Cyclic Voltammetric Stripping

Daily routine for best performance

Metrohm

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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 highest importance. They all contribute to keep the measuring system at best performance.

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. 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.

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 Dosing units

Figure 1 Dosing units included in standard fully automated Professional CVS setups

Actions

Prepare each dosing unit twice with the respective solution. Then rinse the electrodes and tubings in the measuring vessel well with deionized water.

Comments

- The preparation should be done with a waste beaker instead of the measuring vessel below the measuring head and using port 3 (see chapter 5.6: Dosino configuration) for waste. The electrodes and the dosing tips are rinsed thoroughly with deionized water after preparation to avoid carryover.

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

The dosing system, consisting of aspiration tube (port 2), dosing unit and dosing capillary (port 1), has to be filled homogeneously with the solution to be dosed.
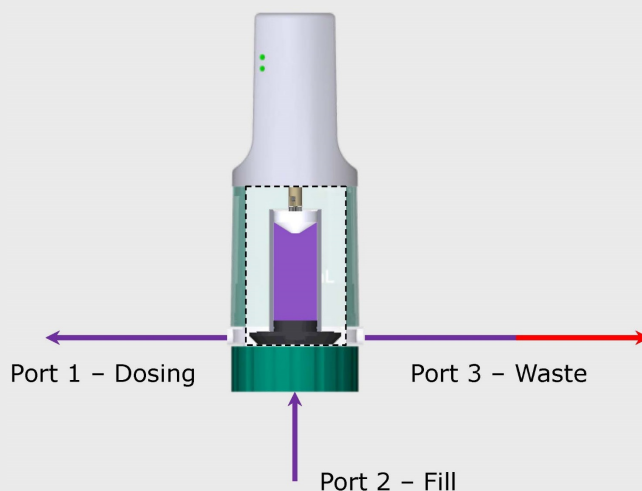
When the same dosing unit is used for different solutions with different compounds and concentrations the old solution has to be replaced in all parts of the dosing system by the new solution. Preparation means that all of these parts are subsequently filled with the new solution and the old solution 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 Bridge electrolyte vessel

Figure 2 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 as online version (*http://va-electrodes.metrohm.com*).

- If the maintenance-free reference electrode (6.0730.000/6.0730.100) is used no actions are necessary.

2.3   Working electrode – WE (Pt RDE)

Figure 3 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: Conditioning of the WE.

Comments

- In case of accidental metallization 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 is neither recommended nor necessary, this 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 as online version (*http://va-electrodes.metrohm.com*).

2.3.1 Conditioning of the WE

It is recommended to run the conditioning at least once per day after all electrodes are installed and the Dosinos 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 charge is smaller (or higher) than usual, it can be an indicator for Dosino leakage (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: Problems and possible solutions).

If conditioning takes too long because the charge 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 conditioned. Thereby it is immersed in VMS and cyclic voltammograms are recorded until the measured curves are stable. During this conditioning procedure Cu is deposited and removed from the working electrode, until the amount of deposited Cu on the working electrode is reproducible.

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

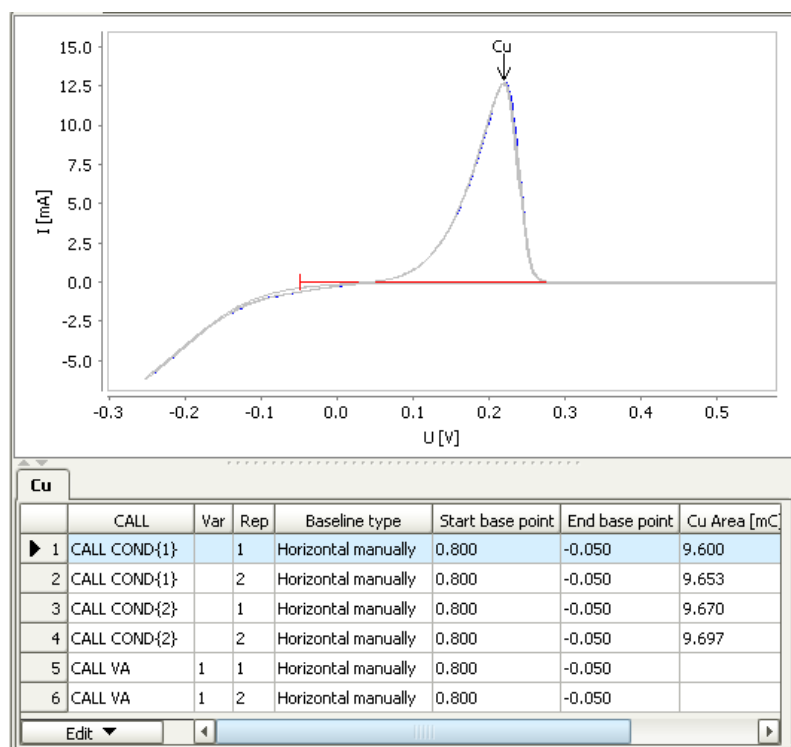|	CALL	Var	Rep	Baseline type	Start base point	End base point	Cu Area [mC]
▶ 1	CALL COND{1}		1	Horizontal manually	0.800	-0.050	9.600
2	CALL COND{1}		2	Horizontal manually	0.800	-0.050	9.653
3	CALL COND{2}		1	Horizontal manually	0.800	-0.050	9.670
4	CALL COND{2}		2	Horizontal manually	0.800	-0.050	9.697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

