TEA 4000

Method Manual

EN3.B

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Jaroslav Heyrovský invented polarography – a subclass of the voltametry – in the early 20th-century. Since that time a lot of methods have been invented and redeveloped by several experts in the field of polarography. The methods collected in this Method Manual reflects a wide range of possible applications for our polarograph TEA 4000.

For their work, help and support we like to express our special thanks and gratitude to:

Prof. Dr. Jaroslav Heyrovský
Father of the polarography and Nobel Prize laureate

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A. Polarography

1. Basic Principles

Polarography is a technique in which an electric potential (or voltage) is varied in a regular manner between two or three electrodes (working, reference, and auxiliary) while the current is monitored. The working electrode can be solid (gold, platinum or glassy carbon) or formed by a drop of mercury hanging from a tip of a capillary. If the electrode is formed by a drop of mercury rhythmically dropping from a capillary, the analytical technique is called Polarography. At a specific potential oxidation or reduction of the analyte occurs, which causes an increase of the current which depends on the concentration of the analyte. The shape of a polarogram depends on the method of analysis selected, the type of working electrode used, and the potential ramp that is applied.

Most common techniques are DC (Direct Current, linear sweep) and DP (Differential Pulse, linear sweep with pulses superimposed). Classical polarography uses a dropping mercury electrode, which causes a high consumption of mercury. Modern Instruments as our TEA 4000 are working with a hanging mercury drop, which minimizes the mercury consumption, and allows to do “Stripping Voltammetry”.

Stripping voltammetry means, that the analyte is accumulated in a first step at the surface of the working electrode. To do so an appropriate accumulation potential is applied to the electrode for a defined time intervall (accumulation time). The analyte is then stripped back into the solution in a second step. The enrichment of the analyte effects the high sensitivity.

The most sensitive methods are anodic, cathodic and adsorptive stripping voltammetry, combined with the differential pulse technique. The detection limits using stripping voltammetry depends on the analyte, the best detection limits are about 0,01 µg/l (ppb).

2. Sample Treatment: Digestion Methods for Organic Substances

In general, natural samples have to be digested before performing electrochemical analysis. The reasons are:

a.) trace elements must be present as ions in aqueous solutions,

b.) organic compounds can form complexes with the trace elements and thus prevent their quantitative determination,

c.) many organic compounds show great tendency to adsorb at the surface of the hydrophobic surface of mercury.

Mainly, two methods can be used depending on the nature of the sample and on the content of organic substances:

- Digestion with concentrated acids

- UV digestion

2.1. Digestion with concentrated acids for samples with higher organic loads and for solid samples

Principle	The organic matrix is destroyed by high-temperature oxidation with the help of a concentrated mineral acid (H_2SO_4, HNO_3, $HCLO_4$)
Reagents	**conc. mineral acid** (H_2SO_4 96 %, HNO_3 65 %), **H_2O_2 30 %**, of highest available quality (suprapur) in order to minimize blank values.

Procedure in an open system
10 ml or 2 g of the sample are given in a Kjeldahl flask made of quartz. 6 ml of the mineral acid are added. If possible, the mixture is allowed to stand for several hours at room temperature (e.g. overnight) in the closed flask. Then, it has to undergo slow heating. After a certain period, liquid samples should turn into a brown colour. Solid samples should be liquefied. Now, hydrogen peroxide can be added dropwise to the mixture and the mixture is to be heated again until the solution becomes clear and colourless.

Attention
The addition of hydrogen peroxide has to be performed dropwise and very carefully (e.g., by letting the drop flow on the wall of the flask into the digestion mixture). The reaction of the hydrogen peroxide with the hot mineral acid can be very vigorous.

Procedure in a closed system
The digestion in a closed system is performed under high pressure and high temperature. It requires a special device (e. g. a microwave digestion apparatus). This kind of digestion is recommended in the case of solid materials and volatile metals like lead and mercury. 0.5 g of the sample are filled into the digestion vessel. Concentrated mineral acid and hydrogen peroxide are added and the digestion program is started.

Attention
High pressure digestion with nitric acid is very often not complete. Additionally, very stable organic nitro compounds can be formed. These substances can influence the electroanalytic determinations. To avoid these problems, a post-treatment with UV radiation is recommended.

2.2. UV digestion for slightly polluted samples and as post-treatment

Principle	photolysis with UV-light, radical oxidation
Reagents	**H_2O_2** **HCl**

Procedure
The liquid samples are filled into quartz vessels, which are then placed around a mercury lamp. The device must be cooled with water to avoid sample temperatures higher than 80 °C. An addition of hydrogen peroxide (max. 1 %) is suitable for a more effective oxidation of organic substances. The digestion period depends on the pollution level and on the characteristics of the UV-lamp. It can be shortened if a small amount of hydrochloric acid (0.1 %) is added to the sample.

B. Application in water analysis

1. Determination of nitrates

1.1. Determination of nitrate I

Principle

Reduction of the nitrate ion on the hanging mercury drop electrode with the help of cerium (III) ions.

The cerium (III) ions support the transport of negatively charged nitrate ions to the negatively charged electrode. The cerium (III) ions are adsorbed at the mercury surface. Consequently, the nitrate ions are drawn nearer to the surface of the cathode. The nitrate ion will be deformed in the strong electric field and reduced at the end to ammonia.

Reagents

Supporting Electrolyte:
aqueous 0.4 M Ce^{3+} solution
14.9 g $CeCl_3$ $7H_2O$/ 100 ml, fill up with H_2O

Nitrate Standard Solution (620 mg/l):
0.1011 g KNO_3/ 100 ml, fill up with H_2O

Method

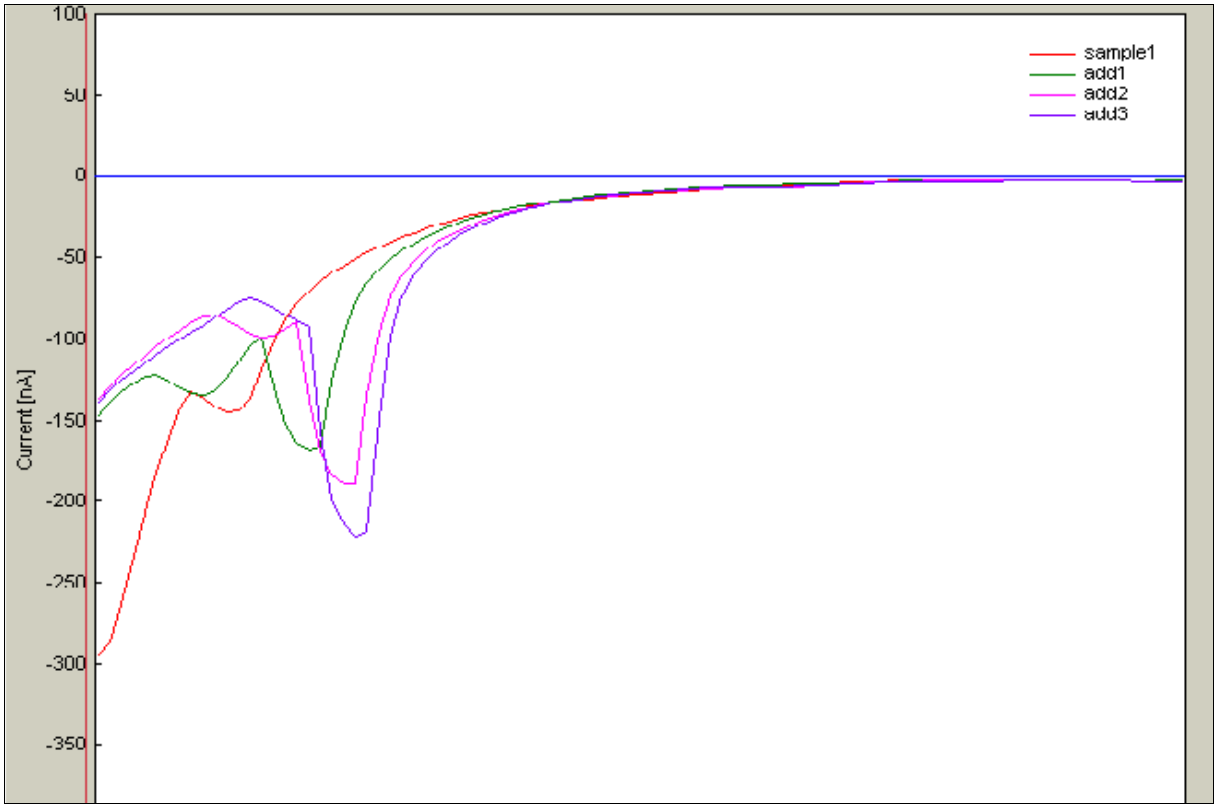
DP voltammetry

Solution

- 4 ml aqueous sample
- 2 ml supporting electrolyte
- 14 ml bidistilled water

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1200		Inert gas [s]	300-600
Final E_{fin} [mV]	-1900		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	10		Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential of NO_3^- is obtained at –1.6 V.
- Method of standard addition is used for evaluation.
- The cerium (III) chloride used must be free of any nitrates.
- The peak can shift to more positive values during standard addition.
- Two peaks can appear under the conditions given above. The more positive peak is used for evaluation.
- Detection limit 0.04 mg/l

