Task 4 **Analytical chemistry lab. I**

COULOMETRIC DETERMINATION OF ASCORBIC ACID

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Introduction

Coulometry is an electroanalytic method where the determined compound is completely converted into another form in a different oxidation state at the electrode. Coulometric determination is based on the measurement of the charge requiredfor the completion of the reaction. The electrode reaction occurring at the working electrode has to proceed with 100% yield. Other side reactions are not allowed, e.g. the decomposition of water can be a side reaction. Coulometric analysis can be performed with constant potential or constant current (coulometric titration). Coulometric titrations can be divided into two major groups – *primary and secondary coulometric titrations*. *Primary titration* is an analysis where the determined compound reacts directly at the electrode. Only a limited amount of compounds can electrochemically react (e.g. acids). In secondary coulometric titration the determined compound reacts with the titrant, which is generated by the electrochemical reaction at the electrode . The method is similar to classical volumetric titration, but the titrant is not added from a burette, but is generated at the electrode [1].

Faradays Law enables the calculation of the amount of the compound created at the electrode by electrochemical reaction:

$$Q = I\,t = z\,n\,F$$

where I is the generation current [A], t – the time required to reach the end point of the titration [s], z – the number of exchanged electrons in the electrochemical reaction, n – amount of titrant, F –Faradays constant (F = 96 485.31 C mol^{-1}).

Then the mass of the compound can be calculated via the following equation:

$$m = Q\,M / (z\,F)$$

where m is the mass of the determined compound [g], M – the molecular weight of the compound being tested [g mol^{-1}].

The end point of the titration can be determined visually or by tracking a physical quantity over time (potentiometry, amperometry, biamperometry, spectrophotometry, etc.).

The advantage of coulometric titration is the possibility of using non-stable or volatile titrants (e.g. Mn^{3+}, Br_2), the titrants have not been standardized, and titration can be automatized easily. The time can be measured more precisely than volume; it is possible to reach lower detection limits than with classical titration (10 μg – 100 mg) [1].

Biamperometric indication

Biamperometric indication of the equivalence point (end of titration) is applicable where the titrant or the analyte forms a reversible redox couple. On the two same electrodes in the solution with dissolved redox system potential E_r occurs. This potential is (with a reversible system) determined by the intercept of the polarisation curve with the potential axis (fig. 1A); for an irreversible system the intercept will be located between

the cathodic and anodic wave and its value will be controlled by the cathodic η_a^k and anodic η_a^a overpotential (fig. 1B).

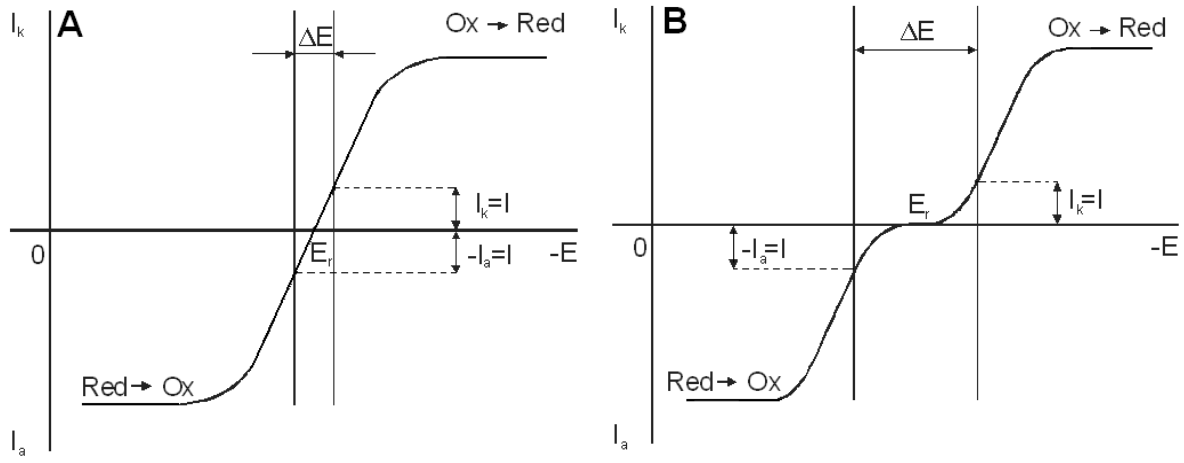


Figure 1. Polarization curves of reversible (A) and irreversible (B) redox system. E_r – equilibrium potential, ΔE – inserted potential on the electrodes, I_k – cathodic, I_a – anodic, I – measured current, η_a^a - anodic, η_a^k - cathodic overpotential.

When the potential ΔE (*polarization potential*) is applied to the electrodes from an external voltage source, the potentials of the electrodes are shifted and the current starts to pass through the electrode system. The concentration of the reduced (*Red.*) form of the compound will increase near the cathode and vice versa at the anode to reach equilibrium with the actual system voltage. The overall concentration change is zero. The value of the current $I = I_a = -I_k$ is limited by the diffusion toward the electrode surface.

With an irreversible system, the current cannot pass until the voltage is lower than the sum of the overvoltages: $\eta_a^a + \eta_a^k = \eta_a$

The condition for the passage of current is the presence of both forms of the redox system. If the concentration of one form decreases, then the current also decreases. When only one form is present in the solution, then the current is almost zero.

The shape of biamperometric curves (fig. 2) depends on the nature of the redox system. Close to equivalence point the current falls to zero*. This leads to the end of the titration being determined as the intercept of the decreasing (or increasing) part of calibration curve with the X-axis (I=0) or with the value of the residual current.

The choice of polarization voltage is a critical factor in biamperometric indication. The optimal polarization voltage is usually in the range from 100 to 350 mV, its value should be determined experimentally. Too low a polarization voltage results in a very low indication current, which is difficult to measure due to electronic noise. On the other hand, too high a voltage can overtake the decomposition voltage and begins to induce side reactions at the indicator electrodes (e.g. decomposition of the supporting electrolyte). Electrode reactions will thus take place both at the generation electrodes (correctly) and also at the indicator electrodes (incorrectly). The result of the determination will be lower by the unknown amount that reacts at the indicator electrodes (shortened analysis time).

* This fact can be used to stop the generation of current at the equivalence point and stop the titration. This method is called „dead stop titration“.