Figure 4 A well-conditioned working electrode gives highly reproducible measuring curves and stabilizes fast.

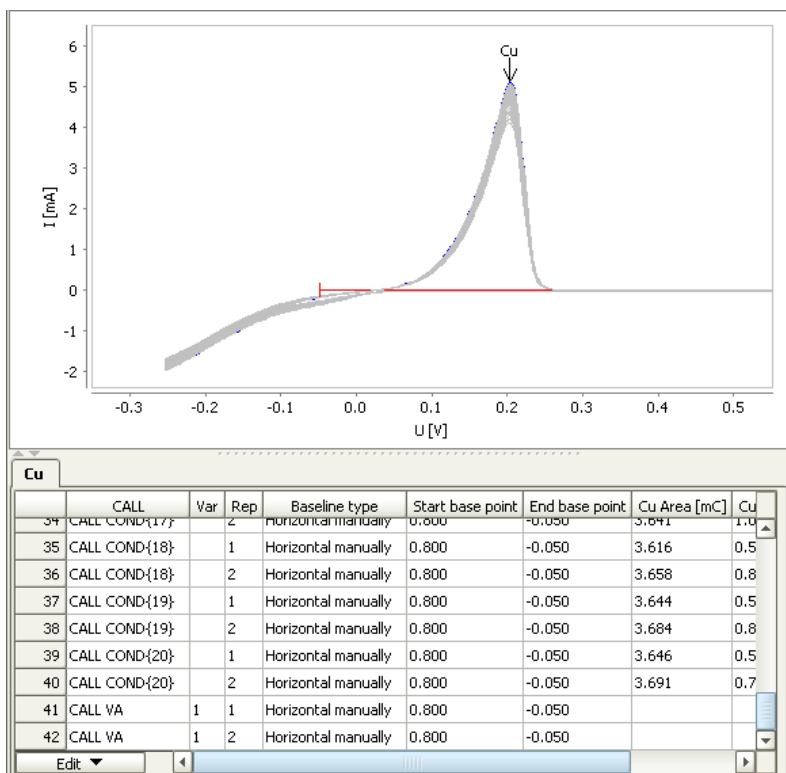|	CALL	Var	Rep	Baseline type	Start base point	End base point	Cu Area [mC]	Cu
34	CALL COND{17}		2	Horizontal manually	0.800	-0.050	3.641	1.0
35	CALL COND{18}		1	Horizontal manually	0.800	-0.050	3.616	0.5
36	CALL COND{18}		2	Horizontal manually	0.800	-0.050	3.658	0.8
37	CALL COND{19}		1	Horizontal manually	0.800	-0.050	3.644	0.5
38	CALL COND{19}		2	Horizontal manually	0.800	-0.050	3.684	0.8
39	CALL COND{20}		1	Horizontal manually	0.800	-0.050	3.646	0.5
40	CALL COND{20}		2	Horizontal manually	0.800	-0.050	3.691	0.7
41	CALL VA	1	1	Horizontal manually	0.800	-0.050		
42	CALL VA	1	2	Horizontal manually	0.800	-0.050		

Figure 5 A working electrode in bad condition gives less reproducible measuring curves and takes long for stabilization.