1.2. Determination of nitrate II

Principle Voltammetric determination of nitrated benzoic acid.
Benzoic acid react with nitrate in concentrated sulfuric acid to give nitrobenzoic acid. This compound can be reduced to aminobenzoic acid at the cathode.

Reagents **Supporting Electrolyte:**
0.01 M benzoic acid dissolved in conc. H_2SO_4
0.1221 g benzoic acid / 100 ml, fill up with H_2SO_4

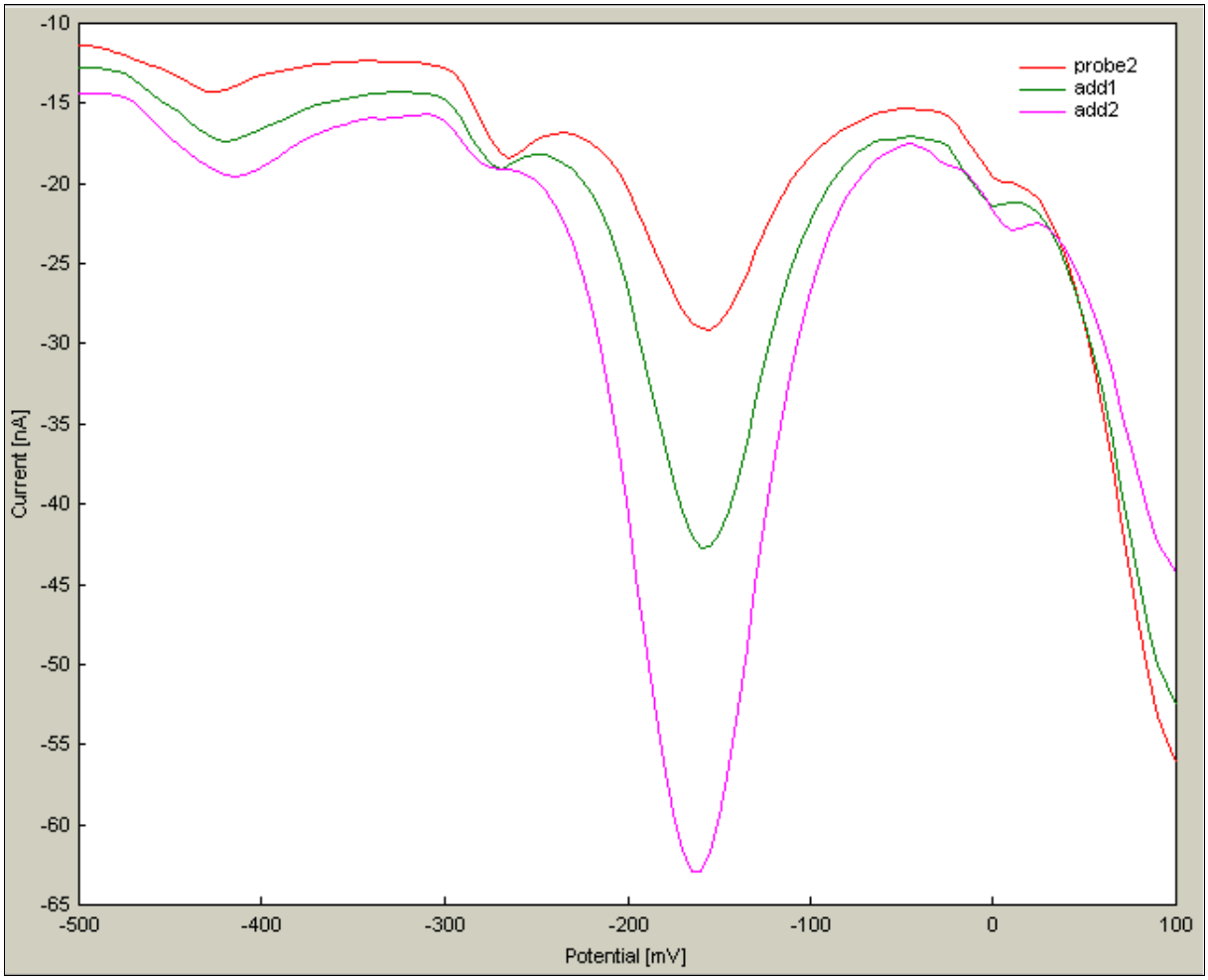
Nitrate Standard Solution (620 mg/l):
0.1011 g KNO_3/ 100 ml, fill up with H_2O

Method DP stripping-HMDE

Solution Preparation in a 25 ml volumetric flask:
- 6 ml supporting electrolyte
- 2 ml sample (or sample + nitrate standard addition)
- stir vigorously for 80 s
- add 10 ml distilled water
- fill up with water after cooling down and transfer quantitatively into the electrolytic cell

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	+100		Inert gas [s]	300-600
Final E_{fin} [mV]	-500		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	10		Accumulation potential [mV]	+100
			Accumulation time [s]	300
			Rest [s]	15
			Pulse height [mV]	-50
			Pulse width [ms]	80



- Peak appears at –158 mV
- Standard addition is used for evaluation
- Detection limit 0.01 mg/l

2. Determination of nitrites

Principle The nitrites react with diphenylamine. The nitrosodiphenylamine thus formed can be determined voltammetrically. The nitrosogroup is reduced at the cathode.

Reagents **Supporting Electrolyte:**
0.01 M diphenylamine solution
in a mixture of acetic acid and methanol (1:1)
0.17 g diphenylamine/ 100ml, fill up with the mixture