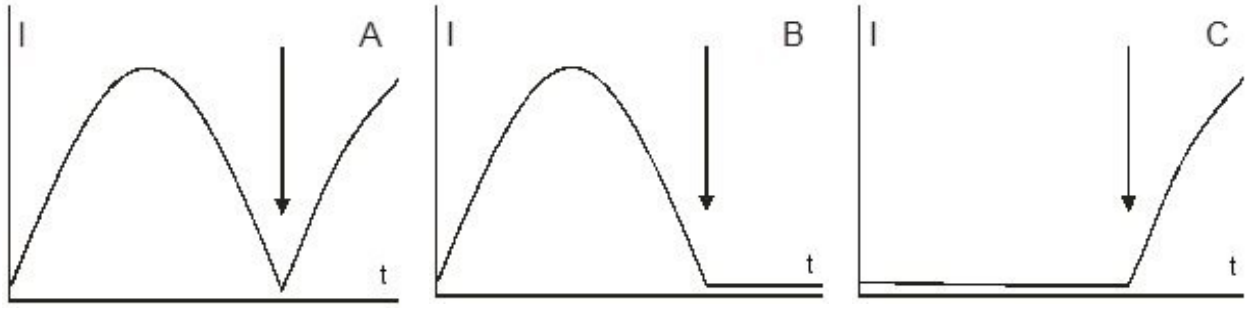


Figure 2. Coulometric titration record with biamperometric indication where indication current (I) is plotted on Y axis and time (t) on X axis. Evaluation of the end of the titration (equivalence point) is marked with an arrow. Individual cases of coulometric titration:
A: titration of reversible system (analyte) with reversible (titration agent) $\Rightarrow \eta_a < \Delta E$ for both systems,
B: titration of reversible system (analyte) with irreversible (titration agent) $\Rightarrow \eta_a$ of analyte is lower than voltage ΔE applied to the electrodes, η_a of titrant > ΔE
C: titration of the irreversible system (analyte) with reversible (titration agent) $\Rightarrow \eta_a$ of analyte > ΔE, η_a of titrant < ΔE.

Technical equipment

The coulometric system Unicoulo ("Nightfly systems s.r.o." represented by Ing. Ivan Pavelka, CR) is designed for constant current coulometry with biamperometric, amperometric and potentiometric indication (Fig. 3). The device is newly implemented as a separate measuring unit (A) which is completely controlled by a computer program (B and C). The electrode system (D) is compatible with Metrohm equipment (Switzerland).

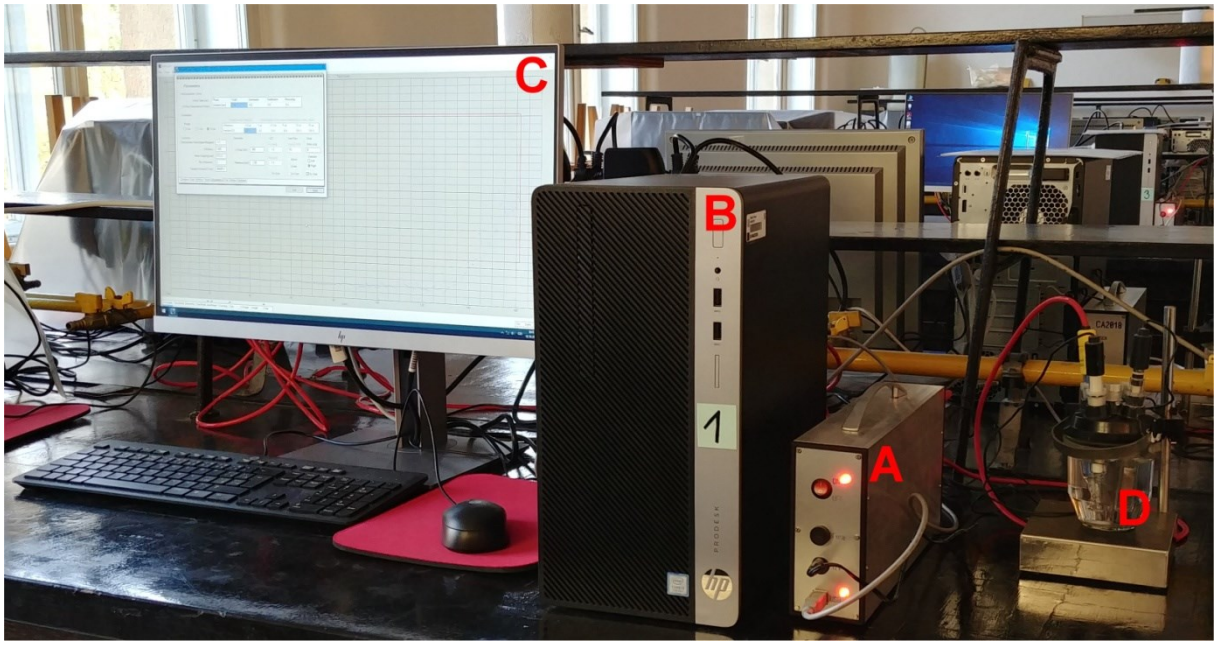


Figure 3: Complete coulometry equipment: (measuring unit containing measuring card (A), computer (B), monitor (C) and electrochemical cell (D)).

The measuring unit (A) is now a separate box about 30x10x5 cm which communicates with the PC via a USB interface, and contains a control unit consisting of a new interface board, a measuring board, a power supply and a voltage and current source necessary for coulometric measurements, as well as indicator electrodes and a USB port to connect to your computer.

The current source (1 mA and 10 mA) is located on the plug-in card. The current value differs for every single instrument and the right value, which has to be used for the calculation, is shown on the monitor of the computer (ask the teacher if you are unable to find it). This current is applied to the generation electrodes. If the current is unable to pass through the cell due to too high resistance, the indicator above I_{Gen} turns red. The most common reason is the absence of sodium sulphate solution in the space of the counter electrode or the electrode being disconnected from the instrument. The indication system is activated by applying the voltage to the indicator electrodes. The indication electrodes are mechanically connected to the same holder but they must not be in direct contact with each other. This can occur when insufficient care is taken when handling the cell*.

The electrode system consists of a generation and indication cell. The generation cell consists of two flat platinum electrodes: a **working electrode** and a **counter electrode**. The counter electrode is separated from the solution by a porous glass frit to prevent the mixing of electrolysis products and side reactions. The tube is filled with 0.5 $mol \cdot l^{-1}$ sodium sulphate solution. The signal is recorded through two platinum indication electrodes, which are mounted in the same holder. The electrode set is placed into the titration vessel (fig. 4). The arrangement *i*) prevents the mixing of electrolysis products, *ii*) ensures that the electric field of the generation electrodes does not affect the indication system, *iii*) enables solution stirring to ensure the rapid response of the system [1].