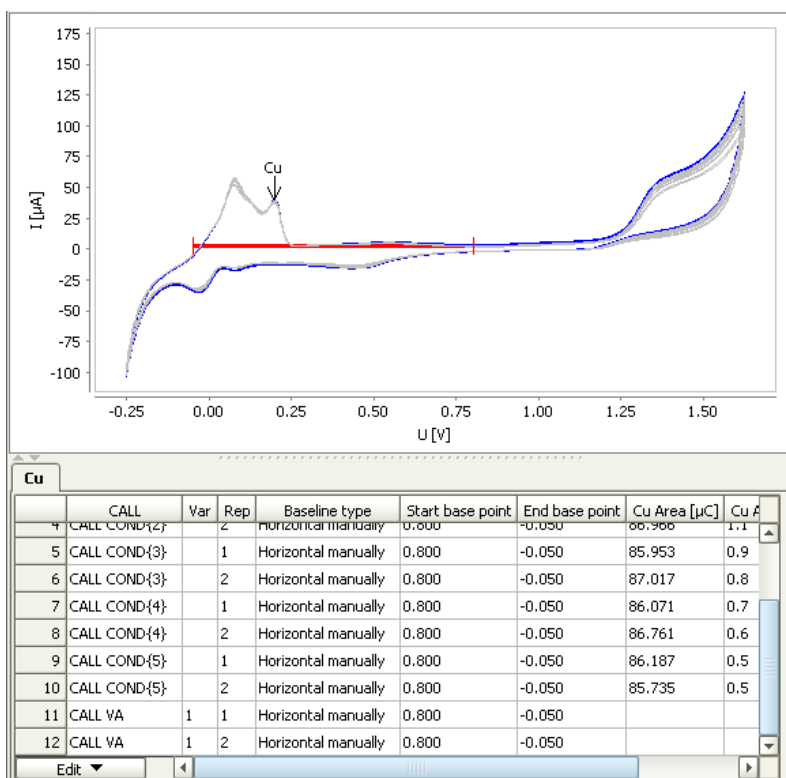|	CALL	Var	Rep	Baseline type	Start base point	End base point	Cu Area [µC]	Cu A
4	CALL COND{2}		2	Horizontal manually	0.800	-0.050	86.966	1.1
5	CALL COND{3}		1	Horizontal manually	0.800	-0.050	85.953	0.9
6	CALL COND{3}		2	Horizontal manually	0.800	-0.050	87.017	0.8
7	CALL COND{4}		1	Horizontal manually	0.800	-0.050	86.071	0.7
8	CALL COND{4}		2	Horizontal manually	0.800	-0.050	86.761	0.6
9	CALL COND{5}		1	Horizontal manually	0.800	-0.050	86.187	0.5
10	CALL COND{5}		2	Horizontal manually	0.800	-0.050	85.735	0.5
11	CALL VA	1	1	Horizontal manually	0.800	-0.050		
12	CALL VA	1	2	Horizontal manually	0.800	-0.050		

Figure 6 Example measuring curves for conditioning with contamination in the measuring vessel. If a stripping area is obtained, which is much smaller than usual, it can be an indicator for a contaminated measuring vessel or additives leaking from a dosing unit.

2.4   Auxiliary electrode – AE (Pt rod)

Figure 7 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 turned.
- In case of accidental metallization 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 a conditioning is carried out as described in chapter 2.3.1.

2.5   Check standard

Actions

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

Comments

- A check standard only consists of VMS and known concentrations of organic additives. It does not contain contaminations and breakdown products, which are present in a real sample.
- A check standard solution should be freshly prepared before the analysis. Especially brighteners are not stable for a longer period of time in dilute solutions.
- The validity of DT calibration curves, intercept 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 Dosing units

Actions

Prepare a dosing unit twice each time a new solution is used.

Comments

- When a dosing unit has to be filled with a different solution, e.g. a sample for the suppressor determination, different VMS or another additive concentrate the dosing unit has to be thoroughly rinsed with the new solution.
- If possible the preparation should be done without the measuring vessel below the measuring head and using port 3 for waste (see chapter 5.6: Dosino configuration). A beaker can be placed below the measuring head.
- Rinse electrodes and tubings thoroughly with deionized water after preparation to avoid carryover.

3.2 Temperature

Actions

Make sure to maintain a stable temperature throughout the working day and during determinations. Plating baths are often operated at elevated temperature, e.g. 50 °C. Thus 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 in the measuring vessel is used. This is the case in brightener determinations by LAT or MLAT or some leveler applications.
- For determinations using an external calibration curve (dilution titration, response curve) it is important that the temperature of the measuring solution during calibration does not significantly differ (<5 °C) form the temperature during determination.
- The measuring system should not be exposed to direct sunlight or placed below an air conditioner.
- Measuring vessels with a thermostat jacket can be used in combination with a water bath circulator to ensure a stable temperature.

