

# Polarographie

## Set Up:

1. Start the computer and the Polarograph (Turn on button on the rear left side)
2. Open the vent for the nitrogen left to the manometer and set it to 1 bar
3. Fill right wash flask with  $\text{H}_2\text{O}_{\text{dest.}}$  2cm if empty (to saturate the nitrogen with humidity)
4. Start the program „797 VA Computrace“ (On the Desktop) and click „Start measurements“
5. The assistant will explain the device and set up the reference electrode

## Waste Deposition:

1. Quicksilver has to be deposited in the appropriate flask
2. Due to practical and safety regulations the quicksilver should be decanted over a beaker before deposition
3. Inform the assistant in case of quicksilver containment

## Assignment:

- 1. Become acquainted with different measurement methods (Theoretic principles have to be known)**
- 2. Determination of Ascorbic Acid in a matrix**
- 3. Writing the protocol with discussion of the methods and discussion of results.**

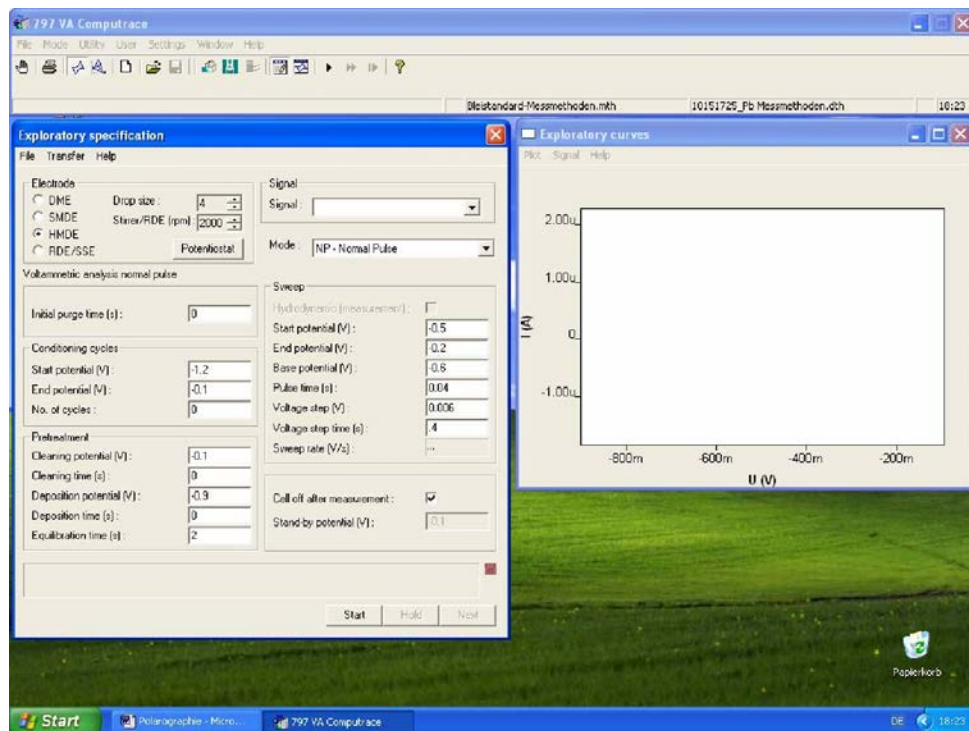
## Inventory:

797 VA Computrace Polarograph  
Working electrode, auxiliary electrode and reference electrode  
(Ag/AgCl) saturated KCl  
Ion Standard (1g/l Pb)  
100  $\mu\text{l}$  Gilson

## A. Introduction

### 1. Measuring Programm and Modes

- Click Mode/„Exploratory“ (to measure unknown substances); „Determination“ is for known substances
- Click the Button „Exploratory specifications“ (Icon with pencil) and „Monitor“ (Icon tot he right); the settings fort he different modes can be obtained from the protocoll below. You can follow the measurement in the Monitor window.



### 2. Laden der Elektrodenart:

- „DME“ (dropping), „SMDE“ (static) or „HMDE“ (hanging)
- Explanenation in Addendum
- Drop size: „4“
- Stirrer : „2000 rpm“

### 3. Vorlegen der Probe

- Collect Hg Waste; Clean required glass instruments
- Preparing Pb Standard:  
**20 ml H<sub>2</sub>O<sub>dest.</sub> (approx.) + 0.5 ml 3M KCl + 300 µl Pb-Std. (1 g/l)**

## B. Measuring Methods

- Follow the instructions and perform the experiments (theoretical background is described in the addendum)
- Set up parameters in the „**Exploratory specifications**” window
- Start the measurements via the „Start“ Button. Results will be plotted and saved as .sig files.  
(Attention: Remember the file name if you want to load it again)
- Load files via the menu „Files Files/Load signal“
- „Stop“ allow you to cancel the measurement
- „Purge Time“ (to remove oxygen) has to be set to 60s for the first measurement then to 5s.
- The results should be copied in a word file (right mouse/copy to clipboard)
- Use (.) as decimal separator.

## I. Gleichstrompolarographie mit unterschiedlichen Elektroden

- **PARAMETER:**  
Start Pot. (-0.6V), End Pot. (-0.1V), Base Pot. (-0.6), Pulse Time (0.04s), Voltage Step (0.004V), Voltage Step Time (0.4s), Deposition Time (0s)

Versuch	Mode	Elektrode
1	NP	DME
2	NP	SMDE
3	NP	HMDE

- **Protocol:**  
Interpret the results in terms of selectivity and base line drift  
Protocol the results  
(Plot/Copy to Clipboard).  
Why do you have to add KCl?  
Why an increasing current is observed before the Pb-Reduction?  
Which information can you get from  $E_{1/2}$ ?

