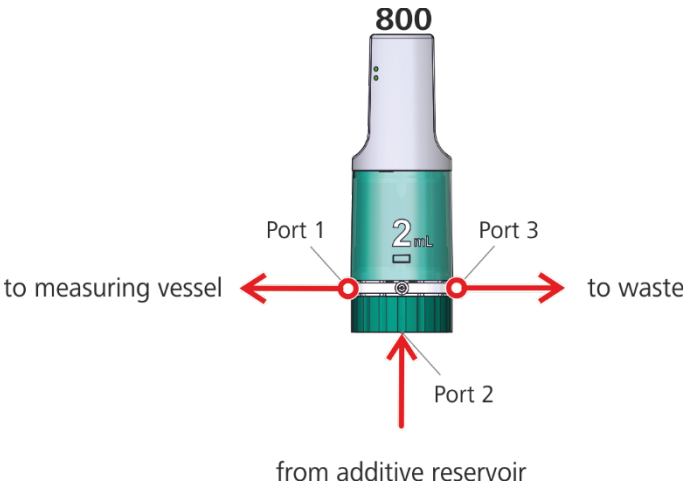


Figure 20: Tubing configuration on the 807 Dosing Unit for preparation via port 3

Info: *What is the benefit of preparing an 807 Dosing Unit via port 3?*

- Faster: Since an FEP tubing of 2 mm inner diameter can be used on port 3 the dispensing of solution to the waste is much faster than into the measuring vessel via e.g. a capillary of 0.3 mm inner diameter as used in the four-way micro dosing tip 6.1824.000. Smaller diameters limit the dosing speed.
- Less contamination: If the preparation is done via port 1 a very high volume of the respective solution goes into the measuring vessel. This can result in memory effects, if rinsing is done insufficiently.

In addition to the aspiration tubing at port 2, where the additive or VMS is filled into the 807 Dosing Unit and port 1, where the dosing is carried out port 3 should be used for preparation. An FEP tubing with an inner diameter of 2 mm is connected there, which leads to a waste container.

The use of port 3 for preparation needs to be defined in the software.

In the **viva** software this setting is found under the properties of the respective 807 Dosing Unit. Note that the length of the waste tubing should be specified as 0 cm to avoid that this tubing will also be completely filled during preparation.

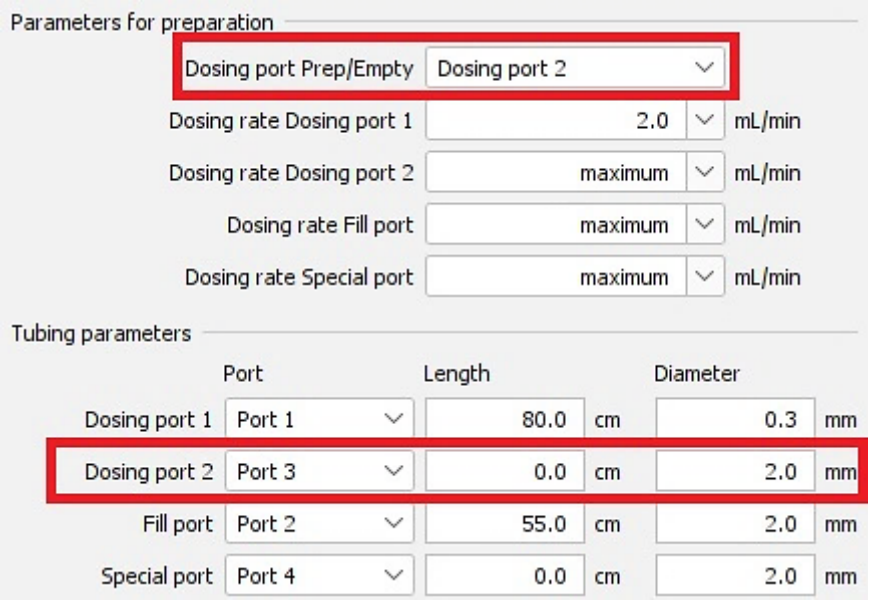


Figure 21: Settings for preparation via port 3 in the **viva** software

In the VA Computrace software the setting is found under «Settings/General settings».