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 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 the result is too high.

An example from the Metrohm technical poster «Temperature dependence of CVS determinations» (8.000.6027) 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.

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	99.3%	117.5%	125.7%
21.6	51.9	20	48.1	101.0%	113.4%	117.4%
26.6	63.9	15	36.1	101.5%	109.1%	109.9%
31.6	76.0	10	24.0	101.2%	100.9%	104.0%
36.6	88.0	5	12.0	99.4%	99.7%	99.4%

3.3   Solution addition

Actions

During a determination the electrodes must not be removed from the measuring solution. 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 for this purpose.

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 not to remove the electrodes from 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 Reference electrode – RE

Figure 8 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 to third day. This should be done at the end of a working day, when shutting down the instrument, to allow 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 as online version (*http://va-electrodes.metrohm.com*).

- If the maintenance-free reference electrode (6.0730.000/6.0730.100) is used, no actions are necessary.

4.2   Electrode storage

Actions

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, the electrodes have to be stored separately. The reference electrode assembled with the bridge electrolyte vessel is taken out of the measuring head and stored in a separate vessel (e.g. 6.2008.040 or 6.2743.057). The storage vessel has to be filled with deionized water or a solution of $c(KNO_3) = 1$ mol/L. The bridge electrolyte vessel should be filled with $c(KNO_3) = 1$ mol/L to the mark prior to storage. The working electrode and the auxiliary electrode can be stored dry.

Comments

- More important than the used storage solution for the reference electrode is that the reference electrode does not run dry. A storage vessel should 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 should be filled with deionized water after the last determination. The measuring vessel must not be emptied after a determination series because the reference electrode will dry out. The electrodes should furthermore not be stored in VMS or in the measuring solution.

- If the completely maintenance-free reference electrode (6.0730.000, 6.0730.100) is used, it is recommended to store it in $c(KCl) = 3$ mol/L, when the instrument is not in use. Under no circumstances may the reference electrode dry out as this will destroy it irreparably.

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 the latter 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 gel-filled reference electrodes (6.0728.040, 6.0728.140, 6.0730.000, 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 electrodes without gel filling (6.0728.030, 6.0728.130) dry out they 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 as online version (*http://va-electrodes.metrohm.com*).

4.3   Dosing units

Actions

Prepare the dosing units with deionized water at the end of the working day and leave the dosing units filled.

Comments

- Preparing the dosing units with deionized water prevents blockage due to crystallization.

- Do not empty the dosing units with the «Empty» function for storage overnight. Otherwise small residual amounts of solution will remain inside the cylinder, tubings and other compartments of the dosing unit. Then crystallization will occur more easily due to facilitated water evaporation.

- If the 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 and stored dry. See also chapter 5.3 Maintenance of dosing units - Procedure of this document and «Manual 807 Dosing Unit», 8.807.8002, chapter 3.7.

5 General tips

5.1 Solutions

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

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 a 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 and intercept values

Values which are used for multiple determinations, such as the calibration factor for a suppressor determination, intercept value for a brightener determination by LAT 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.

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 dosing units

Actions

Carry out a regular maintenance of the dosing units, e.g. every 2-4 weeks.

Comments

- Dosing units are very useful devices which allow highly precise automatic addition of solutions, even down to very small volumes. This high precision requires proper handling and taking care of the 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 dosing unit. To avoid this we recommend a regular maintenance of the dosing units.

- In this procedure they are disassembled completely and thoroughly cleaned. After complete drying the necessary parts are greased and the 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 dosing unit is emptied and disassembled completely (see also «Manual 807 Dosing Unit», 8.807.8002, chapter 3.7).
- 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, dosing piston and the housing are greased as indicated.

contact area to the housing
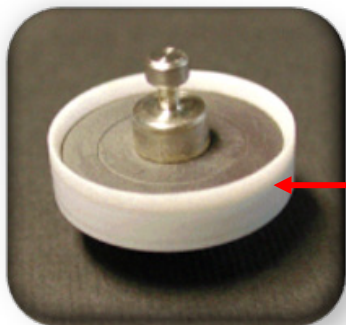
grease the contact area to the glass cylinder and remove excess grease with a soft tissue
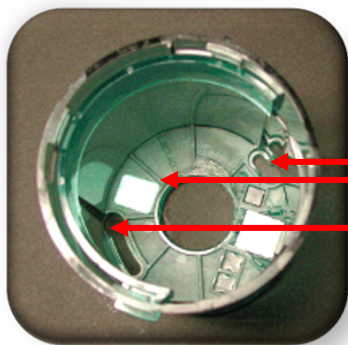
openings for the guide pins of the
800 Dosino and contact area to the
centering tube