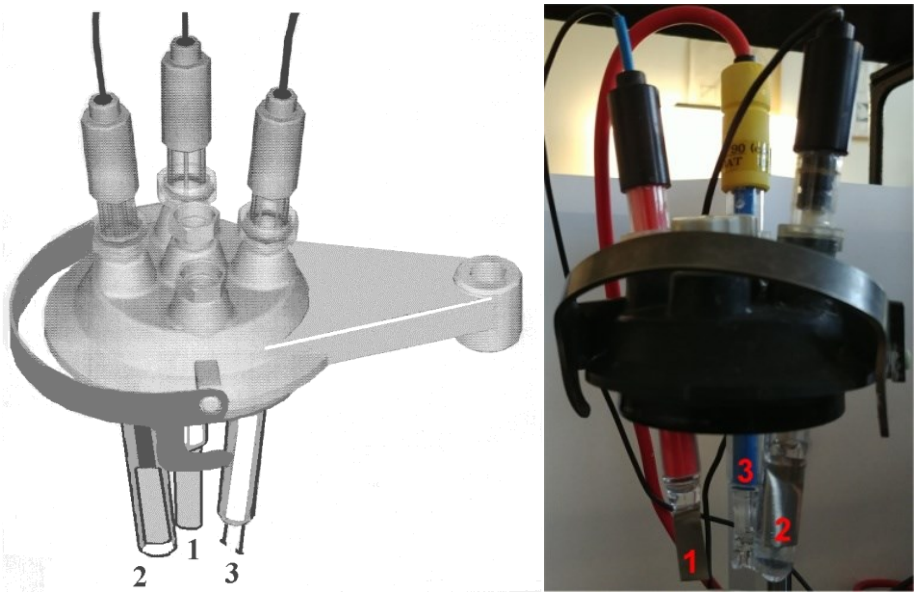


Figure 4. Electrode system: **1** – working generation electrode (anode), **2 –** counter generation electrode (cathode), **3** – indication electrode.

* Platinum is very soft material, which is easy to bend.

COULOMETRIC DETERMINATION OF ASCORBIC ACID (VITAMIN C)

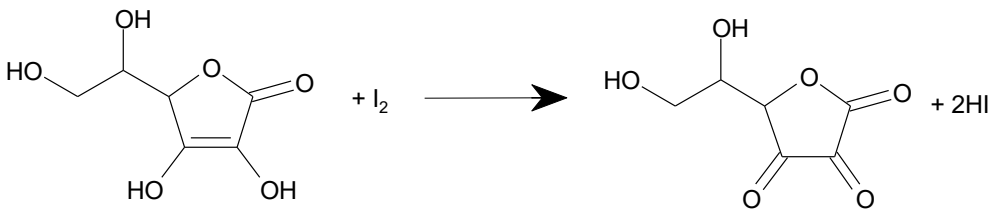
Tasks

1. Determine the correct polarization potential for determining the level of ascorbic acid.
2. Determine the level of impurities in the chemicals on the basis of the blank measurement.
3. Determine the concentration of vitamin C in samples.
4. Process the results according to the protocol.

Principle

Ascorbic acid is one of the first vitamins to be discovered. Its content in the fruit and vegetables decreases with storage and if we want to supply an organism with vitamin C, a more concentrated synthetic form has to be used. The recommended daily dose and average content in some meals is in *supplement 1*[*].

Your objective is to determine the content of ascorbic acid in industry vitamins by coulometric titration based on the oxidation of ascorbic acid by iodine. The scheme of oxidation is:



The titration agent is generated by the electrolysis of NaI at the working electrode (anode).

The working electrode (anode): $2I^- \leftrightarrow I_2 + 2e^-$

The counter electrode (cathode): $Na^+ + e^- \leftrightarrow Na$

$2Na + 2H_2O \leftrightarrow 2NaOH + H_2$

Its concentration is zero until the equivalence point is reached, and as a result there is no current in the indication circuit. The generated iodine (titration agent) is consumed by ascorbic acid (analyte) that is added to the titration vessel and behaves irreversibly, so the indicating system will show a practically zero current value up to the equivalence point. Beyond the equivalence point the indication current increases, because both iodine and iodide are present and the redox system I_2/I^- is reversible. The solubility of iodine in the water is low, but in the presence of iodide the solubility is higher. The triiodide ion is created I_3^- (red-brown colour, yellow in very dilute solution).

The pH should be under 8, because in more alkali solution the iodine dissociates into hypoiodite or even iodate. In highly acidic solutions the HI can be oxidized to iodine by atmospheric oxygen.

$$2I_2 + OH^- \leftrightarrow HIO + I^-$$
$$3HIO + 3OH^- \leftrightarrow IO_3^- + 2I^- + 3H_2O$$
$$4I^- + O_2 + 4H^+ \leftrightarrow 2I_2 + 2H_2O$$

[*] Information from this supplement is NOT in the test and will be NOT assessed.

Ascorbic acid is not very stable, so the determination conditions are very important to prevent gross errors. Ascorbic acid decomposes when heated in the presence of oxygen, and this decomposition is catalyzed in the presence of some metals (e.g. copper). Ascorbic acid is stabilized by low pH, the presence of complexing agents and presence of reductans. A solution of oxalic acid is a good choice, since it maintains a low pH and also has a weak complexing ability. The use of a nitrogen atmosphere and short extraction time eliminates the influence of atmospheric oxygen. The influence of metals can be reduced by EDTA (ethylendiaminetetraacetate, complexon 3) or by using extraction into organic solvents. Never use a high temperature to increase extraction speed, because of the thermal instability of ascorbic acid [2]. Sometimes dilute hyperchloric acid [3], phosphoric acid with EDTA and sodium sulphite is used for the extraction [4].

In this exercise the pH of all samples is around 4, so no correction is necessary. Also commercially available pills do not contain iron or copper, so the addition of EDTA is not essential.

Working guide

Agents

Solution	Application	C [mol/l]	Volume [ml]
Na_2SO_4	Cathode space filling	0.5	*
NaI	Basic electrolyte	0.2	*
Oxalic acid	Basic electrolyte	0.5	*
Ascorbic acid – standard solution	For analysis	**0.01**	**50**
Sample A (Vitamin C - powder)	For analysis		**50**
Sample B (Vitamin C - pill)	For analysis		**100**
Sample C (Lemon)	For analysis		**50**

* The solution is prepared in the laboratory

Working with UniCoulo software

Most of the functions are available via the drop menus, and their utilization is clear from their names. The interface follows the standards of MS Windows*.

- Adjusting analysis parameters: Analyze > Parameters, or Setup > **Parameters**. First, you need to set three parameter windows according to the tables and figures in *supplement 2* and *3*:
  1. Method/Mode,
  2. Parameters and
  3. Chart Setting.

The most frequently used functions are:
- Stirrer: **Monitor** > **stirrer on**
- Start of analysis: **Analyze** > **Start**
- Stirrer off: **Monitor** > **stirrer off**
- End of analysis: **Analyze** > **Stop**
- Store results in a file: **File** > **Save A**s
- Equivalence point determination: **Process** > **Two Lines**.

1. Cleaning the electrodes

The electrodes need to be cleaned for the electrode system to function correctly. Carry out electrode cleaning before the first measurement and after every measurement. **Change the polarity of the working electrode from positive to negative** (in the "Method" drop menu), **change the reference current from 3 to 100 μA** (in the "Parameters" drop menu) and **change the maximum of the Y-axis from 3 to 100** (list "Chart setting").

For the first cleaning (before the first measurement) run the analysis for 180s and stop it manually. For subsequent cleanings, run the analysis for 90s and stop it manually.

* See Computer sciences in the first and second semester.