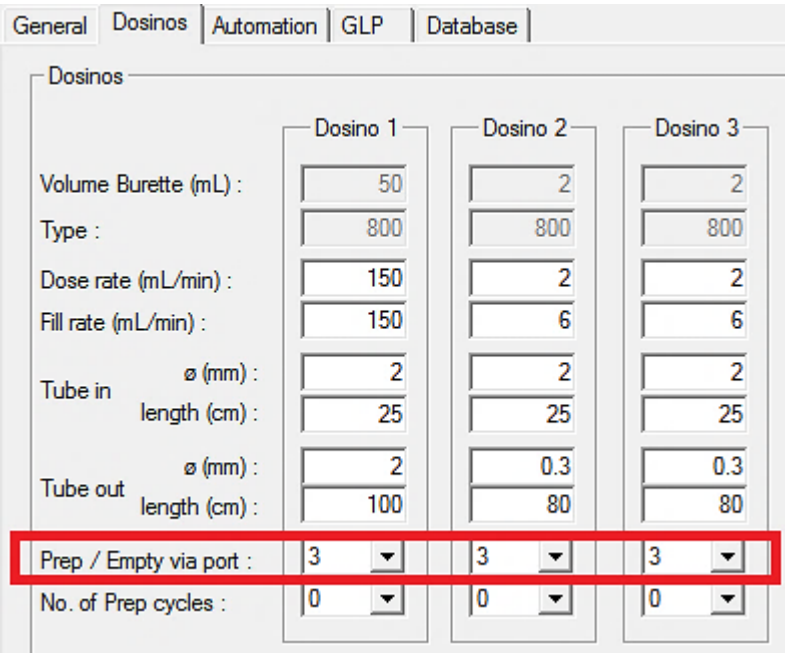


Figure 22: Settings for preparation via port 3 in the VA Computrace software

6 Troubleshooting

6.1 Checklist

In case of problems (unusual measuring curves, results out of the expected range, bad reproducibility) please check the following items.

	Check	Nominal condition	Action, if condition is not met
☐	Are the electrode cables correctly connected?	AE – Auxiliary electrode WE – Working electrode RE – Reference electrode	Connect correctly
☐	Is the RE filled correctly?	Internal reference system filled with c(KCl) = 3 mol/L. Outer electrolyte solution $c(KNO_3)$ = 1 mol/L.	See chapter 4.1: Refilling of the reference electrode and 2.2: Replacing the bridge electrolyte
☐	Has the peak area of the VMS/intercept changed?	The peak area has to be stable.	Check the WE, clean the WE See chapter 6.2.1: • «Instable signal» • «Area of the stripping peak is higher than usual»
☐	Is the cyclic voltammetric test in H_2SO_4 OK?	Example and criteria: see chapter 5.4.2.	Clean the WE See chapter 6.2.1: • «Instable signal» • «Area of the stripping peak is higher than usual»
☐	Is the VMS clean?	Besides $CuSO_4$, H_2SO_4, Cl^- (HCl or NaCl), and sometimes Fe species, no other substances must be present, especially no organics.	Use clean glassware for the preparation of solutions. Chemicals with a quality of analytical grade or better have to be used to avoid contaminations.
☐	Has the temperature of the used solutions changed?	The temperature has to be stable during the determination. Temperature	Stabilize the temperature (e.g. with a measuring vessel with a thermostat jacket).

		changes influence the CVS measurement.	
☐	Was the check standard freshly prepared?	The check standard should be freshly prepared prior to the determination. Organic additives can decompose when stored in diluted solutions.	Prepare a new check standard solution.
☐	Is the recovery in a check standard OK?	• ±10 % of the expected value for suppressor • ±20 % of the expected value for brightener or leveler	Check the used method, check the standard solution.
☐	Are the concentrates of brightener, suppressor and leveler from the same batch as used in the production process?	Additive concentrates should be from the same batch as used in the production process. Concentration fluctuations and slight composition changes may occur with different additive batches.	Use the same batches of additives for the analysis and the production process.
☐	Was the sample taken correctly?	A proper sampling procedure is necessary to obtain correct results.	• Rinse the sampling tubing sufficiently. • The sample should be as fresh as possible.
☐	Is the recovery in a spiked plating bath sample OK?	• ±10 % of the expected value for suppressor • ±20 % of the expected value for brightener or leveler	Check the standard solution, optimize the method.