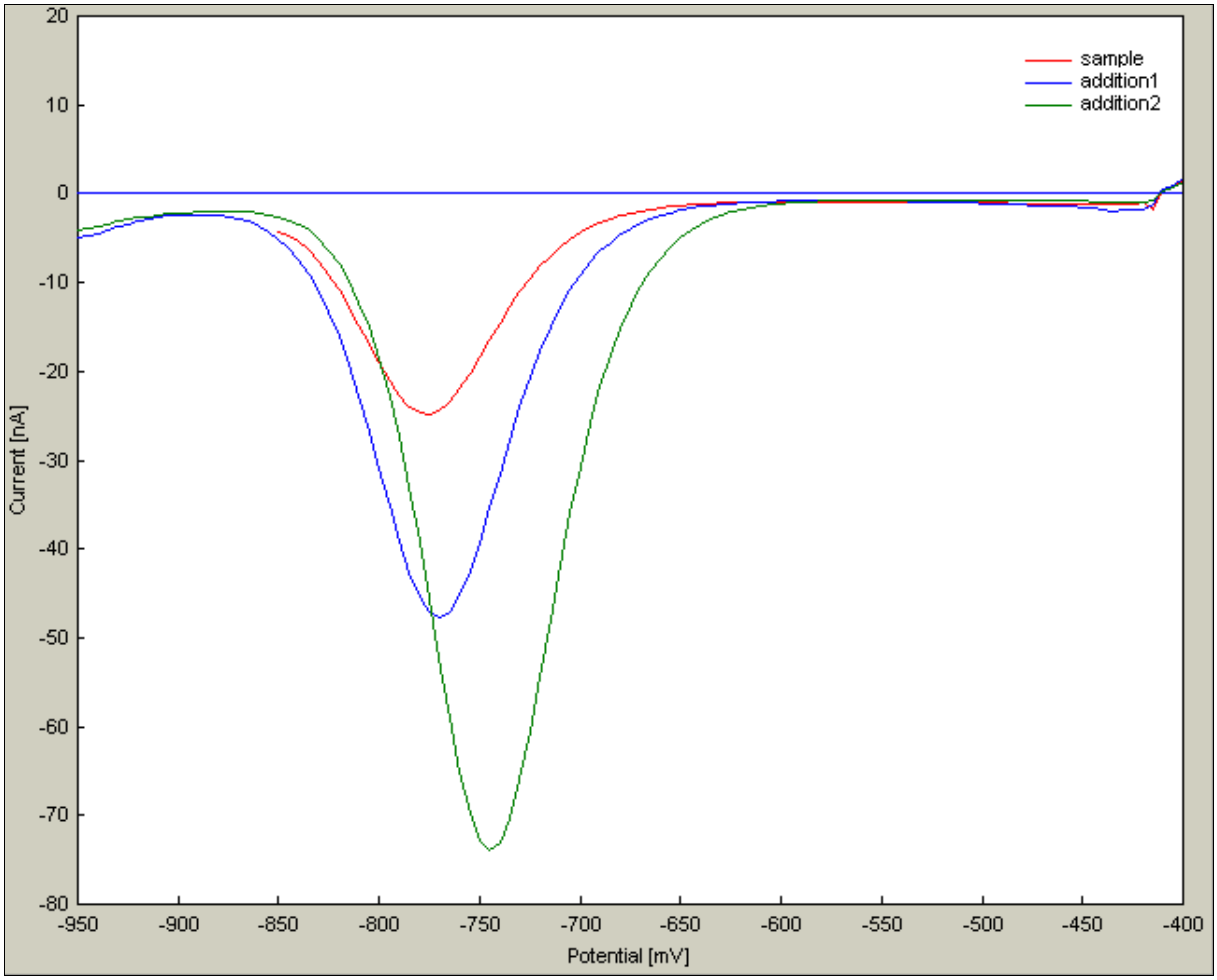
Nitrite Standard Solution (1 mg/ml):
0.14997 g $NaNO_2$/ 100 ml, fill up with H_2O
must be prepared fresh each day

Method DP-Voltammetrie

Solution
- 16 ml aqueous sample
- 4 ml diphenylamine solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-400		Inert gas [s]	300-600
Final E_{fin} [mV]	-950		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Pulse height [mV]	50
			Pulse width [ms]	80



- The peak appears at -0.75 V.
- At higher concentrations of nitrite the peak shifts into positive direction.
- Standard addition is used for evaluation.
- Detection limit 8 µg/l

3. Determination of sulfites and thiosulfates

Principle The anions SO_3^{2-} und $S_2O_3^{2-}$ are determined by the cathodic stripping voltammetry (CSV).

Reagents

Supporting Electrolytes:
2 M NaOH
8 g/ 100 ml, fill up with H_2O
2 M acetic acid
11.4 ml conc. acetic acid/ 100 ml, fill up with H_2O

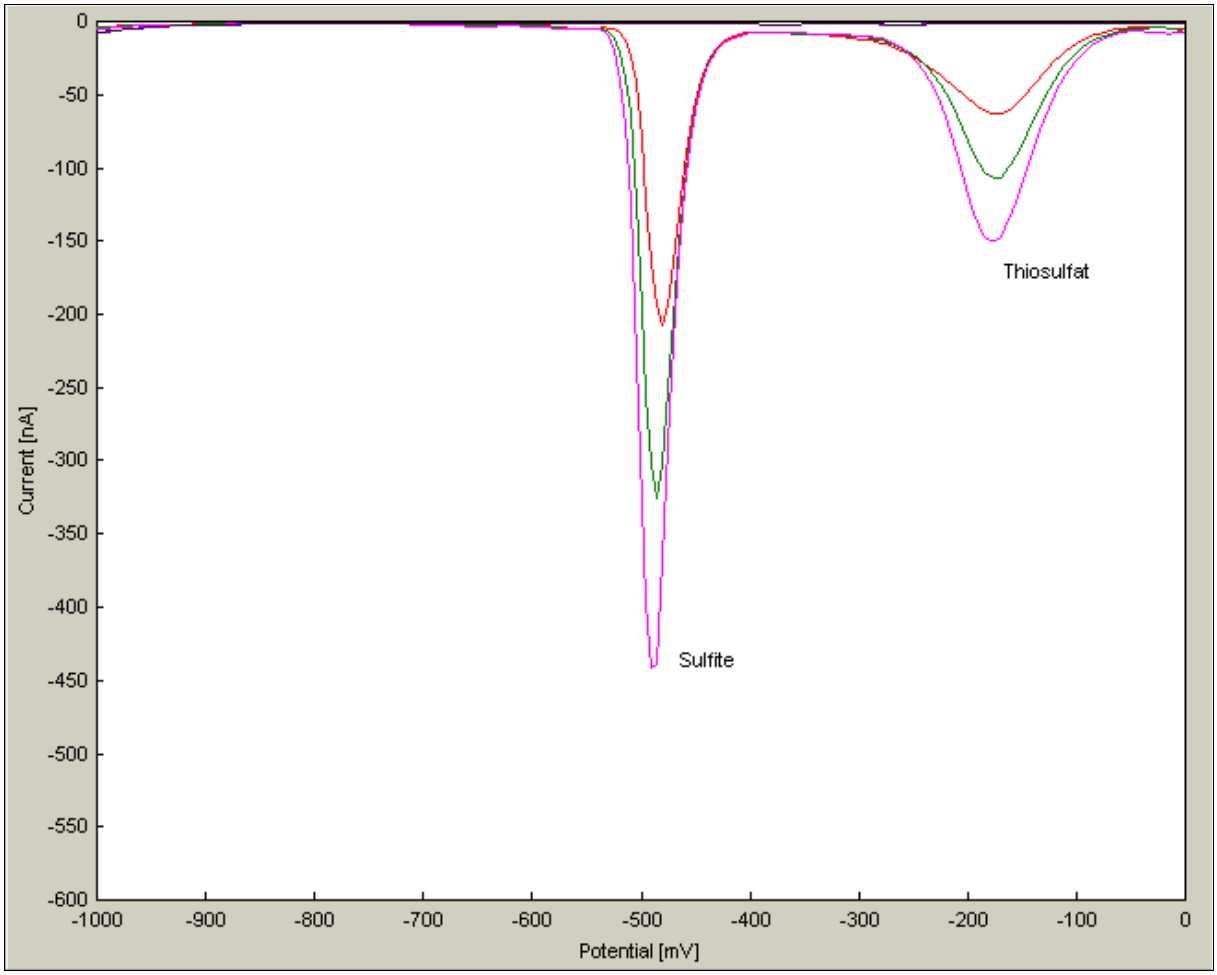
Standard Solutions (1 mg/ml):
Sulfite: 0.15742 g Na_2SO_3/ 100 ml, fill up with H_2O
Thiosulfate: 0.22133 g $Na_2S_2O_3.5H_2O$/ 100 ml, fill up with H_2O

Method DP stripping - HMDE

Solution
- 20 ml bidistilled water
- 1 ml 2 M NaOH
- 2 ml 2 M acetic acid
- purge 5 min with nitrogen
- 1 - 10 ml aqueous sample

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	0		Inert gas [s]	300-600
Final E_{fin} [mV]	-1000		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	0
			Accumulation time [s]	60
			Rest [s]	10
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak due to sulfite appears at -480 mV. The peak due to thiosulfate is at -173 mV.
- With increasing concentrations of the anions the peaks shift into negative direction.
- An accumulation time of 60 s is recommended.
- Standard addition is used for evaluation.
- Detection limits: sulfite 5 µg/l, thiosulfate 20.5 µg/l

4. Determination of cyanides

Principle Free cyanide ions can be determine by voltammetry with the hanging mercury drop electrode. In the case of analysis of a complex material, the cyanide is separated by destillation.