- Those parts that are in contact with solution should only be greased slightly. The valve disk is greased slightly. Grease the valve disk and remove excess grease with a soft tissue. Excess grease would be introduced into the dosing channel and is eventually transported into the measuring vessel, which has to be avoided. When a finger is put on the valve disk no fingerprint should be visible.

- The dosing unit is reassembled (see also «Manual 807 Dosing Unit», 8.807.8002, chapter 3.8).

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 in a glass shaft (see Figure 3). 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 life time 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 charge 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 charge of electrode conditioning

As a measure for the performance of the electrode the charge obtained during conditioning should be monitored over time (see chapter 2.3.1 Conditioning of the WE). A variation in the charge in the range of ±20% is acceptable. If suddenly the area increases or decreases drastically, it can be an indication that the end of the lifetime has been reached.
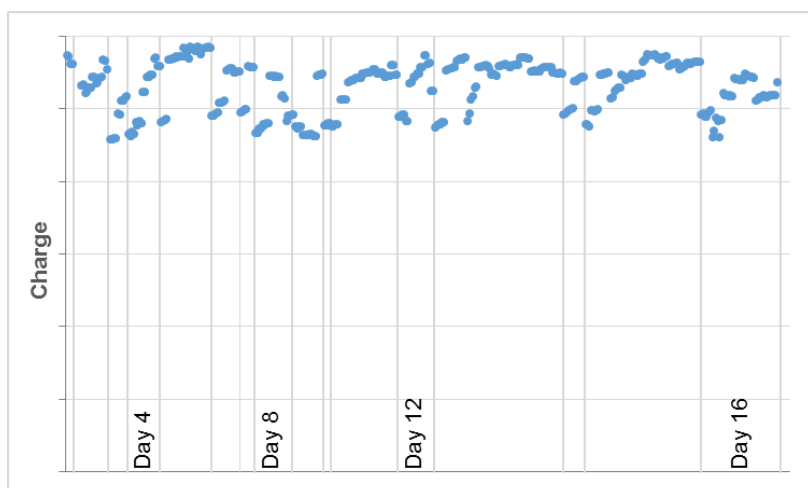
Figure 9 Example for the charge obtained during conditioning over a period of 16 days

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) or in the program data path of the 797 VA Computrace (Windows 7, 32 bit: %ProgramData%\Metrohm\797 VA Computrace\Method\CVS …). 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 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)
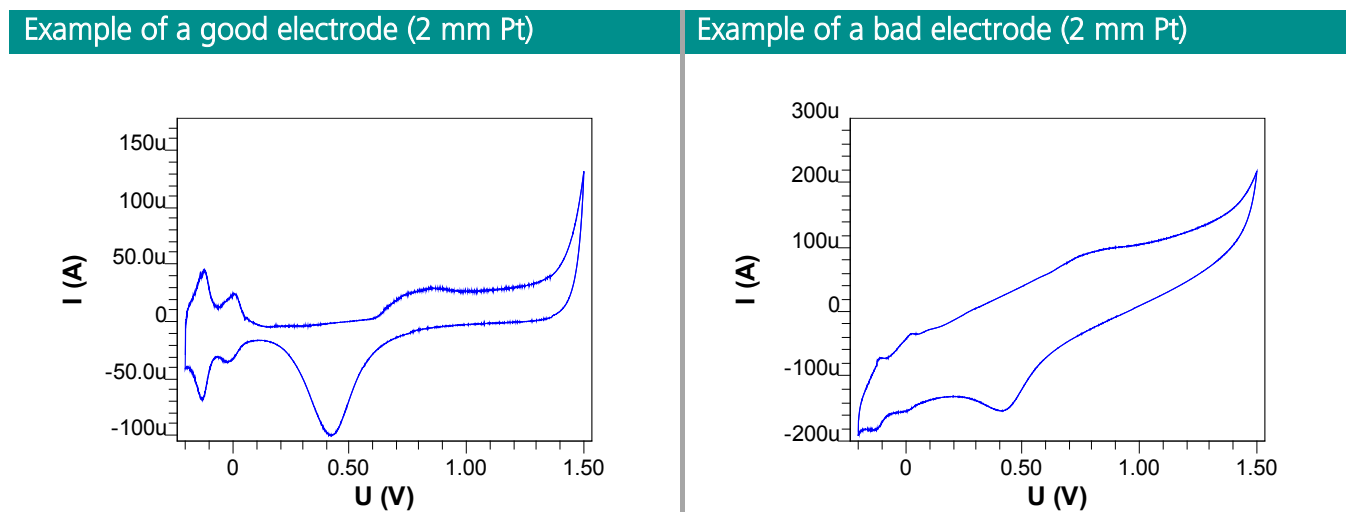
5.5 Driving axle