6.2 Problems and possible solutions

The following lists contain typical problematic phenomenons, their possible causes and solution proposals.

6.2.1 General

Problem	Possible cause	Suggested solutions
WE surface is scratched	Bad storage or handling	• Manual polishing of the Pt surface can be done as the last option to recover an RDE. Note that the original performance cannot be restored afterwards! • Replace the working electrode.
Signal is noisy	Air bubble on the WE	• Remove the air bubble by repeated lifting and lowering of the measuring head, so that the WE is immersed and removed from the measuring solution. Then repeat the measurement.
	WE is in bad condition	• Conditioning (see chapter 2.3.1)
	Adsorption of additives on the WE surface	• Conditioning (see chapter 2.3.1) • Rinse electrode with ethanol • Soak electrode in c(NaOH) = 1 mol/L for 60 minutes
	Abrasion at the driving axle.	• Replace the driving axle.
	Broken sliding contact.	• Replace the driving axle.
	Lifetime of the Hg contact driving axle expired.	• Replace the Hg contact driving axle (6.1204.220/6.1204.520).
Driving axle is blocked	Crystallization of $CuSO_4$, corrosion by H_2SO_4 or abrasion particles around the titanium axle	• Replace the driving axle. • Do not overfill the measuring vessel. • Do not touch the driving axle with contaminated fingers/gloves. • Careful operation during rinsing. • Use of automatic rinsing equipment.

Instable signal	Bad condition of the WE	• Clean the WE with ethanol and/or acetone. • Soak the WE for min. 60 minutes in c(NaOH) = 1 mol/L. • Use a new electrode.
	Leakage from 807 Dosing Unit	• Tighten the connection of the dosing capillaries with the dedicated wrench (6.2739.000). • Clean the 807 Dosing Unit as described in chapter 5.3. • Exchange the 807 Dosing Unit.
	Temperature	• Use of a measuring vessel with thermostat jacket and a water bath circulator.
	Contaminated VMS	• Prepare new VMS using clean glassware and correct concentrations. • Reagents quality at least analytical grade
	Wrong (bad) RE filling or insufficient time for equilibration of the reference potential	• Refill the RE and give it sufficient time for equilibration (see chapter 4.1)
Area of the stripping peak is higher than usual	Incorrect VMS composition	• Use correct concentrations of the VMS components.
	Wrong voltammetric parameters	• Use the correct method settings.
	Contaminated VMS	• Prepare new VMS using clean glassware and correct concentrations. • Reagents quality at least analytical grade
	Wrong (bad) RE filling	• Refill the RE and give it sufficient time for equilibration (see chapter 4.1)
	Temperature	• Maintain a stable lab temperature. • Use a measuring vessel with thermostat jacket and a water bath circulator.
	Pt RDE (WE) surface changed, scratched, rough	• Handle with care • Exchange the Pt RDE.
	WE defective	• Exchange the WE.

Copper layer on the WE	Wrong voltammetric parameters or manual stop of the measurement	• Check the voltammetric parameters • Do not use the «Standby potential» in the method. • Dip working electrode in w(HNO_3) = 65 % for a few seconds
	Reference or auxiliary electrode cable not or wrongly connected	• Connect cables correctly
	Wrong filling or air bubble in the RE	• Fill RE correctly (see chapter 4.1)
Copper layer on the AE	Wrong voltammetric parameters or manual stop of the measurement	• Check the voltammetric parameters. • Do not use the «Standby potential» in the method. • Dip auxiliary electrode in w(HNO_3) = 65% for a few seconds to remove the Cu.
	Auxiliary electrode cable wrongly connected	• Connect the cables correctly.
	Wrong filling or air bubble in the RE	• Fill RE correctly (see chapter 4.1).
Dosino is blocked • No solution is dosed • Cylinder does not turn	Precipitation/ crystallization in the cylinder or tubings	• Disassemble the 807 Dosing Unit. If the valve disk and distributor disk stick together check under the respective point «Valve disk and distributor disk stick together», further below. • Clean the 807 Dosing Unit, let it dry and reassemble it. • To prevent crystallization fill the 807 Dosing Units with H_2O, if they are not in use. • If the 807 Dosing Unit is not used for a longer time they should be cleaned and stored dry. • If crystallization has occurred in the tubings, try to immerse them in deionized water until the crystals have dissolved or replace the tubings.
	Sample contains particles	• Remove particles or use a tubing with a bigger inner diameter.