Reagents

Supporting Electrolyte:
1.12 g **KOH**
1.24 g **boric acid**
the pH is adjusted to 9.75 by means of KOH addition
fill up with water in a 100 ml volumetric flask

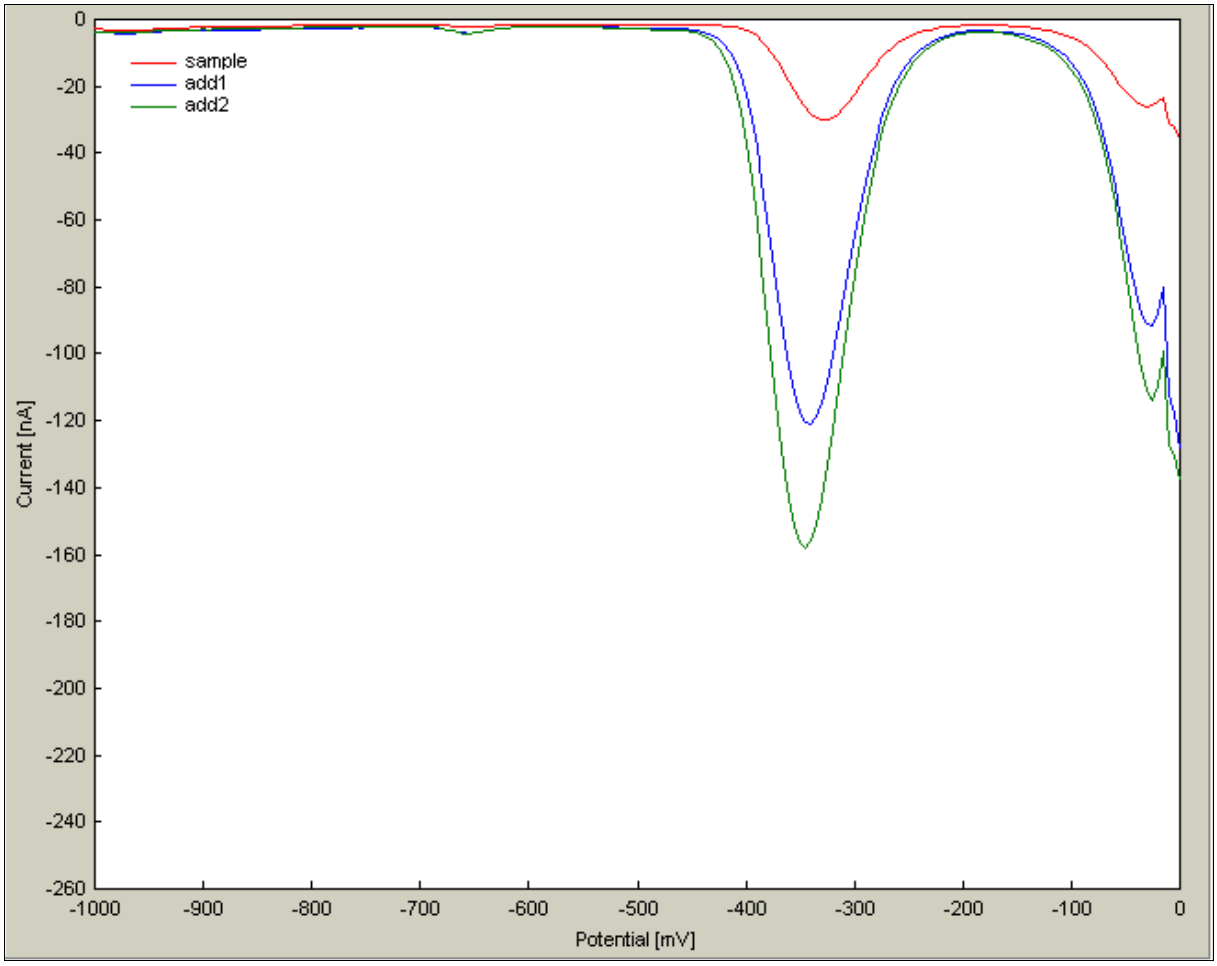
CN^- Standard Solution (1g/l):
0.2503 g KCN, 0.56 g KOH/ 100 ml, fill up with H_2O

Method DP-Voltammetrie

Solution
- 10 ml supporting electrolyte are purge with nitrogen for 5 minutes
- 10 ml aqueous sample solution are added

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	0		Inert gas [s]	300-600
Final E_{fin} [mV]	-1000		Number of scans [1]	1-3
			Pulse height [mV]	50
			Pulse width [ms]	80



- Two peaks appear, the potentials of which are -330 mV and -36 mV.
- The second peak at -330 mV is used for determination. Standard addition is used for evaluation.
- The determination is not disturbed by a 1000 fold excess of sulfates, nitrates and phosphates.
- From the complex cyanides, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ and $K_2Ni(CN)_4$ do not affect the height of the measured peak at all, $Zn(CN)_2$ and $KZn(CN)_3$ interfere when in 10 fold excess.
- When the concentration of the cyanide in the sample is higher than mg/l, it is necessary to decrease the amount of the sample in the measuring solution.
- Detection limit 7 µg/l.

5. Determination of heavy metals in water

5.1. Determination of cadmium, lead and copper in water

Principle The metals are determined by the anodic stripping voltammetry (ASV) with the hanging mercury drop electrode.

Reagents

Supporting Electrolyte:
0.1 M acetate buffer, 0.25 M NaCl
5.7 ml **conc. acetic acid**
8.2034 g **$NaCH_3COO$**
14.611 g **NaCl**
fill up with water to 1 l

Standard Solutions (1 g/l):
Cd^{2+}: 0.2282 g $CdSO_4$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O
Pb^{2+}: 0.1599 g $Pb(NO_3)$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O, **or**
0.1831 g $Pb(CH_3COO)_2$ $3H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O
Cu: 0.3929 g $CuSO_4$ $5H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

The standard solutions are diluted 1:10 and 1:100.

