First aid for polarography and voltammetry

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ion analysis
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Contents

1 Electrodes

The electrodes are described in detail in *section 3.4 - 3.7* of the 693/694 Instructions for Use.

The electrode test is described in *section 4.1.4*.

The stand electronics can be tested with the help of the dummy cell (*section 7.6*).

1.1 RE: "Reference Electrode Faulty"

- Check whether the reference electrode (RE) is connected to the RE cable.
- Top up internal electrolyte (KCl 3 mol/L, if nothing else is specified). Press the wadding in the reference system together with an Eppendorf tip and allow the air to escape.
- Top up external electrolyte (KCl 3 mol/L, if nothing else is specified).
- Check RE for air bubbles. If air bubbles are present shake the electrode like a clinical thermometer.
- It takes approx. 20 min for a new electrode (inner and outer diaphragm) to be come wet (e.g. during installation).
- The mercury at the MME flows out in a thin stream or the drops change colour: the RE should be refilled.
- Check whether the diaphragm is blocked.

1.2 MME: "Working Electrode Faulty"

The electrode does not drop, drops irregularly or continually or the capillary cannot be filled.

- Check whether the MME is connected to the WE cable.
- Check whether there is still some mercury in the electrode. Top up with mercury if necessary.
- Do not fill the MME with more than 6 mL mercury. It is very important that Hg flows around the needle.
- Check mercury quality and filter the mercury if this is necessary.
- Change capillary.
- Protect the new, packed capillary against moisture.
- Insert the capillary immediately after unpacking.
- Check whether there has been a break in contact between the needle and the capillary.
- Clean and adjust the MME needle, exchange it if necessary.
- Check inert gas pressure (1 bar).
- Rub the electrode body dry, clean with distilled water or dilute acid and dry with a lint-free cloth.
- Check whether all internal components are present (parts 94, 95, 96 of the MME, see Instr. for Use page 3-13).
- Check RE.
- Is electrolyte present in the measuring vessel? If none is present a few drops of KCl 3 mol/L can be added.
- Check tapping mechanism on stand.

Detailed information about the MME can be found in *section 3.4* of the 693/694 Instructions for Use.

1.3 RDE "Rotating Disc Electrode“

- Check whether the electrode tip is firmly screwed on to the drive shaft.
- Check whether the RDE is connected to the WE cable.
- Check whether there is electric contact between the RDE and the drive shaft (with the help of an ohmmeter).
- Is the electrode surface clean?
- If necessary polish or clean the electrode; if necessary "strip-off" ultra-trace graphite electrode.

1.4 AE: "Auxiliary Electrode faulty"

- This electrode is also known as the "counter electrode".
- Check whether the auxiliary electrode is correctly connected to the AE cable.
- This electrode is very robust and seldom defective.

1.5 Inert gas

- Check gas pressure (1 bar = 14 psi). The pressure should be extremely constant. N_2 is recommended.
- The purity of the gas should be between 99.996 % and 99.999%.

2 Liquids (general)

The purity of the reagents plays an important role in determining the results. Extremely pure chemicals should be used for determining lower concentrations.

2.1 Electrolytes

- The pH during a determination plays an important role (e.g. for Zn, Cd, Pb, Cu it should be approx. 4.5). For information and parameters for analyses see the Application Bulletins.
- The electrolyte must be sufficiently conductive and concentrated.
- The purity of the electrolytes and the cleanliness of the reagent bottles is very important.
- The electrolyte volume depends on the type of electrode used.
- The working life of the electrolytes is limited, particularly for organic additives (buffer substances, complex formers). It may be necessary to make up fresh solutions every day.

2.2 Standard solutions

- The standard solutions should be made acidic (approx. pH=1…2) and stored in plastic bottles.
- Diluted standard solutions (ppb range) are very unstable and must be freshly made. They must also be made sufficiently acidic.
- The concentration of the standard solutions must be arranged so that a volume between 20 and 500 µL is to be added.
- Standard additions are recommended. The peak height after the last addition should be 2…5 times higher than the sample peak.
- 1000 ppm solutions are often used as stock solutions. They are stable over long periods of time. Dilutions are to be made with dilute acids.