	Valve disk and distributor disk stick together	• Remove the housing and centering tube of the 807 Dosing Unit. • Place the 807 Dosing Unit with the dosing cylinder in warm water (possibly with a small amount of dishwashing detergent) for a few minutes. • Carefully release the cylinder base from the distributor disk by hand (without rotating it) in order to separate the two disks from each other. • Clean the 807 Dosing Unit, let it dry and reassemble it. • If the disks stick together frequently, especially with H_2SO_4 containing solutions, the valve disk should be greased with PTFE paste (6.2803.050).
No peak at expected potential or no peak at all	One or more electrode cable not or wrongly connected	• Connect all electrodes with the correct cables.
	Wrong RE filling	• Fill RE correctly (see chapter 4.1).
Wrong/no peak is evaluated	Wrong peak position defined	• Adapt the peak position under «Substances». Choose a potential, which is as close as possible to the real peak position. • Adapt the tolerance range.
	Wrong sweep direction is chosen	• The peak has to be evaluated in the anodic sweep under «Substances».

Baseline changes for every addition	Wrong baseline setting	• Check the baseline settings:
		  • Evaluation: manually
		  • Start: positive
		  • End: negative
		  • Type: horizontal

6.2.2 DT – Dilution Titration

Problem	Possible cause	Suggested solutions
VMS value is lower than usual/ voltammogram of VMS has an unusual shape	Contamination in the measuring vessel/ leakage from 807 Dosing Unit(s)	• Rinse the measuring vessel thoroughly with deionized water. • Check for leakage from the 807 Dosing Units. • Tighten the connection of the dosing capillaries with the dedicated wrench (6.2739.000). • Clean the 807 Dosing Unit as described in chapter 5.3. • Exchange the 807 Dosing Unit.
Insufficient number of points on the calibration / determination curve (less than 5)	Contamination in the measuring vessel/ leakage from 807 Dosing Unit(s)	• Rinse the measuring vessel thoroughly with deionized water. • Check for leakage from the 807 Dosing Units. • Tighten the connection of the dosing capillaries with the dedicated wrench (6.2739.000). • Clean the 807 Dosing Unit as described in chapter 5.3. • Exchange the 807 Dosing Unit.
	Wrong concentration of standard solution	• Prepare a new calibration standard.
	Too high addition volume	• Decrease the addition volume.
Too many points on the calibration / determination curve (more than 15)	Wrong concentration of standard solution	• Prepare a new calibration standard.
	Too small addition volume	• Increase the addition volume.
	No sample or standard solution is added	• Check if the 807 Dosing Unit is filled. • Prepare the 807 Dosing Unit with the respective solution twice.
	The signal ratio to stop the additions is set too small	• Set the signal ratio 0.05 … 0.1 lower than the «evaluation ratio». (Note: In the

		Computrace software the signal ratio is the «addition ratio».)
Conditioning cycles do not reach a relative standard deviation of 0.5%.	WE is in bad condition	• See chapter 2.3.1
	Wrong (bad) RE filling	• See chapter 4.1
	Contamination in the measuring vessel/ leakage from 807 Dosing Unit(s)	• Rinse the measuring vessel thoroughly with deionized water. • Check for leakage from the 807 Dosing Units. • Tighten the connection of the dosing capillaries with the dedicated wrench (6.2739.000). • Clean the 807 Dosing Unit as described in chapter 5.3. • Exchange the 807 Dosing Unit.