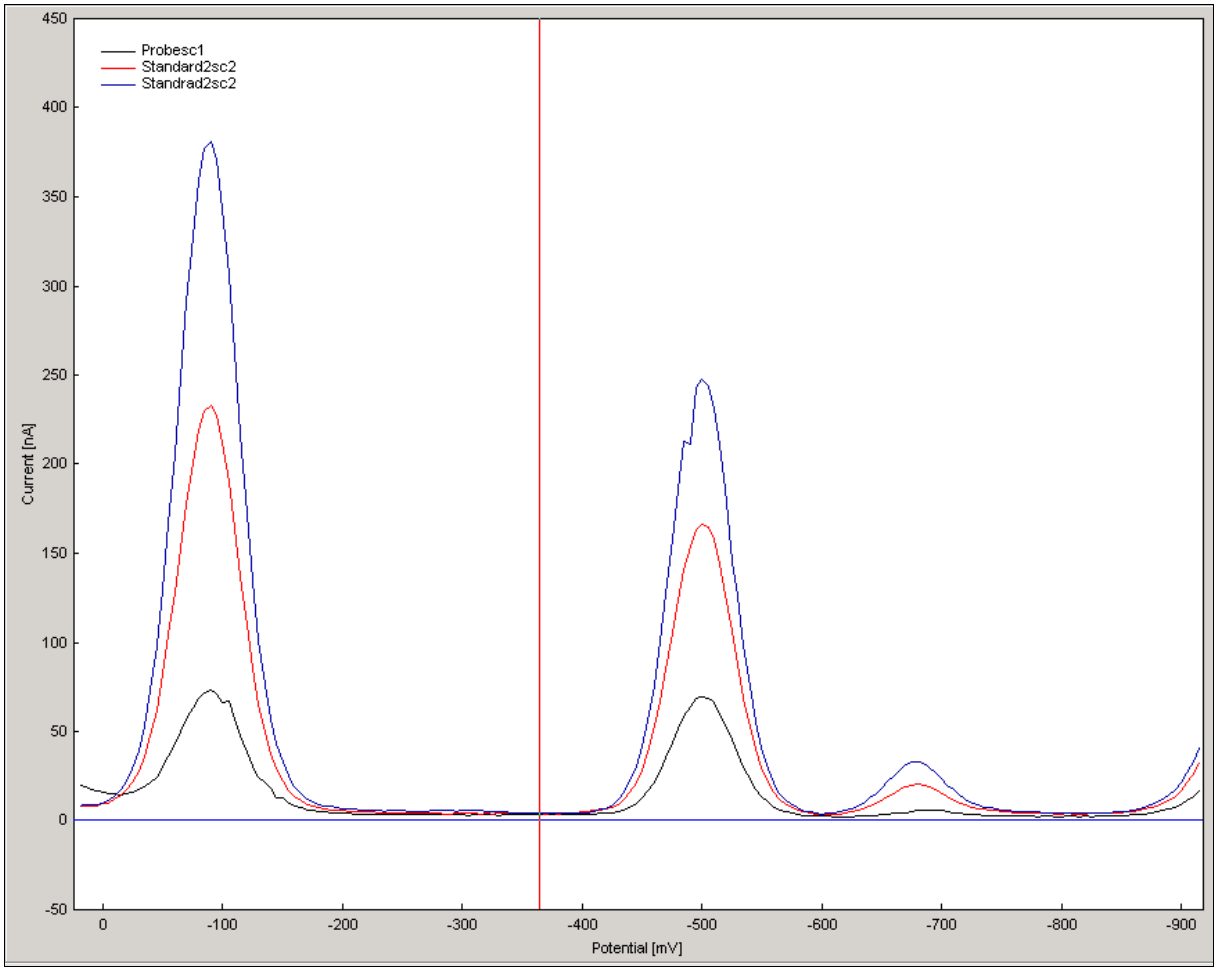
Method DP stripping-HMDE

Solution
- 10 ml water sample
- 10 ml supporting electrolyte

Waters containing minimum amount of dissolved organic substances can be measured directly; water samples containing dissolved organic compounds are first treated according to procedure given in section A.

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-900		Inert gas [s]	300-600
Final E_{fin} [mV]	0		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-900
			Accumulation time [s]	15-300
			Rest [s]	10-15
			Pulse height [mV]	50
			Pulse width [ms]	80



- In the supporting electrolyte given above, peaks are obtainable at the following position: Cu at -100 mV, Pb at -500 mV, Cd at 680 mV.
- Standard addition or calibration curve is used for evaluation.
- Blank experiment is recommended at very low concentrations.
- The accumulation time depends on the concentration of the metals. At higher concentrations, long accumulation times can result in a saturation of the electrode surface. Accumulation times longer than 300 s are not advisable.
- Detection limits depent on the qualitiy of the reagents used, under optimal conditions, the detection limit for Cd, Cu and Pb is 0.05 µg/l.

5.2. Determination of zinc, cadmium, lead and copper

Principle The metals are determined by anodic stripping voltammetry (ASV) at the hanging mercury drop electrode.

Reagents

Supporting Electrolyte:
0.1 M acetat buffer, 0.25 M NaCl
5.7 ml **conc. acetic acid**
8.2034 g **$NaCH_3COO$**
14.611 g **NaCl**
fill up with water to 1 l

Standard Solutions (1 g/l):
Cd^{2+}: 0.2282 g $CdSO_4$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O
Pb^{2+}: 0.1599 g $Pb(NO_3)$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O, **or**
0.1831 g $Pb(CH_3COO)_2$ $3H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O
Cu: 0.3929 g $CuSO_4$ $5H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O
Zn^{2+}: 0.4399 g $ZnSO_4$ $7H_2O$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

The standard solutions are diluted 1:10 and 1:100.

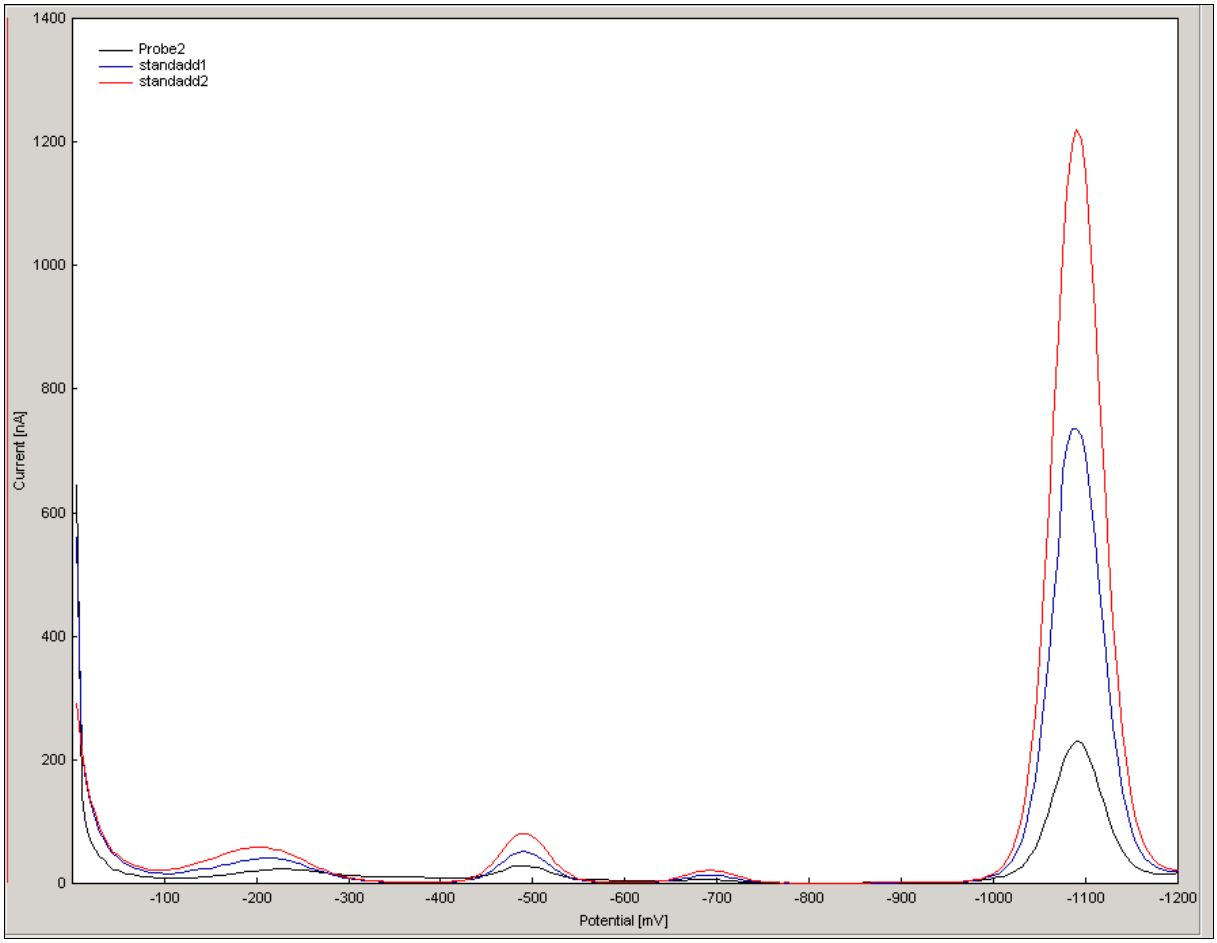
Method DP stripping-HMDE

Solution
- 10 ml water sample
- 10 ml Supporting Electrolyte

Waters containig minimum amount of dissolved organic substances can be measured directly; water samples containing dissolved organic compounds are first treated according to procedure given in section A.