Figure 10 Driving axle 6.1204.510 (left) and 6.1204.520 (right) assembled with a 2 mm Pt RDE tip 6.1204.610, each

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 gap between the driving axle and the RDE, as discussed below.

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.

bottom of the driving axle

maximum fill level (approx. 1 cm below)
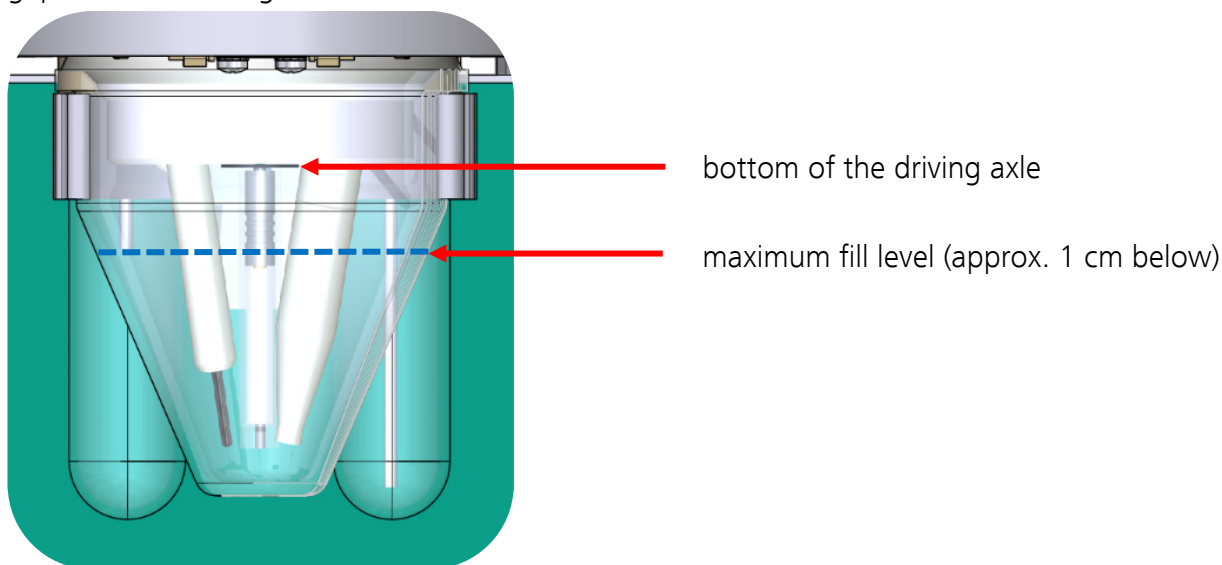
Figure 11 Maximum fill level in the measuring vessel

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. Nevertheless it should be avoided that measuring solution enters the gap between the titanium axle and the PTFE part. Otherwise 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. However, this does not have an influence on the application.

- 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   Dosino configuration

For dosing units it is recommended to use the following setup, where port 3 is used for the preparation.
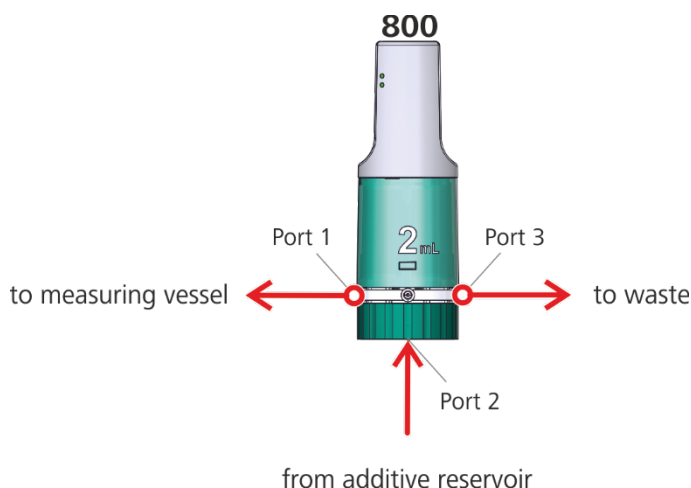
Figure 12 Dosino tubing configuration for preparation via port 3