2. Determination of polarization potential

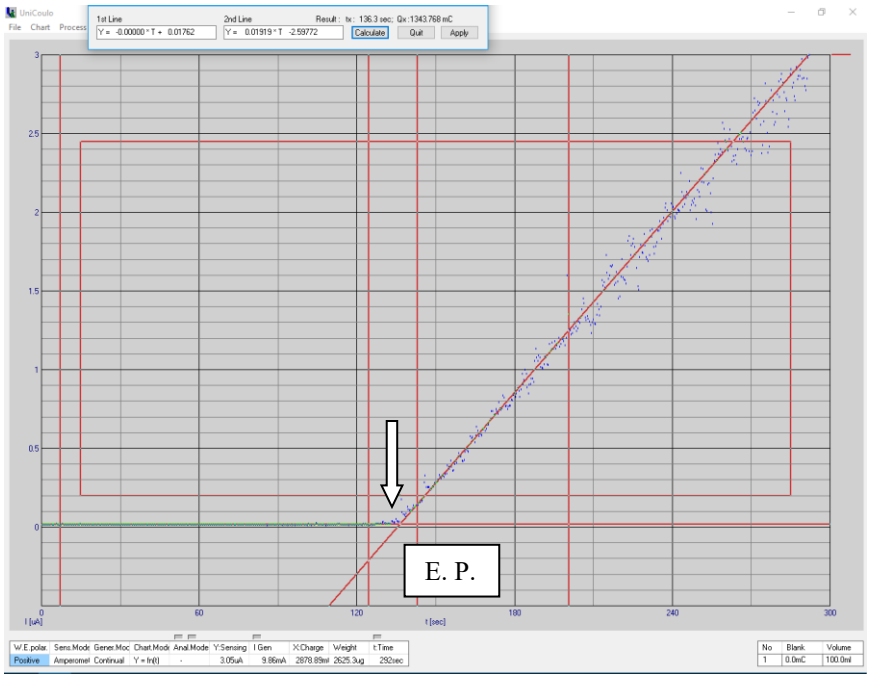
Each student will prepare his/her own standard of ascorbic acid with a concentration of 0.01 mol l^{-1} in the 50 ml volume flask by weighing out ascorbic acid (M_r=176.13 g/mol). Please be careful to work very precisely (weigh accurately into a small, clean and dry beaker (labelled standard)).

- Put basic electrolyte into the titration vessel:
  - 10 ml of NaI,
  - 10 ml of oxalic acid ($H_2C_2O_4$) and
  - H_2O*.

  Then pipette exactly 1 ml 0.01 mol l^{-1} of ascorbic acid solution into the vessel.
- Secure the vessel in the holder and drop the stirrer bar into the vessel.
- Add the 0.5 mol l^{-1} Na_2SO_4 in to the cathode space.
- Turn on the stirrer (**Monitor > Stirrer on**) and check that the mixer rotates continuously and does not jump in the vessel.
- Set „Parameters“ (see. *supplement 2*). Perform the analysis (**Analyze** > **Start**) using polarization potential of 50, 100, 200, 300 and 600 mV. Measure each potential once.
- Evaluate data using „**Two Lines**“ method.
- Calculate the concentration of ascorbic acid (mol l^{-1}) from the results (titration time, charge) and compare with the known concentration.

Choose the optimal polarization potential and use it in all subsequent measurements.

Save the measurement in the Data folder to your created folder according to the task measurement date, for example March 13, 2019 will have the name 0313_2019. The file name should contain the following: **PN50, PN100, PN200, PN300, and PN600**. E.g. analysis with 300 mV potential will be saved to a file with the name **PN300**.



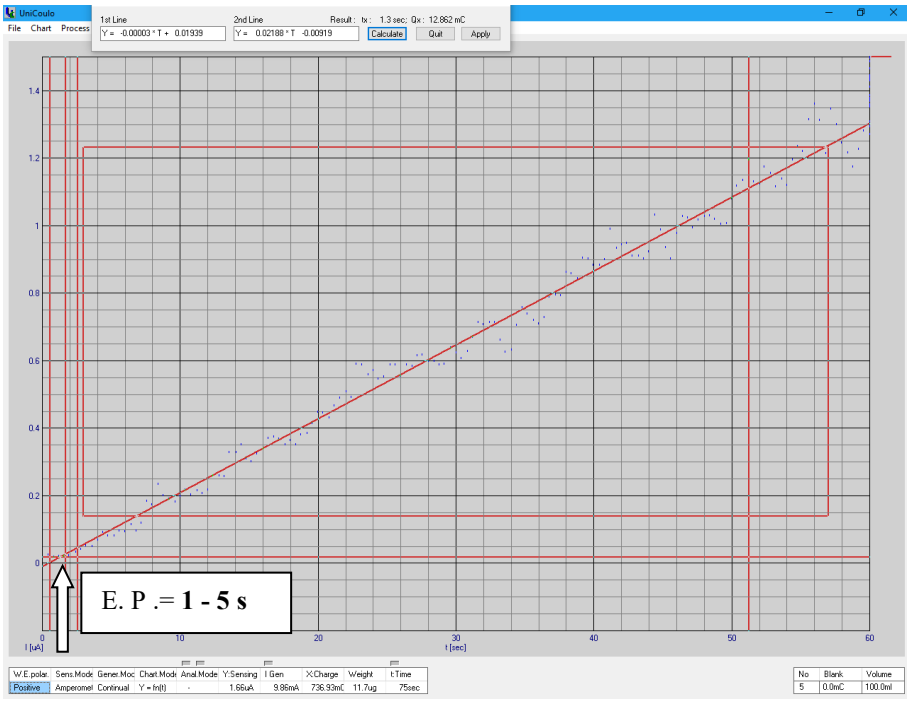
E.P. Equivalence point

* Use a cylinder the first time and mark the level using a felt-tip pen.

3. Blank

The value of the blank provides information about the impurity content in chemicals. Mix the basic electrolyte (10 ml NaI a 10 ml oxalic acid and H_2O) and measure the titration curve using the optimal polarization potential. Repeat it twice. The average will then be used.

The file name will consist of the date and **SL1** to **3**. E.g. the 2nd analysis will be named **SL2**.



4. Sample preparation

Samples B

Weigh the pill. Place it in the 100 ml beaker and add 30 ml of water. Wait until no more sample dissolves (the solution can be turbid, because the sample can contain a filler which is insoluble in water and does not react with iodine). Then transfer all of the solution into the 100-ml flask and add water to the mark.

Sample C

Slice the lemon into quarters and weigh one quarter on a watch glass. Squeeze juice from the lemon quarter. Filter the solution and transfer the extract to a 50-ml flask and add water to the mark.

5. Sample analysis and data evaluation

Samples A and B

For the first measurement, pipette 1.0 ml of sample. For the 2nd to 5th measurements, pipette a volume of sample that will make the end of the titration approximately 200 seconds. File names should contain the name of the sample and the number of analysis, e.g. the 3rd analysis of sample B will be named SB3. Calculate the average (content of vitamin C per 100 g of sample), standard deviation and confidence intervals.

Sample C

Take 10 ml for the analysis, because the content of the vitamin is lower than the synthetic pills. Repeat it once. Only calculate the average in mg per 100 g of sample.