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1200		Inert gas [s]	600-300
Final E_{fin} [mV]	0		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-1200
			Accumulation time [s]	15-300
			Rest [s]	10
			Pulse height [mV]	50
			Pulse width [ms]	80



- In the supporting electrolyte given above the peaks appear at: Cu -200 mV, Pb -500 mV, Cd -680 mV, Zn -1100 mV.
- Standard addition or calibration curve is used for evaluation.
- At low concentrations of the metals a blank experiment is advisable.
- The accumulation time depends on the concentration of the metals. At higher concentrations, long accumulation times can result in a saturation of the electrode surface. Accumulation times longer than 300 s are not advisable.
- Detection limits depend on the qualitiy of the reagents used, under optimal conditions, detection limit for Zn, Cd, Cu and Pb is 0.05 µg/l.
- To prevent the formation of intermetallic compound see section C1.

5.3. Determination of lead

Principle Lead is determined by anodic stripping voltammetry (ASV) with the hanging mercury drop electrode.

Reagents **Supporting Electrolyte:**
1 M HNO3
4.2 ml conc. HNO3/ 100 ml, fill up with H_2O

Standard solution (1mg/1ml):
Pb^{2+}: 0.1599 g $Pb(NO_3)$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O, **or**
0.1831 g $Pb(CH_3COO)_2$ $3H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

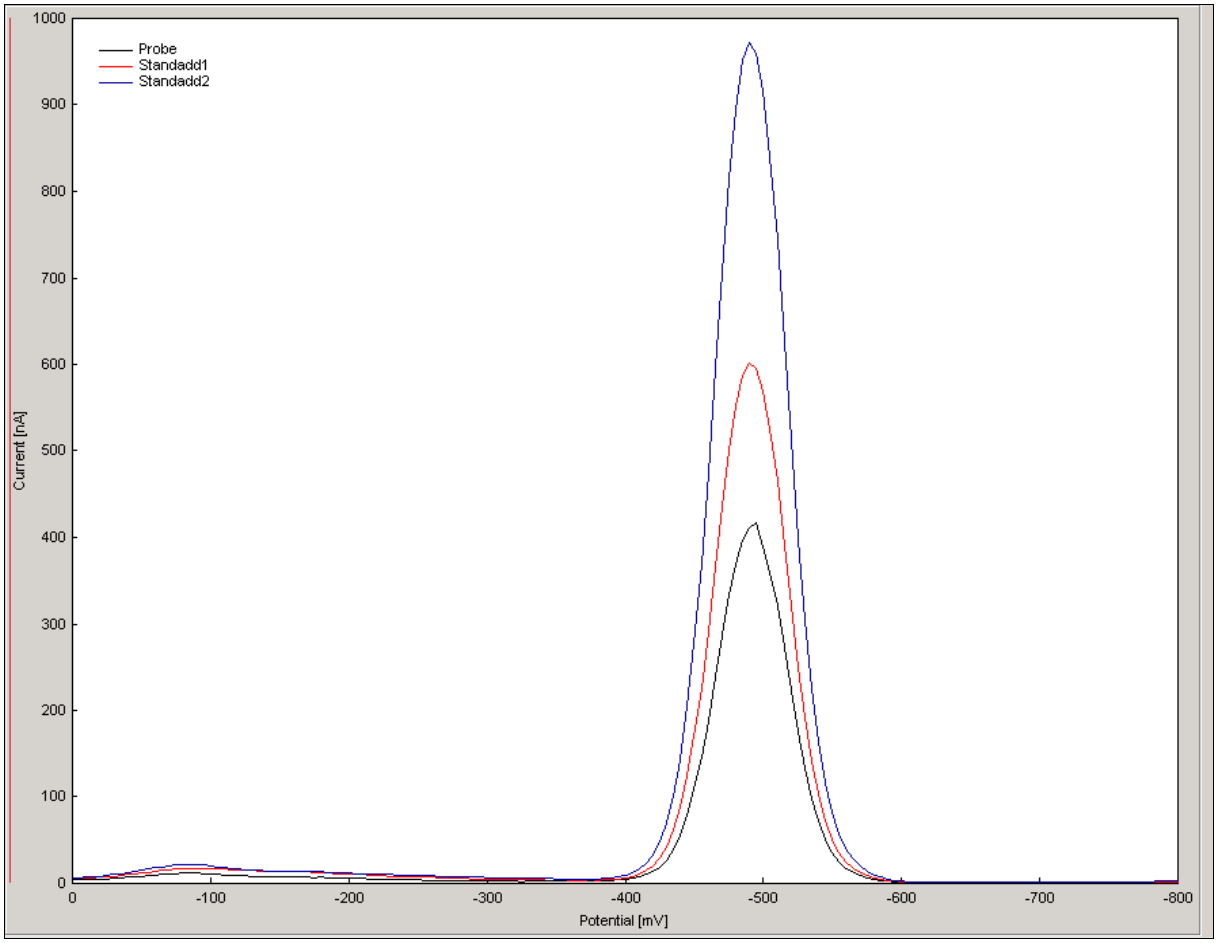
The standard solution is diluted 1:10 and 1:100.

Method DP stripping-HMDE

Solution
- 20 ml sample
- 2 ml 1 M HNO_3

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-800		Inert gas [s]	300-600
Final E_{fin} [mV]	0		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-800
			Accumulation time [s]	15-300
			Rest [s]	10-15
			Pulse height [mV]	50
			Pulse width [ms]	80



- The peak appears at -500 mV.
- Standard addition or calibration curve is used for evaluation.
- At very low concentrations a blank experiment is advisable.
- The accumulation time depends on the concentration of the metals. At higher concentrations, long accumulation times can result in a saturation of the electrode surface. Accumulation times longer than 300 s are not advisable.
- Detection limit 1 µg/l.

5.4. Determination of tin

Principle Tin is determined by anodic stripping voltammetry (ASV) at the hanging mercury drop electrode.

Reagents **Methanol**

4.8 M HCl:
40 ml conc. HCl/ 100 ml, fill up with H_2O

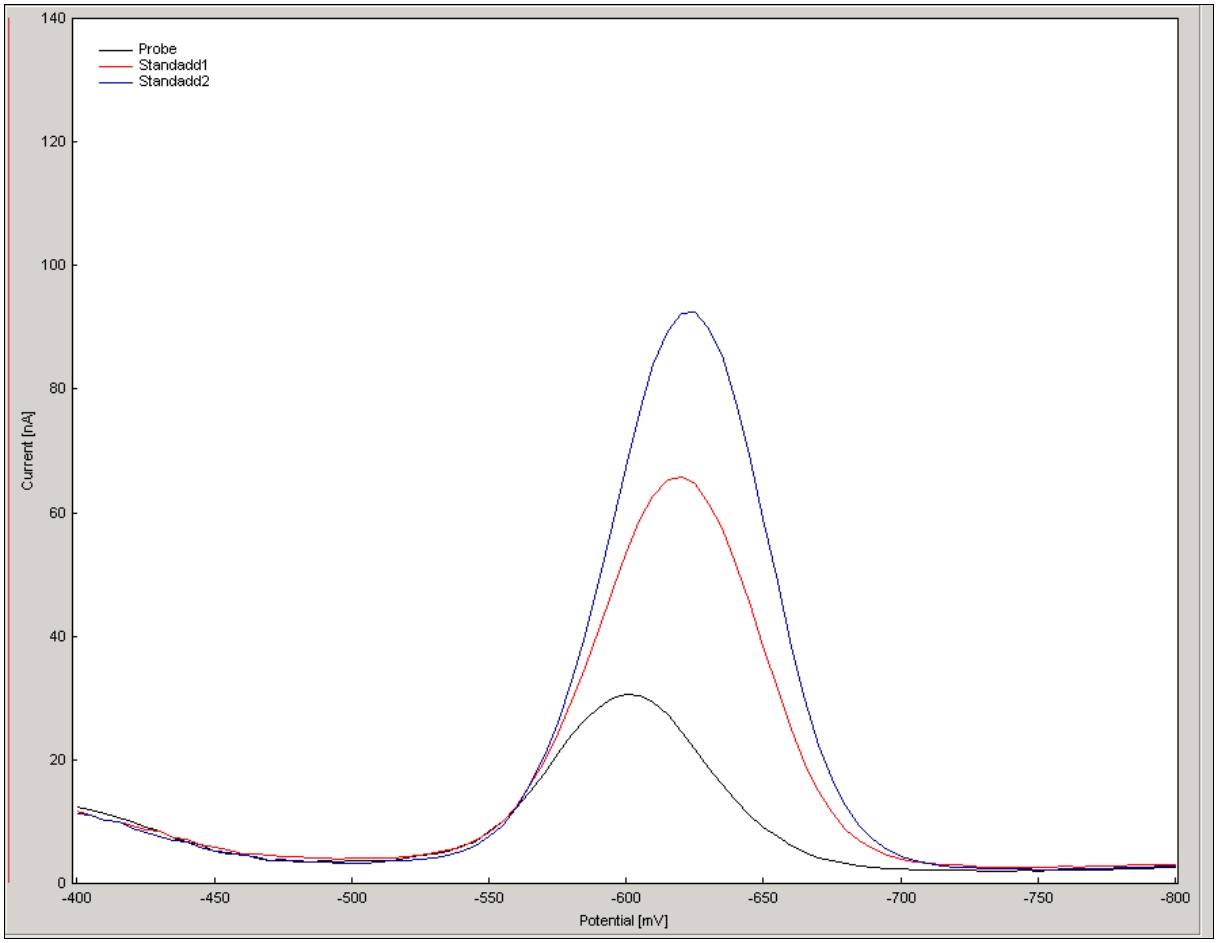
Sn^{2+}-Standard solution (1 g/l):
0.01901g $SnCl_2$ $2H_2O$, 9 ml conc. HCl/ 100 ml, fill up with H_2O