Info: *What is the benefit of preparing a 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 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 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 13 Settings for preparation via port 3 in the **viva** software

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

Figure 14 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 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	
☐	RE is correctly filled?	Internal reference system filled with c(KCl)=3 mol/L. Outer electrolyte solution $c(KNO_3)$ = 1 mol/L	See chapter 4.1: Reference electrode – RE and 2.2: Bridge electrolyte vessel
☐	Has the charge (signal) of the VMS/intercept changed?	The charge has to be stable.	Check the WE, clean the WE. See chapter 6.2.1: General: • «Instable signal» • «Area of the stripping peak is higher than usual»
☐	Cyclic voltammetric test in H_2SO_4 is OK?	Example and criteria: see chapter 5.4.2: Cyclic voltammetric test of platinum RDEs.	Clean the WE. See chapter 6.2.1: General: • «Instable signal» • «Area of the stripping peak is higher than usual»
☐	VMS is clean?	Besides $CuSO_4$, H_2SO_4, Cl^- (HCl or NaCl), and sometimes Fe species no other substances shall 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 changes influence the CVS measurement.	Stabilize the temperature (e.g. with a measuring vessel with thermostat jacket).
☐	Check standard is freshly prepared?	The check standard should be freshly prepared prior to the determination. Organic additives decompose when stored in diluted solutions.	Prepare a new check standard solution.
☐	Recovery test in a check standard is OK?	• ±10 % of the expected value for suppressor	Check the used method, check the standard solution.

		• ±20 % of the expected value for brightener or leveler
☐ Concentrates of brightener, suppressor and leveler are 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 fluctuation may occur with different additive batches.	
☐ 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.
☐ Recovery test in a spiked plating bath sample is 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 solutions.

6.2.1 General

Problem	Possible cause	Possible solution
WE surface is scratched.	Bad storage.	• 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.	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.	Cristallization (predominantly $CuSO_4$)	• Replace the driving axle. • Do not overfill the measuring vessel.

	or abrasion particles around the titanium axle.	• 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.
	Dosino leakage	• Tighten the connection of the dosing capillaries with the dedicated wrench (6.2739.000). • Clean the dosing unit as described in chapter 5.3: Maintenance of dosing units. • Exchange the dosing unit.
	Temperature.	• Use of a measuring vessel with thermostat jacket and a water bath circulator.
	Contaminated VMS.	• Use clean glassware for preparation. • Use correct concentrations. • Reagents quality at least analytical grade.
	Wrong (bad) RE filling or insufficient time for equilibration of the reference potential.	• See chapter 4.1: Reference electrode – RE.
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.
	Contaminated VMS.	• Use clean glassware for preparation. • Reagents quality at least analytical grade.
	Wrong (bad) RE filling.	• See chapter 4.1: Reference electrode – RE.
	Temperature.	• Use of 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»*. • 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: Reference electrode – RE).

Copper layer on the AE.	Wrong voltammetric parameters or manual stop of the measurement.	• Check the voltammetric parameters. • Do not use the «Standby potential»*. • Dip auxiliary electrode in $w(HNO_3) = 65\%$ for a few seconds to remove the Cu.
	Auxiliary electrode cable wrongly connected.	• Connect cable correctly.
	Wrong filling or air bubble in the RE.	• Fill RE correctly (see chapter 4.1: Reference electrode – RE).
Dosino is blocked. • No solution is dosed • Cylinder does not turn	Precipitation, crystallization in the cylinder or tubings.	• Disassemble the 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 dosing unit, let it dry and reassemble it. • To prevent crystallization fill the dosing units with H_2O, if they are not in use. • If the dosing units are not used for a longer time they should be cleaned and stored dry. • If crystallization has occurred in the tubings try to immerse it in dionized water until the crystals have dissolved or replace the tubings.
	Sample contains particles.	• Remove particles or use a tubing with bigger inner diameter.
	Valve disk and distributor disk stick together.	• Remove housing and centering tube of the dosing unit. • Place the dosing unit with the dosing cylinder in 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 one another. • Clean the dosing unit, let it dry and reassemble it.
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: Reference electrode – RE).
Peak is not evaluated.	Wrong peak position defined.	• Adapt the peak position under «Sub-stances»*.