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6. Takeover and handover of laboratory working space

Check the laboratory equipment according to the enclosed list. After finishing work:
• clean the residue of crystallized Na2SO4 from the electrode holder,
• **immerse the electrode system in distilled water**, drain and rinse the fritted tube with distilled water and fill with distilled water,
• wash the dishes with detergent, and then rinse with water,
• dry the metal parts,
• dump, wash and wipe the weighing bottles dry.

Literature

1. Štulík K., Barek J.: Elektrochemické analytické metody, UK v Praze, Státní pedagogické nakladatelství Praha, 1985.
2. Woggon H., Köhler V.: Mitt. Lebensmitt. Hyg. 54, 95 (1963).
3. Veazey R.L., Nieman T.A.: J. Chromatogr. 200, 153 (1980).
4. Mason W.D., Amick E.N., Heft W.: Anal. Lett. 13, 813 (1980).

Statistical evaluation

Interval reliability: $L_{1,2} = \bar{x} \pm t_{n-1} s / \sqrt{n}$

Average: $\bar{x} = \frac{\sum x_i}{n}$

Standard deviation: $s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n-1)}}$

Where n is the number of measured values and t_{n-1} is the critical value of Student's distribution for an (n-1) degree of width and level of relevance $\alpha = 0.05$.

n-1	2	3	4	5
t	4.30	3.18	2.78	2.57

Acknowledgements

Development of the task and the new laboratory manual were created with the support of the project Modernization of the Laboratory of Analytical Chemistry I, IGA VŠCHT Praha 2018 (No. C1_VŠCHT_2018_010 (402-17-8641)), the investigator Ing. Gabriela Broncová, Ph.D. (Gabriela.Broncova@vscht.cz). The authors of the manual especially wish to thank DSP students Ing. Štěpán Strnad and Ing. Zuzana Němečková for testing new machines and measuring samples. Special thanks to Ing. Ivan Pavelkovi (i.pavelka@volny.cz, company "NightFly systems s.r.o.", Czech Republic) for the preparation of measuring units.

Questions

1. Describe the principle and conditions of coulometric titration.
2. Write the equations of the electrochemical reactions at the generation electrodes.
3. List 3 factors which affect the precision of coulometric titration.
4. What is the role of the basic electrolyte in the determination of ascorbic acid by coulometric titration?
5. Define the role of the generation and indication current in coulometric titration.
6. Explain the principle of biamperometric indication of the equivalence point. Draw a theoretical titration curve for the following systems:
    a. $C_6H_4(OH)_2$ (hydroquinone) + 2 Mn^{3+} → $C_6H_4O_2$ (quinone) + 2 Mn^{2+} + 2 H^+
    b. $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$
    c. blank

    Hint:
    a. Reversible redox systems are both analyte and titrant
    b. A reversible redox system is analyte only
    c. Reversible redox system is titrant only
7. Explain the advantages and disadvantages of coulometric titration compared to volumetric titration.
8. Write the name of the physical law used to calculate the content of the analyte in coulometric titration.
9. How long is the blank analysis?
10. How many ml of 0.01 mol/l ascorbic acid should be pipetted to obtain an equivalence point time of 200 s for coulometric titration with I_2. Current 10 mA; Faraday constant = 96485,31 C/mol.
11. Write the indication methods used for coulometric titration.
12. Draw the dependence of the generation current on time.
13. What compounds are created at the generation electrodes, Pt-cathode and anode in anaqueous solution of NaCl?

Supplement 1

Recommended daily dose **of vitamin C:**

	Children			**Men**		**Women**			
Age	1-3 years	4 - 8 years	9 - 13 years	14 - 18 years	Over 19 years	14 - 18 years	Over 19 years	Pregnant	Nursing
Vitamin C	15 mg	25 mg	45 mg	75 mg	90 mg	75 mg	90 mg	80-85 mg	115-120 mg

Sources of vitamin C

Vitamin content in some food ingredients (approximate values):

Food ingredients	**Values of vitamin C content in mg**
Orange juice 200 ml	88
Grapefruit juice 200 ml	70
Orange	70
Grapefruit	88
Strawberry 200 ml	82
Tomato	23

Supplement 2

Setup > Parameters > Method/Mode

W. E. Polarity	*Sensing*	*Generation*	*AZC*	*Stirrer*
Negative[a]	**Amperometry**	**Continuous**	On	**On**
Positive[a]	Potenciometry	Constant Discontinuous	**Off**	Off
	pH measuring	Controlled Discontinuous		

W.E. Polarity is the polarity of the positive generation electrode (iodine generation),
[a] For cleaning the electrode system: Negative, for measurement/analysis: Positive.

Setup > Parameters > Parameters

Data acquisition timing (sec)	*Phase*	Wait 1	Generation	Stabilization	Measuring	Wait 2
(of basic measurement period)	*Duration [sec]*	**0.0**	**0.1**	**0.0**	**0.1**	**0.0**

Wait2 is the final parameter of the upper table, which includes the timing of the individual steps during the measurement. This parameter needs to be checked by clicking on the top table.

I generation		
Auto	1 mA	**10 mA**

Constants	
Stoichiometric Ratio	**1/1**
Efficiency	**1**
Molar Weight [g/mol]	**176,13**
No of Electrons	**2**
Faraday Constant [C/mol]	**96485,31**

Electrodes	
U Polar [mV]	*
***Reference* [µA]**[b]	**3**

Stirrer RPMx100
8
Direction:
left
right
On Start

*Polarization potential **U polar** will be changed from 50 to 100 / 200 / 300 and 600 mV. Once you have determined and set the optimal value, you must not change it.
[b] ***Reference*** - for cleaning the electrode system: 100 µA; for measurement: 3µA.

Setup > Parameters > Chart Setting

Chart Mode
Y = f(t)
X = f(t)
Y = f(X)

Plot Mode
dots
dots+lines

Points Style
.
x
o

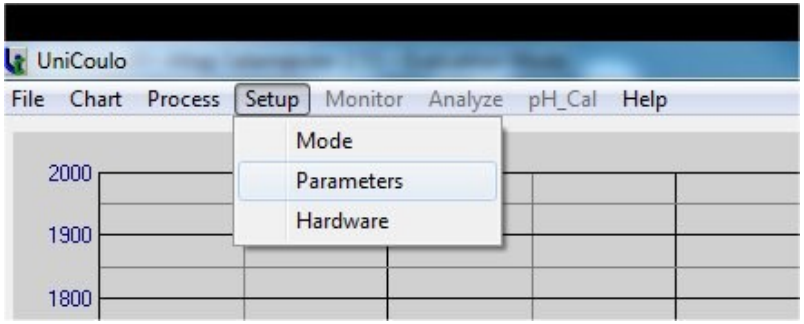
Scrolling

Axes Setup and Titles	*Axe*	*Title*	*Min*	*Max*[c]	*Crosses*	*Tick Marks*
	Y: Sensing	**I [µA]**	**-0.5**	**3**	**100**	**50**
	X: Charge	Q [mC]				
	t: time	**t [sec]**	**0**	**300**	**100**	**50**

