Analytisch-Physikalische Chemie

Teil Analytische Chemie
Sommersemester 2007

Quantitative analysis of zinc and copper in mineral water and ascorbic acid in fruit juice by method of polarography

Gruppe 13:

Simon Breitler, *Studiengang Chemie*, *4. Semester*, brsimon@student.ethz.ch
Daniel A. Frick, *Studiengang Chemie*, *4. Semester*, frickd@student.ethz.ch
Matthias Geibel, *Studiengang Chemie*, *4. Semester*, mgeibel@student.ethz.ch
Florian Glaus, *Studiengang Chemie*, *4. Semester*, glausf@student.ethz.ch

Assistents: Marie-Pierre Collin
Andrea Amantonico

Abstract: The concentration of zinc and copper cations in Prix Garantie Sparkling mineral water was measured by method of anionic stripping, a subclass of polarography. The result for Cu^{2+} was 5 ± 3 µg/L and the concentration of Zn^{2+} was 133 ± 18 µg/L.

In a second experiment, the concentration of Vitamin C (ascorbic acid) in blood orange juice by Michel was determined, using the method of differential pulse polarography. It was measured twice, once using the technique of external calibration, which yielded a concentration of 273 ± 3 mg/L and once using standard addition with which we received a concentration of Vitamin C of 275 ± 4 mg/L.

Zürich ZH, 23. Mai 2007

Simon Breitler Daniel A. Frick

Matthias Geibel Florian Glaus

1. Theory [1],[2]

Polarography is a subclass of voltammetry, the electrochemical analytical method where the current in dependence of a time-changing voltage is measured. Polarography uses a liquid working electrode which can be periodically or continually be renewed. In our case, a dropping mercury electrode was used.

Within the field of polarography there exist five different techniques.

- Direct current polarography (DCP)
- Alternating current polarography (ACP)
- Normal pulse polarography (NPP)
- Differential pulse polarography (DPP)
- Stripping methods

DCP was used at the very beginning of the research in polarography. Since this method is not very sensitive, it was abandoned with the raise of ACP. In DCP a linear increasing direct current is applied to the electrode and the current within the cell is measured.

ACP uses a monotonously increasing alternating current instead of the direct one in DCP. It therefore yields peaks rather than cascaded plots. This is due to the induction of an alternating current in the cell by the applied alternating current. Since peaks are far easier to interpret, this method offers an improvement in accuracy.

In pulse polarography instead of a continuous growing current, voltage is applied in form of short pulses. The current within the cell is measured shortly before the pulse and at the end of each pulse, before the electrode drop is dropped. The difference between the two currents, are then plotted. The main advantage of this method is that since the capacitive current decreases exponentially in time, it can be neglected. Furthermore, due to the short pulse, more electrochemically active substance is located near the electrode. This leads to a better resolution and a lower detection limit.
There exist two different methods. In NPP, the current after each pulse drops back to a basis current, giving cascaded plots again, whereas in DPP, the overall applied voltage is increased after each pulse as well, leading to a peak structure in the plot.

Stripping methods offer by far the best detection limits in electrochemical analysis. Traces with as low concentrations as 10^{-12} mol/l can be detected, thus being one of the most sensitive techniques available for trace analysis.
During our lab course, we only used anionic stripping, which will be discussed here.
The name anionic stripping arrives from the fact, that the electrochemical active cations are first concentrated at the electrode by reduction and then “stripped off” using the reverse process of oxidation.

$$Cu^{2+} + 2\,e^{-} + Hg \quad \underset{\text{detection (anionic)}}{\overset{\text{accumulation (cathodic)}}{\rightleftharpoons}} \quad Cu^{\circ}(Hg)$$

The measurement starts with reduction of the analytes by applying a cathodic current to the electrode. The cell is stirred in order to maximize analytes accumulation at the mercury drop. After a certain amount of time, the stirring is stopped. Because of the lack of convection, the accumulation and therefore the current become smaller and the solution calms down. This period is called the rest period and is usually about 5 to 30 seconds long.

An anionic current is then applied to the electrode, oxidizing the analytes. The detection is based on the decomposition of the accumulated analytes. This leads to a certain current peak at the oxidation potential of each ion, which is proportional to the concentration of the analytes.