## II. Differentialpulsolarographie

- **PARAMETER:**  
Start Pot. (-0.6V), End Pot. (-0.2V), Pulse Amplitude (0.02V), Pulse Time (0.04s), Voltage Step (0.004V), Voltage Step Time (0.4s)

Versuch	Mode	Elektrode
4	DP	DME
5	DP	HMDE

- **Protocol:**  
Which current do you measure (Faraday or capacity)?  
Protocol the results (Plot/Copy to Clipboard).  
Interpret the results in terms of selectivity and base line drift

### III. Wechselstrompolarographie

- **PARAMETER:**  
Start Pot. (-0.6V), End Pot. (-0.2V), Voltage Step (0.004V), Voltage Step Time (0.6s), Amplitude (0.01Vrms), Modulation Time (0.05s), Frequency (50Hz), Phase sensitive (0°)

Versuch	Mode	Elektrode
6	AC	DME

- **Protocol:**  
Which current do you measure (Faraday or capacity)?  
Protocol the results (Plot/Copy to Clipboard).  
Interpret the results in terms of selectivity and base line drift

### IV. Cyclovoltammetrie

- **PARAMETER:**  
Start Pot. (-0.6V), First Vertex Pot. (-0.1V), Second Vertex Pot. (-0.6V), Voltage Step (0.004V), No. of Sweeps (1), Save last (1) sweeps

Versuch	Mode	Elektrode	Sweep Rate (s)
7	CV	HDME	0.2
8	CV	HDME	0.1
9	CV	HDME	0.05
10	CV	HDME	0.01
11	CV	HDME	0.005

- **Protocol:**  
Interpret the results in terms of sensitivity and peak maxima.  
Protocol the results (Plot/Copy to Clipboard).  
Interpret the reaction in terms of reversibility.  
Why is  $E_{1/2}$  changing with higher sweep rates?

## V. Inversvoltammetrie

- **Prepare a fresh sample in a cleaned titration vessel (Attention: Also clean the Electrodes):**  
20 ml H<sub>2</sub>O<sub>dest.</sub> + 0.5 ml 3M KCl + 30 µl Pb Standard (1g/l)
- **PARAMETER:**  
Start Pot. (-0.6V), End Pot. (-0.2V), Pulse Amplitude (0.05V), Pulse Time (0.04s), Voltage Step (0.004V), Voltage Step Time (0.4s), Deposition Potential (-0.9V)

Versuch	Mode	Elektrode	Deposition Time (s)
12	DP	HDME	0
13	DP	HDME	10
14	DP	HDME	100

- **Protocol:**  
Interpret the results in terms of sensitivity and peak maxima.  
Protocol the results (Plot/Copy to Clipboard).

## C. Optional: Pb in tap water

1. Use the Inversvoltammetrie to determine the Pb in tap water (Deposition Time **30s**, Parameters **-0.6/-0.1V**, **Addition of internal standard (Pb Standard 1:50; 20µl, add 3 times min. Evaluation see ascorbic acid)**).
2. Determine the concentration of PB in 1L of Tap water (see Ascorbic Acid)
3. Determine the Detection limit of your method if there is no Pb in tap water
4. You can take your own tap water from home to test it.

## D. Determination of Ascorbic Acid

The determination depends on the oxidation of ascorbic acid to dehydroascorbic acid:



The redox potential is depended of the pH Value:

$$E_{1/2} \propto \frac{0,059}{2} V \log(C_{H_3O^+})$$

This phenomena leads to peak broadening. To solve this problem acetate buffer with pH= 4,6 is used in the experiment.

**Sample:** vitamin C fizzy tablet

### Experiment:

1. Solve tablet in 250ml H<sub>2</sub>O<sub>dest.</sub> And degas the solution for 10min in an ultrasonic bath.
2. 20 ml acetat buffer; no KCl necessary
3. Add 100µl sample
4. Use DPP-Method: DME, Start Pot. -0,2V, End Pot +0,2V
5. Quantitative evaluation via standard addition method. Add 20µl of the 1g/l ascorbic acid standard. Minima 4 Times.

### Evaluation:

1. Calculation of the concentration via peak area and peak height.
2. For evaluation  
Choose the corresponding signal in „Exploratory specifications“. It will turn blue.  
In „Exploratory curves“ choose the menu „Signal“ and click „Peak Search“.  
A new window appears  
Klick „Options“ „Manual“  
Choose in „Baseline“ the beginning and the end of the base line  
(Settings will not be saved, so it is useful to write them down on paper)  
Height and Area will be shown. Write them down in a table (Excel)  
(y.yy-00x means y,yy\*10<sup>-x</sup>)
3. Evaluation via standard addition method (Excel)
4. Calculate quantity of Vitamin C in mg/tablet

## **E. To finish the experiment**

1. Close Nitrogen
2. Clean titration vessel and fill it with  $\text{H}_2\text{O}_{\text{dest.}}$
3. Reference Electrode has to be put in saturated KCl solution (3M KCl)
4. Turn of the device and the computer.
5. Tell your supervisor you are leaving
6. On the next Monday the protocol have to be finished.