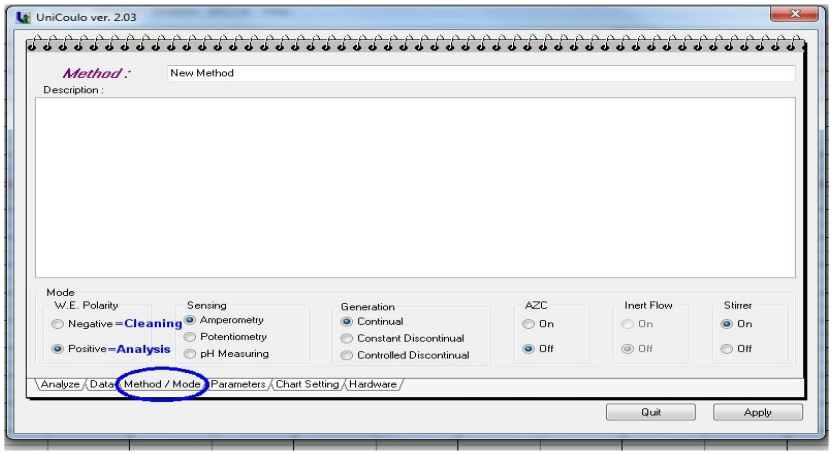
[c] For cleaning the electrode system**- maximum Y:Sensing**: 100; for measurement: 3.

Supplement 3

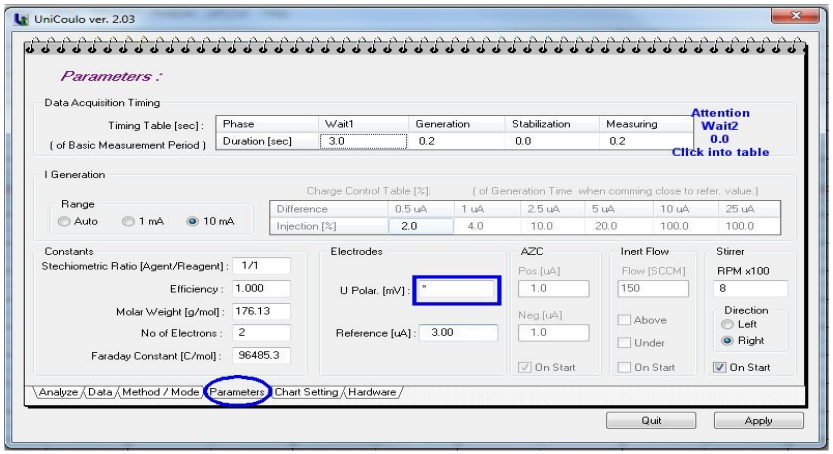
Set method parameters in UniCloulo using the following path:
Setup-Parameters.



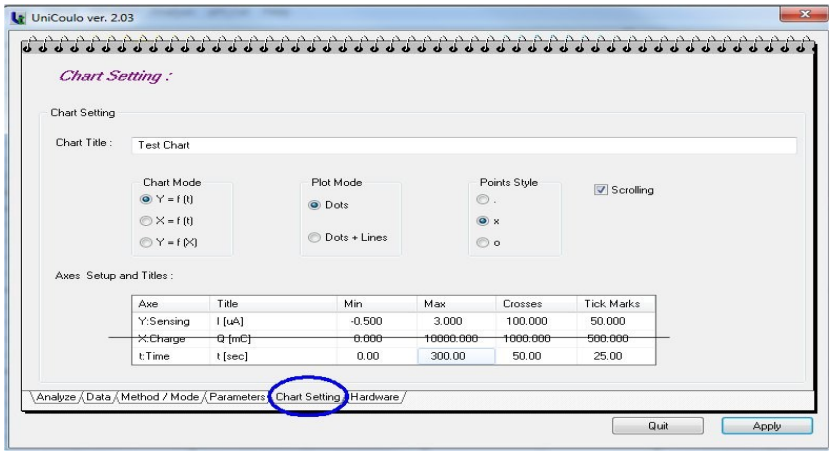
The following must be set in the first three windows:
1. Method/Mode,
2. Parameters and
3. Chart Setting.



W.E. is the polarity of the positive generation electrode (iodine generation), positive polarity is selected during analysis and negative during electrode cleaning.



Wait2 is the final parameter of the upper table, which includes the timing of the individual steps during measurement. This parameter needs to be checked by clicking on the top table.
U Polar. [mV] (highlighted with a blue rectangle) is the polarization potential that you optimize while measuring the ascorbic acid standard.



In the table of values to set the graph of the analysis, ignore the middle line X Charge (***do not delete anything***).

Extension of the laboratory task 4

Voltammetric determination of ascorbic acid

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Acknowledgements: The updated laboratory task was created with the support of the project Innovation of basic laboratory tasks of the subject Analytical Chemistry Laboratories I, PIGA UCT Prague 2025 (No. C1_PIGA_2025_029 (402-02-5645)), researcher Ing. Gabriela Broncová, Ph.D. (Gabriela.Broncova@vscht.cz).

Theoretical part

Voltammetry

Voltammetry is an electroanalytical method in which the current passing through an electrochemical cell is a function of the applied voltage. The electrochemical cell consists of three electrodes that are immersed in a supporting electrolyte. Supporting electrolyte is a solution containing inert salt and ensuring pH, the ionic strength, solubility analyte. The analyte is oxidized or reduced on the working electrode (WE) at determined potential that ~~of which~~ is set/controlled against the reference electrode (RE). The current as result of occurring redox reaction passes between the WE and the counter electrode (CE). The obtained dependence I vs. E is a voltammogram, from which qualitative and quantitative information about the analyte can be obtained.

Voltammetric methods can also be used in the study of electrode processes. The relationship between current (I) and applied potential (E) obtained during voltametric measurements shows graph called voltammogram. Voltammogram gives both qualitative and quantitative information. The potential corresponding the increasing current with changes of concentration is qualitative characteristic. The current (peak height) that is linearly dependent on the analyte concentration is quantitative characteristic.

Cyclic voltammetry

Cyclic voltammetry (CV) is a kind of voltammetric technique showing current response as a function of a triangular potential waveform (Fig. 1) [1]. The rate of change of voltage over time is the scan rate (SR, $V.s^{-1}$). The cycle can be divided into two parts: forward scan and reverse scan. In the forward scan, the potential is linearly increased from the initial potential to the vertex potential. In the reverse scan, the potential is decreased from the vertex potential to the final potential (Ep), which is usually the same as the initial potential. Depending on the requirements, one or more cycles can be used. The resultative graph is called cyclic voltammogram.

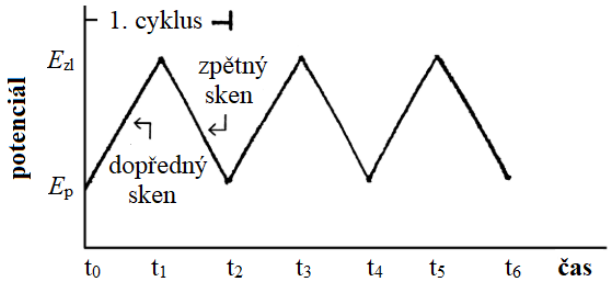


Fig. 1: Dependence of the applied potential on time in cyclic voltammetry.