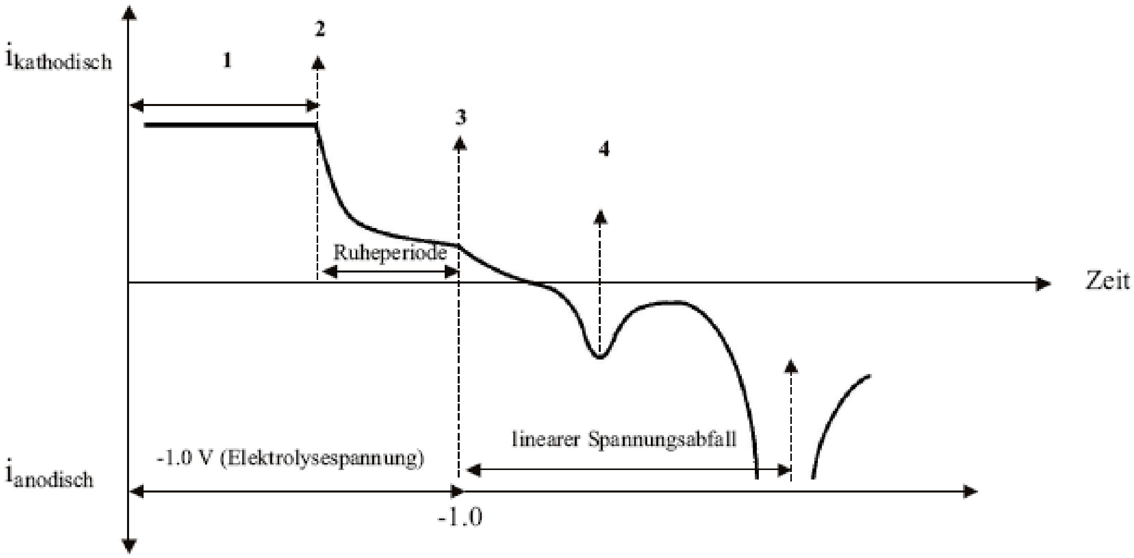


Fig. 1: The voltage versus the time for the anode stripping method. [1]

One big advantage of polarography is the fact, that it offers a big range of applications, since almost every solution can be tested, as long as the conductance is high enough for a measurement and the redox potentials of the analytes are significantly different from each other. For stripping methods an additional condition is, that the ions must form amalgams which have to be soluble in mercury.
It is therefore a widely used technique for quality control in the food industry.

2. Execution of the experiment

2.1. Set up

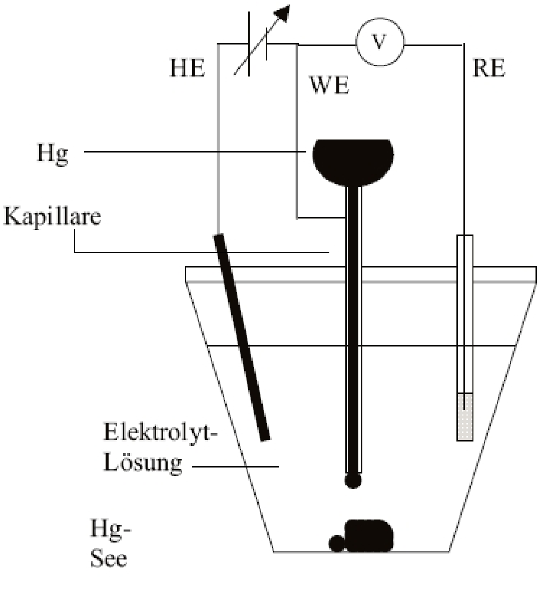
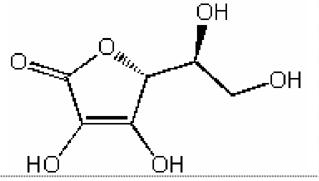
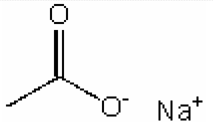
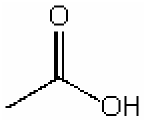
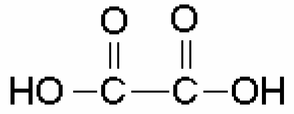


Fig. 2: The used setup for the experiment [1]

The cell consists of three different electrodes. The working electrode, which is a

capillary filled with mercury. As the name implies, this is the electrode where currents are measured.
The reference electrode is usually an Ag/AgCl-electrode, which closes the circuit with the working electrode.
In newer designs, as an improvement, an auxiliary electrode is introduced. Because of the low conductance in aprotic solvents, there is a large resistance in the cell. By introducing a third electrode which is partially discharging the applied current, falsification of the results by the aforementioned effect can be minimized.

2.2. Used Substances [3]

Vitamin C Molecular Formula: Formula Weight: CAS:	 $C_6H_8O_6$ 176.12 g/mol 50-81-7	S24/25	
Sodium acetate Molecular Formula: Formula Weight: CAS:	 $C_2H_3NaO_2$ 82.03 g/mol 127-09-3	S24/25	
Acetic acid Molecular Formula: Formula Weight: CAS:	 $C_2H_4O_2$ 60.05 g/mol 64-19-7	C R10, R35 S2, S23, S26	
Oxalic acid Molecular Formula: Formula Weight: CAS:	 $C_2H_2O_4$ 90.03 g/mol 144-62-7	Xn R21/22 S24/25	 $HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$
Mercury Molecular Formula: Formula Weight: CAS:	 Hg 200.59 g/mol 7439-97-6	T, N R23, R33 S45, S7	Hg

Tab. 1: Verwendete Substanzen.

2.3. Description

Preparations of the solutions were done by using bidestillated water. The cleaning of the cell was done with bidestillated water as well.

2.3.1 Determination of the concentration of Cu^{2+} and Zn^{2+} in mineral water

This measurement was taken by using the method of anionic stripping with standard addition.
The following solutions were prepared:

Solution	**Concentration**
Cu^{2+}:	15 ppm
Zn^{2+}:	101 ppm
Acetat buffer:	50g AcONa 40g AcOH diluted to 1 L.