Method DP stripping-HMDE

Solution
- 10 ml sample
- 5 ml 4.8 M HCl
- purge 5 min with nitrogen
- add 5 ml methanol

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-900		Inert gas [s]	300-600
Final E_{fin} [mV]	-50		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-900
			Accumulation time [s]	15-300
			Rest [s]	10-15
			Pulse height [mV]	50
			Pulse width [ms]	80



- The tin peak is at -600 mV. It shifts to negative potentials at higher concentrations.
- Standard addition is used for evaluation.
- At very low concentrations a blank experiment is advisable.
- Detection limit 10 µg/l.

5.5. Determination of lead and tin

Principle The metals are determined by anodic stripping voltammetry (ASV) at the hanging mercury drop electrode.

Reagents **Supporting Electrolyte:**
1 vol. part conc. HCl and 9 vol. parts methanol or ethanol

Standard Solutions (1mg/1ml):
Sn^{2+}: 0.01901 g $SnCl_2$ $2H_2O$, 9 ml conc. HCl/ 100 ml, fill up with H_2O
Pb^{2+}: 0.1599 g $Pb(NO_3)$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O **or**
0.1831 g $Pb(CH_3COO)_2$ $3H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

The standard solutions are diluted 1:10 and 1:100.

Method DP stripping-HMDE

Solution
- 2 ml sample
- 18 ml supporting electrolyte

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-950		Inert gas [s]	300-600
Final E_{fin} [mV]	-150		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	5-20		Accumulation potential [mV]	-950
			Accumulation time [s]	15-300
			Rest [s]	10-15
			Pulse height [mV]	50
			Pulse width [ms]	80

- The lead peak appears at -500 mV, the tin peak appears at -650 mV.
- Standard addition is used for evaluation.
- At very low concentrations a blank experiment is advisable.
- Detection limits for lead and tin is 10 µg/l.

5.6. Determination of thallium

Principle Thallium is determined by anodic stripping voltammetry (ASV) at the hanging mercury drop electrode.

Reagents **conc. HNO_3 suprapur**

Tl^+- standard solution (1 g/l):
0.1303 g $TlNO_3$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

The standard solution is diluted 1:10 and 1:100.

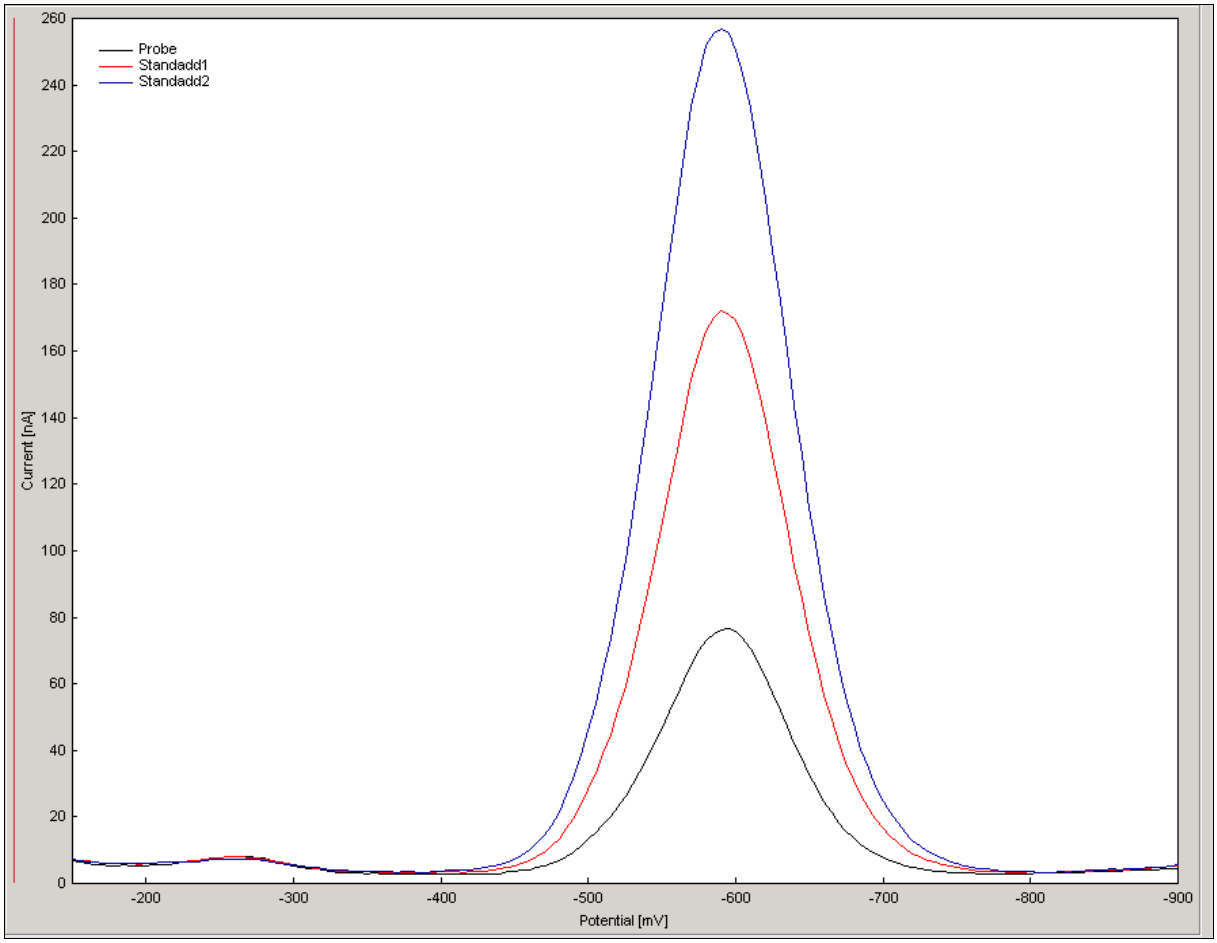
Method DP stripping-HMDE

Solution - 50 ml sample, 1 ml HNO_3/ 100 ml, fill up with H_2O
- from that solution give 20 ml into the electrolytic cell

Waters containig minimum amount of dissolved organic substances can be measured directly; water samples containing dissolved organic compounds are first treated according to procedure given in section A.

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-900		Inert gas [s]	300-600
Final E_{fin} [mV]	-150		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-900
			Accumulation time [s]	15-900
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80



- The thallium peak is at -600 mV.
- Standard addition is used for evaluation.
- At very low concentrations a blank experiment is advisable.
- Detection limit 0.05 µg/l.
- Important: This determination is strongly influenced by cadmium ions, see 5.7.