	Reverse peak is not activated.	• The peak has to be evaluated in the anodic sweep*.

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

Hydrogen formation.	Voltammetric parameters.	• Optimization of the parameters*.
	Air bubble in the RE.	• Check for proper filling of the RE (see chapter 2.2: Bridge electrolyte vessel or 4.1: Reference electrode – RE).

*Part of method development.

6.2.2   DT – Dilution Titration

Problem	Possible cause	Possible solution
Insufficient number of points on the calibration / determination curve.	Too high addition volume.	• Decrease addition volume*. • Increase V_{VMS}*. • Use of the smartDT technique for dynamic addition volumes (Metrohm Application Bulletin 422)*.
Too many points on the calibration / determination curve.	Too small addition volume.	• Increase addition volume*. • Decrease V_{VMS}*. • Use of the smartDT technique for dynamic addition volumes (Metrohm Application Bulletin 422)*.
Error after 20 additions (only 797 VA Computrace) or more than 20 additions (884 Professional VA).	No sample or standard solution is added	• Check if the dosing unit is filled. • Prepare the dosing unit with the respective solution twice.
	Too small addition volume.	• Increase addition volume*.
	Too flat DT curve.	• Increase first vertex potential (more positive)*.
Evaluation ratio is already reached after addition of 10 µL.	Suppressor is too concentrated.	• Prepare a standard solution with smaller suppressor concentration*. • Dilute sample in VMS*. • Increase V_{VMS}*.
Cannot reach the evaluation ratio.	Too flat DT curve.	• Increase first vertex potential (more positive)*.
	To small addition volume.	• Increase addition volume*. • Decrease V_{VMS}*.

	Addition ratio is set too small.	• Set the addition ratio to «evaluation ratio – 0.01»*.
Conditioning cycles do not reach relative standard deviation of 0.5%.	WE is in bad condition.	• See chapter 2.3.1: Conditioning of the WE
	Wrong (bad) RE filling.	• See chapter 4.1: Reference electrode – RE
	Contaminated measuring vessel.	• Check for leakage from the dosing units. • Rinse the measuring vessel thoroughly with deionized water.

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 (only 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 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 a normal behavior. Successful determination of recoveries in spiked samples validates the chosen method.

*Part of method development.

6.2.3 MLAT / LAT – (Modified) Linear Approximation Technique

Problem	Possible cause	Possible solution
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.
	Electrodes are not conditioned.	• Perform conditioning cycles (see chapter 2.3.1: Conditioning of the WE).

Bad cyclic voltammogram reproducibility.	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 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.	• Optimization of the parameters*.
	Manual standard additions.	• Use a Dosino for highly reproducible additions.
	Electrodes in bad condition.	• See chapter 2.3.1: Conditioning of the WE • See chapter 4.1: Reference electrode – RE
The system performs endless cycles to obtain the intercept value.	% Rel. std. dev. for the initial electrode conditioning is too low (cannot be reached).	• Increase the value to 2%*.
	WE electrode is contaminated.	• Clean WE with ethanol and/or acetone. • Soak the electrode for 60 min in c(NaOH) = 1 mol/L. • Use a new electrode.

*Part of method development.

6.2.4   RC – Response Curve

Problem	Possible cause	Possible solution
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
Can I run CPVS in iron free solutions?	Yes.
Can I run a brightener determination by CVS in iron containing solutions (> 1 g/L Fe total)?	Most certainly not, use CPVS.
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 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 set 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 797 VA Computrace software one 846 Dosing Interface can be operated, with the 884 Professional VA and viva it is possible to control multiple.
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 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 some hours. It is not recommended to store them in VMS or used 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 charge 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 (in presence of suppressor).
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	Decreasing copper deposition as a suppressor, but less strong.
MLAT	Modified Linear Approximation Technique	Calibration technique for additive types which increase the copper deposition.
Q	Charge (unit: Coulomb)	Integrated area of the stripping peak.
RC	Response Curve	Calibration technique for additive types which decrease the copper deposition.
RDE	Rotating Disk Electrode	Working electrode type used in CVS.
RE	Reference electrode	E.g. 6.0728.130 + 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 Chloride
WE	Working electrode	E.g. 6.1204.510 + 6.1204.610

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