Baseline changes for every addition	Wrong baseline settings	• Check the baseline settings:
		  • Evaluation: manually
		  • Start: positive
		  • End: negative
		  • Type: horizontal

The evaluation ratio is reached but no results are being displayed.	Wrong sample type (viva)	• The sample type for a suppressor determination has to be «Sample». • For a calibration the sample type has to be «Standard».
	No calibration available	• In viva a calibration curve has to be recorded with the same method name.
	In rare cases the evaluation algorithm is not able to calculate the results with «Nonlinear regression technique».	• Linear interpolation as a regression technique helps to overcome such problems.
The curve obtained from the sample looks different to that from the calibration.	Breakdown products in the sample can cause this effect.	• This is normal behavior. Successful determination of recoveries in spiked samples validates the chosen method.

6.2.3 MLAT / LAT – (Modified) Linear Approximation Technique

Problem	Possible cause	Suggested solutions
Bad result reproducibility	Electrodes were lifted out of the measuring solution during the measurement	• Use the pipetting opening to add the sample.
	Temperature is unstable	• Use of a measuring vessel with thermostat jacket and a water bath circulator.
	Manual standard additions	• Use a Dosino for highly reproducible additions.
Bad reproducibility of measuring curve	Electrodes are not conditioned	• Perform conditioning cycles (see chapter 2.3.1).
	Temperature is unstable	• Use of a measuring vessel with thermostat jacket and a water bath circulator.
Negative result (no result)	No sample was added	• Add sample
	Sample contains no brightener	• Use fresh sample
	Automatic brightener addition	• Check for air bubbles • Prepare the 807 Dosing Unit twice with brightener concentrate.
Additions are not linear	Too high addition volume	• Use smaller addition volume.
	Out of the linear range	• Check the linear range.
	Voltammetric parameters	• Check, if correct voltammetric parameters were used.
	Manual standard additions	• Use a Dosino for highly reproducible additions.
	WE in bad condition	• Condition the WE (see chapter 2.3.1)
	Wrong reference potential	• Refill the RE and give sufficient time for equilibration (see chapter 4.1)
Conditioning takes too long	Relative standard deviation for the initial electrode conditioning is set too low	• For brightener determinations use a value of 2%.
	WE in bad condition	• Condition the WE (see chapter 2.3.1)

		• Clean WE with ethanol and/or acetone • Soak the electrode for 60 min in c(NaOH) = 1 mol/L • Use a new electrode

6.2.4 RC – Response Curve

Problem	Possible cause	Suggested solutions
Bad result reproducibility	Electrodes were lifted out of the measuring solution during the measurement	• Use the pipetting opening to add the sample.
	Temperature is unstable	• Use of a measuring vessel with thermostat jacket and a water bath circulator.
Bad reproducibility of measuring curve	Electrodes are not conditioned	• Perform conditioning cycles (see chapter 2.3.1).
	Temperature is unstable	• Use of a measuring vessel with thermostat jacket and a water bath circulator.
Conditioning takes too long	Relative standard deviation for the initial electrode conditioning is set too low	• For a leveler determinations typically a value of 1 or 2% is used.
	WE in bad condition	• Condition the WE (see chapter 2.3.1) • Clean WE with ethanol and/or acetone • Soak the electrode for 60 min in c(NaOH) = 1 mol/L • Use a new electrode
The result is too high and out of the calibration range.	Additive concentration is too high	• Dilution of the sample • Record a new calibration curve in a different concentration range.