2.3 Samples

- The amount of sample depends on the concentration of the element to be determined.
- If the sample matrix is known, a better assessment of the analysis can be made (organic components?).
- A digestion must be carried out on contaminated samples and on samples where contamination is suspected.
- A lot of errors are made during sampling and when storing the sample. Caution and a critical approach are required.
- The sample should have a good solubility in the electrolyte and be mixable with it.

3 Problems with the analysis

3.1 Dropping electrode (DME/SMDE)

3.1.1 Base line

Low background current or unstable base line

- The electrode drops irregularly: check MME. Adjust needle and capillary.
- Check electrolyte concentration and pH of the solution.
- Check initial potential and final potential of the analysis.
- If the ion concentration in the solution is too high: dilute the electrolyte.
- If the concentration to be determined is considerably lower than anticipated: increase sample volume or change mode (e.g. HMDE).
- Has the sample been degassed? Degassing with nitrogen for at least 5 min is recommended, for alkaline solutions approx. 10 min is recommended.
- Check tapping mechanism on stand.
- Is the gas pressure correctly set (1 bar)?
- Is the reference electrode sufficiently full (inside and outside)?

3.1.2 Curves

Curves look like a "starry night"

- The electrode drops irregularly: check MME.
- Check contact between needle and capillary.
- Have stirring or degassing been switched off during the measurement?
- If the electrode drops much too quickly: reduce “sweep rate“ in program.
- Check tapping mechanism on stand.

Standard addition curves are not reproducible

- Check program in the instrument (stirring time, etc.).
- Check MME, change capillary if necessary.
- The pipetting process was not correct: was the pipetting unit used properly?
- Repeat the analysis again or try out automatic standard addition with Dosimat or Dosino.
- Pipetting the standard solutions must be carried out by one and the same person or with the same instrument or the same pipette.
- Check and test pipetting process. When were the pipettes last calibrated (GLP)?
- Organic components interfere with the analysis: carry out a UV-digestion or similar sample preparation.
- Are the calibration solutions too old?
- Would a calibration curve be more suitable?

3.1.3 Peak displacement

- Check and adjust the pH of the solution.
- Check electrolyte composition and correct if necessary.
- Carry out a standard addition to check whether the correct peak has been evaluated.
- Organic components interfere with the analysis: carry out a UV-digestion or similar sample preparation.
- Enter a new half-wave potential in the instrument and recalculate the results.
- Check RE.

3.1.4 No peak found

- The peak is only displaced: adjust the half-wave potential and recalculate the results.
- The sample concentration is too low: increase the sample volume or the amount of sample.
- The concentration of the ion to be determined is too low: use HMDE (inverse voltammetry) instead of DME or SMDE.
- Are the initial and final potentials correct ?

3.1.5 Peak is in the highest µA range

- The concentration of the ion to be determined is too high: reduce the sample volume and carry out the analysis again.

3.1.6 Double peak

- Check MME.
- Organic components interfere with the analysis: carry out a UV-digestion or other suitable sample preparation.
- If a second element is present at the same potential: add this element to the sample and carry out the analysis again. If the second peak has become higher then the second element is present.
- Has any substance been precipitated out in the measuring vessel (e.g. lead perchlorate standard with KCl as electrolyte)?
- Try out eluents with different compositions (addition of complex formers).
- Check analysis parameters.

3.1.7 Standard addition peaks displaced

- Standard solutions have been made too acidic.
- Buffering capacity of the electrolyte is not sufficient: increase electrolyte volume.