The main advantage of CV technique is the studying of reversibility of the redox processes that can reversible, irreversible and quasi-reversible (Fig. 2). The characteristic peaks observed in

the cyclic voltammogram are result of the redox processes occurring in the diffusion layer formed near the electrode surface.

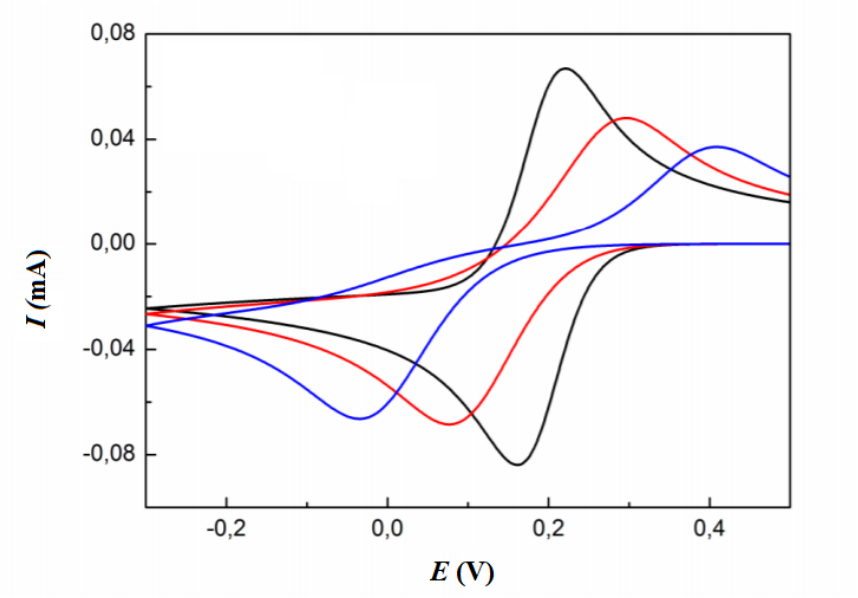


Fig. 2: Cyclic voltammograms for reversible (black), quasi-reversible (red), and irreversible (blue) redox processes.

In the case of reversible processes, the oxidation-reduction peaks are symmetric ones of the same intensity (Fig. 2, black). The potential difference between the cathodic and anodic peaks (ΔEp) can be used as a criterion for Nernstian behavior. For one-electron process, ΔEp is 59 mV. In the case of reversible systems, it is observed a significant separation between the cathodic and anodic peak (Fig. 2, red). In the case of quasi-reversible processes, in which electrons are exchanged slowly, the individual peaks are less distinct and more distant from each other, and often one of the peaks is completely absent (Fig. 2, blue).

Practical part

Apparatus

A PalmSens4 potentiostat (PalmSens BV, Netherlands) with an electrochemical cell arranged in a three-electrode system (Fig. 3) is used for CV measurements. WE (red) is a glassy carbon (GC) electrode, RE (blue) is silver/silver chloride (Ag/AgCl (3 mol·L^{-1} KCl)) and CE (black) is a platinum plate electrode (BVT Technologies, a.s. Strážek, Czech Republic).

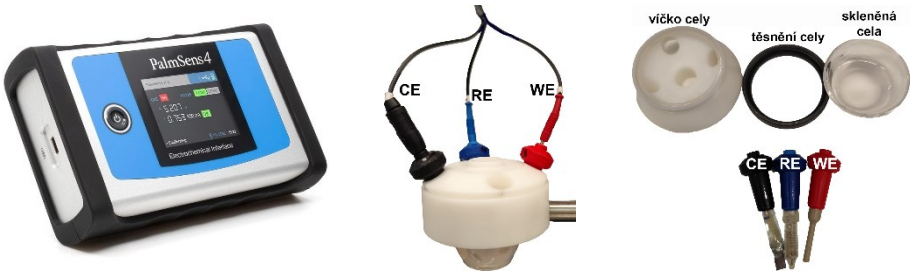


Fig. 3: PalmSens4 potentiostat used for CV measurements, including the electrochemical cell and individual electrodes.

Chemicals:

- ascorbic acid (AA) (analyte)
- oxalic acid 0.03 mol·L^{-1} (supporting electrolyte)
- distilled water
- alumina (polishing suspension)

Electrode polishing

Before starting the measurements, the surface of WE electrode (GC electrode) must be thoroughly cleaned. The cleaning restores the active surface of the electrode through removing adsorbed impurities. Fig. 4 demonstrates the procedure of mechanical cleaning. The surface of GC electrode (WE) is mechanically polished on a pad using alumina suspension. Polishing is performed in a figure-eight motion to minimize uneven wear of the electrode surface.

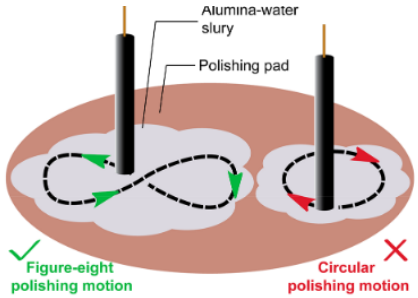


Fig. 4: Schematic representation of procedure mechanical polishing surface of the working electrode [2].

After polishing, the surface of GC electrode should be thoroughly rinsed with distilled water and wiped dry with cellulose tissue.

Preparation of solutions

In this experiment, it is used the same standard AA solution (c= 0.01 mol·L^{-1}) (see part "Coulometry"). The supporting electrolyte (V=5 mL) is mixture of 0.3 mL of 5 mol·L^{-1} oxalic acid and 4.7 mL of redistilled water. Use corresponding micropipettes for pipetting mentioned.

Instrument control and measurement parameter settings

- Turn on the instrument (TEACHER)
- Open the PSTrace program on the computer
- Select the option "PalmSens 4" and Click "Connect"
- Select "Technique", "Cyclic Voltammetry"
- Select program mode "Analytical mode"
- Specify parameters:

Parametr	Hodnota	Jednotka
t equilibration	5	s
E begin	0.0	V
E vertex 1	0.0	V
E vertex 2	0.9	V
E step	0.00244	V
Scan rate	0.05	V/s
Number of scans	1	

1. Pipette 5 mL of supporting electrolyte (0.3 mL of oxalic acid + 4.7 mL of distilled water with) into the cell. Measure the CV voltammogram (blank).

2. Add 200 µL of effervescent tablet sample (identical for coulometry, prepared in a 100 mL volumetric flask). Measure the CV voltammogram (Sample). Evaluate the anodic (oxidation) peak (its position and height).

3. Add 100 µL of AA standard (identical for coulometry, prepared in a 50 mL volumetric flask) to the sample. Measure the CV voltammogram (Standard 1). Evaluate the anodic (oxidation) peak (its position and height).