7 FAQ – Frequently asked questions

Question	Answer
How do I have to store the concentrated additives?	Avoid direct sunlight, use glassware, avoid heating
Does Metrohm provide additives?	No
I always used a Pt WE with bigger diameter. Does this influence my results?	No, the signals with a bigger diameter will be bigger, but at the same time the background current is also higher. More important than the disk diameter is that the signal-to-noise ratio is good enough and the current resolution of the potentiostat is suitable.
Is a Pt WE with a bigger diameter than 2 mm available?	Yes, with 3 mm, order number 6.1246.170. However, the 3 mm Pt RDE is only available with a PEEK shaft. Compared to an RDE with PEEK shaft the use of an RDE in glass has the advantages of better chemical resistivity, better reproducibility of measuring curves and thus faster conditioning.
I want to see the contamination and chloride current. How can I obtain these values?	The contamination and chloride current can be read out from the CVS measuring curve at 1.125 V or 1.475 V, respectively. If CPVS is used additional stripping steps at 1.125 V and 1.475 V are added for 1 second, each. The values can then be read out of the chronoamperogram.
Is it possible to attach more than 4 Dosinos to the 884 Professional VA or more than 3 Dosinos to the 797 VA Computrace?	Yes, it is possible with the 846 Dosing Interface (4 additional ports). With the 884 Professional VA and viva it is possible to control multiple 846 Dosing Interfaces. With the 797 VA Computrace software, only one can be operated.
The preparation of the Dosinos is so slow. How can I speed it up?	The specified dosing rate has to be checked in the configuration. With an FEP tubing of 2 mm inner diameter the maximum dosing rate is the cylinder volume (in mL) multiplied by 3, which gives the dosing rate in mL/min. E.g. with a 2 mL 807 Dosing Unit the maximum dosing rate is 6 mL/min. If a dosing capillary with an inner diameter of 0.3 mm is used the maximum

	permissible dosing rate is 4 mL/min. Our recommendation is to use 2 mL/min. Preparation can be done faster by using port 3, as described in chapter 5.6.
I am used to work with H_2SO_4 10% v/v as outer electrolyte solution. Metrohm uses 1 mol/L KNO_3. Why?	There is no difference in the results. Since KNO_3 is not corrosive and has good electrical conductivity that solution is used. H_2SO_4 as outer electrolyte has the disadvantage that H^+ easily diffuses into the reference system where it changes the reference potential.
How do I store the electrodes when the instrument is not in use?	Store the electrodes in deionized water, if the instrument is not used for a few hours. It is not recommended to store them in VMS or measuring solution. For long-term storage (overnight or longer) the reference electrode should be taken out of the measuring head and stored in deionized water or c(KNO_3) = 1 mol/L. The auxiliary electrode and the working electrode can be stored dry.
How do I check if my WE is still OK?	Monitor the peak area obtained during conditioning of the electrode (2.3.1, 5.4.1) Perform a cyclic voltammetric test on the Pt RDE (5.4.2).

8 Glossary – Terms

Term/Abbreviation	Explanation	Description
Addition ratio	Stop criterion of the dilution titration	The addition ratio is a certain Q/Q(0) ratio at which the additions of standard solution or sample in the «dilution titration technique» are stopped. It has to be smaller than the evaluation ratio.
AE	Auxiliary electrode	E.g. 6.0343.100
Brightener	Additive type	Increases the stripping peak area
CPVS	Cyclic Pulse Voltammetric Stripping	Measuring mode
CVS	Cyclic Voltammetric Stripping	Measuring mode
DT	Dilution Titration	Calibration technique for additive types, which decrease the copper deposition
Evaluation ratio	Point of evaluation for the dilution titration	The Evaluation ratio is a certain Q/Q(0) ratio at which the volume of standard (for the calibration curve) or sample is evaluated in a dilution titration (DT). For many applications it is 0.5.
LAT	Linear Approximation Technique	Calibration technique for additive types which increase the copper deposition
Leveler	Additive type	Decreases the copper deposition like a suppressor, but is typically less strong
MLAT	Modified Linear Approximation Technique	Calibration technique for additive types which increase the copper deposition
Q	Charge (peak area, unit: Coulomb)	Integrated area of the stripping peak
RC	Response Curve	Calibration technique normally used for additive types, which decrease the copper deposition rate, especially leveler. Can also be used for increasing signals with small linear range or nonlinear calibration curve (brighteners by brightRC)
RDE	Rotating Disk Electrode	Working electrode type used in CVS
RE	Reference electrode	E.g. 6.0728.130 (with electrolyte vessel 6.1245.010)

Suppressor	Additive type	Decreases the stripping peak area
VMS	Virgin Makeup solution	Has the identical composition like a plating bath, but without any additives. E.g. acid copper plating bath: $CuSO_4 \cdot 5\ H_2O$ H_2SO_4 Cl^-
WE	Working electrode	E.g. 6.1204.610 (with driving axle 6.1204.510/6.1204.520)

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