3.1.8 No addition

- Has the correct standard solution been used or is the concentration of the solution too low: increase the volume of the standard addition or use a higher concentration or reduce the sample amount accordingly.
- If organic components are present: carry out a UV-digestion or similar.
- Could it be possible that the peak is not the peak which is being looked for?
- Concentration of the analyte is too high: dilute.

3.2 HMDE

3.2.1 Base line

Low background current or unstable base line

- The electrode drops or the drops do not remain hanging: check MME. Change capillary if necessary.
- Has the sample been properly degassed?
- Check the concentration of the electrolyte and the pH of the solution.
- Check the initial potential and final potential of the analysis.
- If the ion concentration in the solution is too high: dilute the electrolyte.
- If the concentration to be determined is considerably higher than expected: reduce sample volume or change the mode (e.g. from HMDE to SMDE or DME).
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

3.2.2 Curves

Curves look like a "starry night"

- Check MME. Check for break in contact between needle and capillary.
- If the electrode surface is overcharged: check deposition potential and time.
- No drops at the capillary: change the capillary.
- Have stirring and degassing been switched off during the measurement?
- Check tapping mechanism on stand.
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

Standard addition curves are not reproducible or non-linear (see section 3.1.2).

- The linearity at the HMDE is naturally not as good as with the DME. The linear range is in general no larger than 1 - 2 decimal powers.

3.2.3 Peak displacement

- Check and adjust the pH of the solution.
- Check electrolyte composition and correct if necessary.
- Organic components interfere with the analysis: carry out a UV-digestion or equivalent sample preparation.
- Carry out a standard addition to check if the correct peak is present.
- Enter a new half-wave potential in the instrument and recalculate the results.
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

3.2.4 No peak found

- The peak is only displaced: adjust the half-wave potential and recalculate.
- The sample concentration is too small: increase the sample volume.
- Has the complex former been forgotten? (adsorptive voltammetry).
- The deposition time under "MEAS" in "Op. Sequence" in the inverse voltammetry is too short: increase the time.
- No Hg drops at the capillary: check MME.
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.
- Are organic components present? Carry out a UV-digestion or similar.

3.2.5 Peak is in the highest µA range

- The sample volume is too large: reduce the volume. Carry out the analysis again.
- The enrichment period (for HMDE) is too long: Reduce the time.
- If necessary use a SMDE or DME electrode instead of HMDE.

3.2.6 Double peak

- Check MME.
- Organic components interfere with the analysis? Carry out a UV-digestion or other suitable sample preparation.
- If a second element is present at the same potential: add this element to the sample and carry out the analysis again. If the second peak has become higher then the second element is present.
- Might it be possible to selectively mask this second element with a complex former?
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.
- For Cu: work without chlorides in the electrolyte or increase the chloride concentration massively.

3.2.7 Standard addition peaks displaced

If HMDE is used potential displacements of more than 20…30 mV are often normal and have to be accepted; particularly in adsorption voltammetry.

- Standard solutions have been made too acidic.
- Buffering capacity of the electrolyte is not sufficient: increase electrolyte volume.

3.2.8 No addition

- Has the correct standard solution been used or is the concentration of the solution too low: increase the volume of the standard addition or use a higher concentration or reduce the sample amount accordingly.
- If organic components are present: carry out a UV-digestion or similar.
- Concentration of the analyte is too high: dilute.
- Addition solution with metal complexing solution (time reaction).

3.3 RDE

There are various different types of RDE:

- **GC**: (Glassy carbon electrode), can be polished with aluminium oxide, glossy surface.
- **Au**: (Gold) can be polished with aluminium oxide, glossy surface.
- **UT**: (Ultra-trace graphite electrode), can be scraped and polished with aluminium oxide, matt surface.
- **Ag**: (Silver), can be polished with aluminium oxide, glossy surface.
- **Pt**: (Platinum), looks very similar to Ag, glossy surface, slightly more matt than Ag.