20 ml of the “PrixGarantie Sparkling Mineral Water” by Coop was added to 5 ml of the acetate buffer in the cell. The solution was degassed for 5 minutes. A polarogram was measured after the degassing process, each polarogram was measured three times. After the third measurement, 50 µl of each standard solution (Cu^{2+} and Zn^{2+}) was added and measurements started again after a brief degassing phase. The standard addition was repeated 4 times.

2.3.2 Determination of the concentration of ascorbic acid (Vitamin C) in blood orange juice.

This measurement was taken by using the method DPP with standard addition and external calibration.

A standard solution of Vitamin C and Oxalic acid was prepared:

0.2000 g Vitamin C
0.1002 g Oxalic acid
Diluted to 100 ml

This standard solution (2.00 g/l) was then used for the preparation of the following solutions:

Number	Standard	Concentration
1	50 mg/l	49.97 mg/l
2	100 mg/l	100.4 mg/l
3	200 mg/l	200.4 mg/l
4	300 mg/l	304.3 mg/l
5	400 mg/l	400.8 mg/l
6	500 mg/l	502.0 mg/l

First a calibration curve was measured by adding 25 ml of acetate buffer and 1 ml of **1** to the cell. The solution was degassed for 5 minutes, and again, three polarograms were measured. The solution was then changed against a new one with 25 ml acetate buffer and 1 ml of **2**. This was repeated until the solution **6** was measured for the third time.
The calibration curve was saved and a sample of 25 ml acetate buffer and 1 ml of Blood orange juice from Michel was measured.
This sample was then used for the standard addition method. After a cycle of three measurements, 1 ml of **2** was then added. This standard addition was repeated 5 times.

The evaluation was done automatically by the supplied computer program. Nevertheless, all calculations were redone by using a complementary Mathematica notebook.

3. Results

3.1. Concentration of Cu^{2+} and Zn^{2+} in mineral water

Output provided by the Mathematica notebook (see Appendix)

Concentration of Cu^{2+} in Coop Prix Garantie Sparkling Mineral Water:

C_{Cu} = 5 ± 3 µg/L (95%, 12 degrees of freedom, Standard deviation = 1.34 µg/L)

Concentration of Zn^{2+} in Coop Prix Garantie Sparkling Mineral Water:

C_{Zn} = 133 ± 18 µg/L (95%, 12 degrees of freedom, Standard deviation = 8.04 µg/L)

Concentration of Vitamin C in Michel Blood Orange Juice:

External Calibration:

$C_{Vit\ C}$ = 273 ± 3 mg/L (95%, 12 degrees of freedom, Standard deviation = 1.24 µg/L)

Standard addition:

$C_{Vit\ C}$ = 275 ± 4 mg/L (95%, 14 degrees of freedom, Standard deviation = 1.79 µg/L)

4. Discussion

At the beginning, the polarograph showed abnormal behavior. The potential of zinc was measured four times at different voltages and copper didn't show up at all. Therefore, we switched to the other polarograph.

Our results for the concentrations of copper and zinc cations in our mineral water are well below the recommendations of the World Health Organization. However, the result for copper can be considered suspiciously low. Either the mineral water has a extremely low copper concentration, or there has to be a systematic error in the determination of the copper concentration. Since the curves for the standard addition show a normal and regular behavior, a systematic error is unlikely.
No reference value for these cations is given.
Our results for the concentration of Vitamin C are both in the right range. They are however twice as high as the reference value stated by the producer. This could be due to matrix effects, which is highly unlikely since both methods yield the same results. Another possibility would be, that the reference values are minimum values and that the actual concentration in the bottle can be far higher and are not strictly controlled in the manufacturing process.
Noticeable is, that both methods show practically the same results. One would expect them to differ to a greater extent since the external calibration doesn't take matrix effects into account. We therefore assume that this particular orange juice consists mainly of water and lacks other substances whose matrix effects could distort our results.
Another point of interest is the small confidence interval and standard deviation. This can be explained by the fact, that during our measurements, we encountered several "spikes" i.e. current values which were far too high. In our Mathematica evaluation, we dropped these values completely, therefore receiving several data points which consisted of less than three values.

During the afternoon, the question of the advantages of a dropping electrode came up. The main advantage can be found by the absence of a memory effect. Unlike a stationary electrode, there will be no accumulations of unwanted substances on the electrode which would distort the measurements, since after each measurement, the electrode drop can be dropped and a new one is formed. A second advantage is, that with a precise capillary, the size (i.e. the volume) of the drop is well-defined over time.

By using the rapid technique, where the drop is shaken off after each measurement at a certain interval, one can calculate the surface of the drop which is proportional to the measured current.

5. References

[1] Praktikum Analytische Chemie (4. Semester), *Polarographie*, März 2007
[2] Univ.-Prof. Dr. Günter Henze, "Einführung in die Polarographie und Voltammetrie", Metrohm Ionenanalytik, Herisau, 2003
[3] www.inventory-loc.ethz.ch, 22.05.2007