4. Then continue with three more additions (Standard 2, Standard 3 and Standard 4) and evaluate them (Fig. 5).

After the measurement is completed, the electrodes must be mechanically cleaned again, rinsed with distilled water and wiped with cellulose tissue.

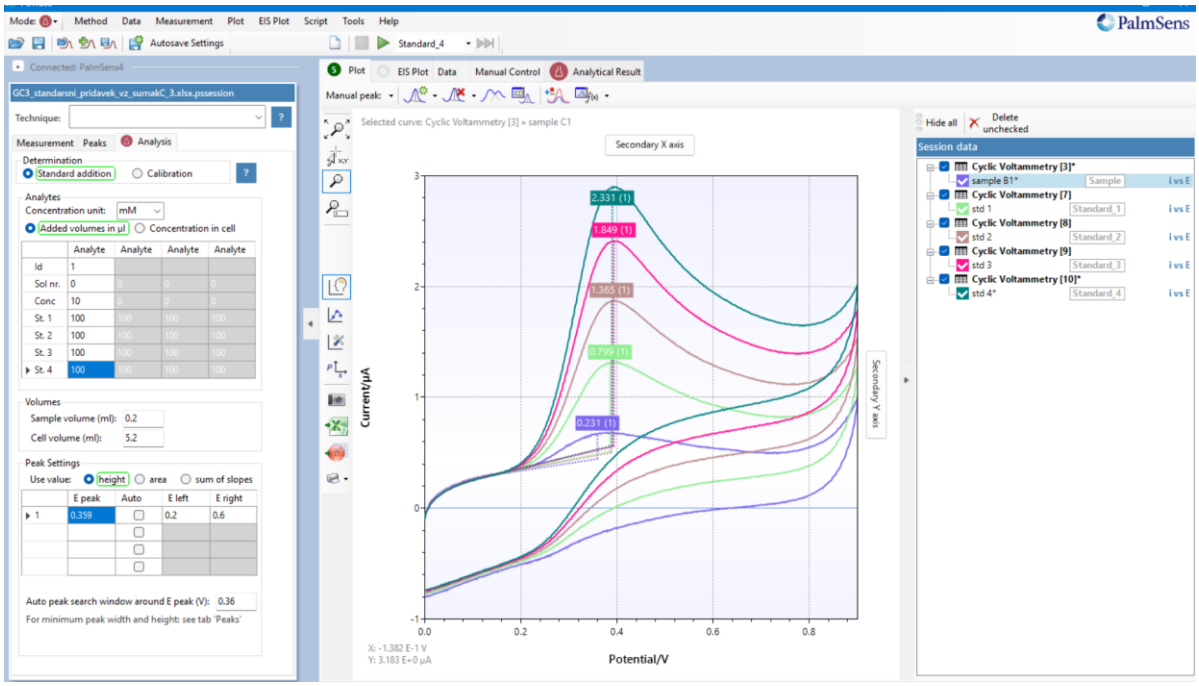
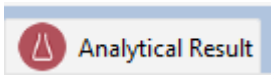


Fig. 5: Setting parameters for the measurement of an effervescent tablet sample using the standard addition method (left part), its subsequent measurement (middle) and data display and description (right).

Then, select the corresponding icon, 

, where the evaluation of the concentration of the effervescent tablet sample using the standard addition method will be displayed in a table and a graph (Fig. 6).

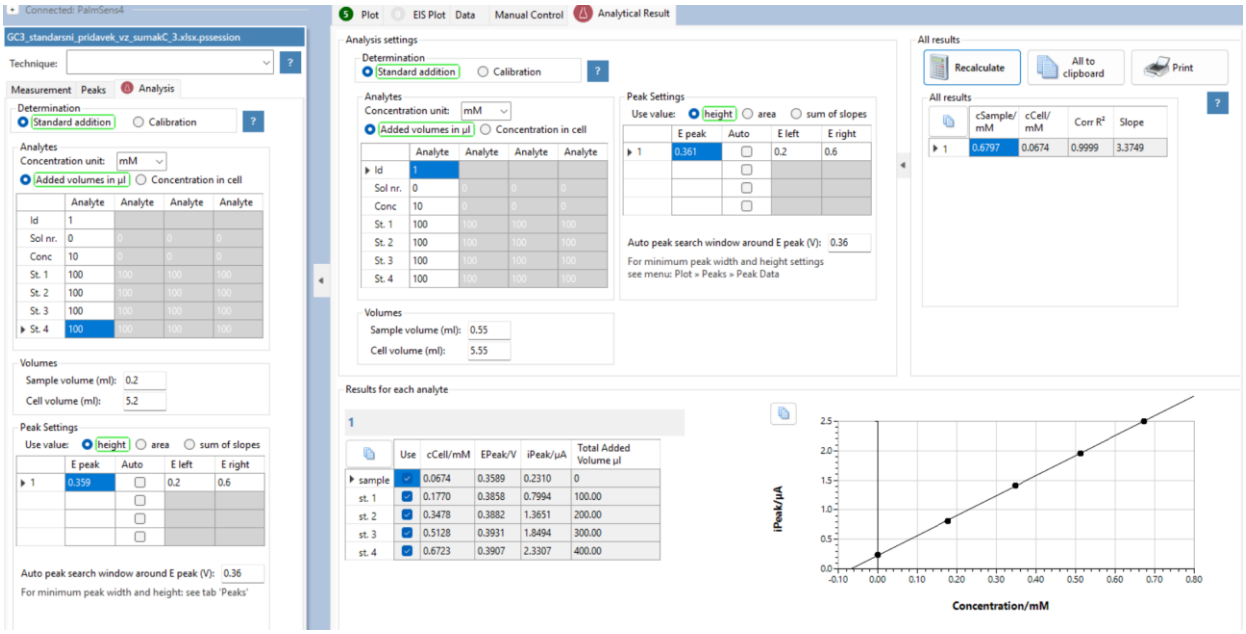


Fig. 6: Evaluation of data obtained from the measurement of an effervescent tablet sample using the standard addition method.

Based on the results obtained, compare both determination methods in terms of accuracy and speed of analysis.

References

[1] Wang J.: Analytical Electrochemistry. Wiley-VCH, US 2000.

[2] Elgrishi N., Rountree K.J., McCarthy B.D., Rountree E.S., Eisenhart T.T., Dempsey J.L.: J. Chem. Educ. 2018, 95, 197−206. DOI: 10.1021/acs.jchemed.7b00361

Review questions for the test

1. What is the principle of voltammetry?
2. What is the name of the voltammogram obtained during voltammetric measurements?
3. How many and what types of electrodes are used in voltammetry? Name each electrode.
4. What are the functions of the individual electrodes used for?
5. What is the principle of cyclic voltammetry?
6. How can an irreversible system be recognized in a cyclic voltammogram?
7. How can a reversible system be recognized in a cyclic voltammogram?
8. What evaluation method is used to calculate the concentration of an analyte in a real sample?
9. What parameters on a cyclic voltammogram are used for qualitative and quantitative analysis?