3.3.1 Base line

Low background current or unstable base line

- The electrode surface must be repolished.
- Has the correct RDE been used?
- Exchange RDE.
- Check concentration of electrolyte and pH of the solution.
- Has the electrode been conditioned (e.g. with "CONDC") ?
- Check initial and final potential of the analysis.
- If the ion concentration in the solution is too high: dilute the electrolyte.
- If the concentration to be determined is considerably higher than expected: reduce sample volume.
- The background current is normally higher if RDE is used in place of MME.
- A background current of several 100 nA is entirely possible.
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

3.3.2 Curves

The standard addition curves are not reproducible (see section 3.1.2).

- Check RDE.

3.3.3 Peak displacement

- Check and adjust pH of the solution.
- Check electrolyte composition and correct if necessary.
- Organic components interfere with the analysis: carry out a UV-digestion or an equivalent sample preparation.
- Enter a new half-wave potential in the instrument and recalculate the results.
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

3.3.4 No peak found

- The peak is only displaced: adjust the half-wave potential and recalculate.
- The background current is too high: repolish the electrode.
- The sample concentration is too low: increase sample volume.
- The deposition time under "MEAS" in "Op. Sequence" in the inverse voltammetry is too short: increase the time.
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

3.3.5 Peak is in the highest µA range

- The sample volume is too large: reduce the volume. Carry out the analysis again.
- The background current is too high: repolish the electrode.
- The deposition time is too long: reduce the time.
- Is the deposition potential correct?

3.3.6 Double peak

- Check RDE and polish if necessary.
- If organic components are present: carry out a UV-digestion or similar.
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less (see section 3.2.6).

3.3.7 Standard addition peaks displaced

See *section 3.2.7*.

- Standard solutions have been made too acidic.
- Buffering capacity of the electrolyte is not sufficient: increase electrolyte volume.
- Electrode surface overcharged: reduce sample volume.

3.3.8 No addition

- Has the correct standard solution been used or is the concentration of the solution too low: increase the volume of the standard addition or use a higher concentration or reduce the sample amount accordingly.
- If organic components are present: carry out a UV-digestion or similar.
- Concentration of the analyte too high: dilute.
- Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

4 Results

The analyses do not supply the required results.

4.1 Instrument operation

- Has the instrument evaluated the correct peaks?
- Are the instrument data correct (concentrations of solutions)?
- Standard addition volumes? Sample amounts? Total volume in vessel? etc.
- ***Example 1:*** 693 VA-Processor

  1.02 g sample is dissolved in 50 mL. From this solution 10 mL are pipetted into the measuring vessel and 5 mL electrolyte are added to it.

  The entries are:

`DOS>M`	5 mL	
`S0` (Monitoring page)		1.02 g (`S2`=1)
`V.fraction`	10 mL	
`V.total`	50 mL	

  The instrument calculates directly back to the sample and gives the concentration in the sample as "Final results". "`V.fraction`" and "`V.total`" are used as "aliquot" data.

- ***Example 2:*** 693 VA-Processor

  1.50 mL sample were pipetted into the measuring vessel and 10 mL electrolyte added to it.

  The entries are:

`DOS>M`	10 mL	
`S0` (Monitoring page)		1.5 mL
`V.fraction`	empty	
`V.total`	empty	

  The instrument then calculates directly back to the sample.

4.2 Blank values, contamination, carrying out the analysis

Results too high

- Have the dilutions been made correctly?
- Have contamination risks been excluded?
- Contamination risks are very high at low concentrations: measuring vessels should be conditioned with dilute HNO_3 solution.
- Are the chemicals pure enough? "Suprapur" grade reagents should be used at low concentrations.
- Very high concentrations were measured in the previous analysis: electrodes and measuring vessels must be carefully cleaned and conditioned (memory effects).
- Has the standard addition been carried out properly? Was the volume set correctly on the pipetting unit?

Results too low

- Concentration too high? HMDE overloaded, use DME/SMDE instead ?
- Buffer not correct ? Make up new one if necessary.
- Addition ratio too low?
- Addition ratio too high?