5.7. Determination thallium in the presence of cadmium

Principle Thallium is determined by anodic stripping voltammetry (ASV) at the hanging mercury drop electrode

Reagents

Supporting Electrolyte:
0.2 M acetate buffer, pH = 4.4
11.4 ml **conc. acetic acid**
16.407 g **CH_3COONa**
fill up to 1 l with H_2O

Tl^+-Standard solution (1 g/l):
0.1303 g $TlNO_3$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

10 mM EDTA:
0.292 g/ 100 ml, fill up with H_2O

The standard solution is diluted 1:10 and 1:100.

Method DP stripping-HMDE

Solution
- 50 ml sample
- 10 ml 10 mM EDTA
- fill up to 100 ml with 0.2 M acetate buffer
- fill 20 ml of that solution into the electrolytic cell

The water samples are digested according to the procedure given in section A.

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-900		Inert gas [s]	300-600
Final E_{fin} [mV]	-150		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-900
			Accumulation time [s]	15-900
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80

- The thallium peak is at -550 mV.
- Standard addition is used for evaluation.
- At very low concentrations a blank experiment is advisable.
- Detection limit 0.05 µg/l.

5.8. Determination of nickel

Principle Nickel is determined by AdSV (adsorptive stripping voltammetry). Nickel form a complex with DMG. This complex can be adsorbed and hence enriched at the mercury surface. In the determination step, the nickel ions are reduced.

Reagents **NH_3 conc.**

NH_4Cl

0.1 % dimethylglyoxime (DMG) solution in ethanol:
0.1 g DMG/ 100 ml, fill up with Ethanol

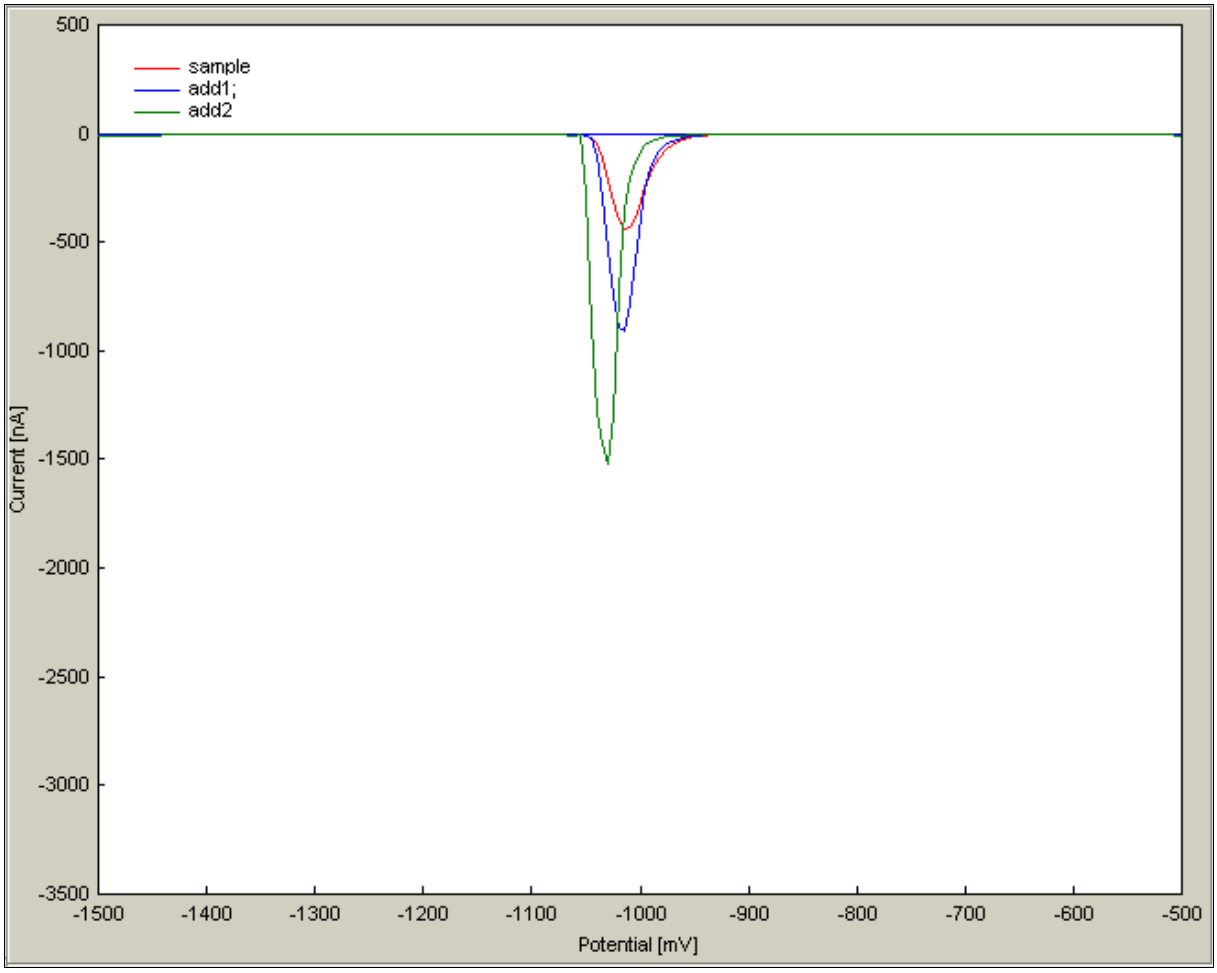
Ni^{2+}-Standard Solution (1 g/l):
0.4784 g $NiSO_4$ $7H_2O$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

Method DP stripping-HMDE

Solution
- 50 ml sample
- 1 ml conc. NH_3
- 0.5 g NH_4Cl
- fill up to 100 ml with H_2O
- 20 ml of the prepared solution are filled in the electrolytic cell with 0.1 ml of the DMG solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-500		Inert gas [s]	300-600
Final E_{fin} [mV]	-1500		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-900
			Accumulation time [s]	10
			Rest [s]	20
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential of the nickel reduction appears at -1.014 V, standard addition is used for evaluation.
- In case of low nickel concentrations, the parameters can be changed as follows: accumulation potential -500mV; accumulation time 30 – 300; sec Rest 15 sec
- The peak potential of the nickel reduction shifts to more negative potentials when the accumulation time increases.
- At very low concentrations a blank experiment is advisable.
- Detection limit 0.2 µg/l

5.9. Determination of cobalt

Principle Cobalt is determined in the same way as nickel by AdSV (adsorptive stripping voltammetry) (cf. 5.8).

Reagents **NH_3 conc.**

NH_4Cl

0.1 % dimethylglyoxime (DMG) solution in Ethanol:
0.1 g DMG/ 100 ml, fill up with Ethanol

Co^{2+}-Standard Solution (1 g/l):
0.4037 g $CoCl_2$ $6H_2O$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

Method DP stripping-HMDE

Solution
- 50 ml sample
- 1 ml conc. NH_3
- 0.5 g NH_4Cl
- fill up to 100 ml with H_2O
- 20 ml of the prepared solution and 0.1 ml of the DMG solution are given in the electrolytic cell

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-500		Inert gas [s]	300-600
Final E_{fin} [mV]	-1500		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-900
			Accumulation time [s]	10
			Rest [s]	20
			Pulse height [mV]	-50
			Pulse width [ms]	80

- The peak potential of the cobalt reduction appears at -1.2 V, standard addition is used for evaluation.
- In case of low cobalt concentrations a blank experiment is advisable.
- Detection limit 0.2 µg/l
- Nickel and cobalt can be detected simultaneously because of the good peak separation.

5.10. Determination of selenium in drinking water

Principle

Selenium is determined by cathodic stripping voltammetry (CSV). At the accumulation potential Se^{2-} is formed. This can react with metal ions in the solution to give sparingly soluble metal selenides. If copper (II) ions are present in the solution, they are reduced to copper (I) ions and Cu_2Se is formed. The copper (I) ions are reduced to metallic copper in the determination step.

Reagents

conc. H_2SO_4

NaOH solution 32%

$(NH_4)_2SO_4$

0.1 M Na_2EDTA
3.72 g/ 100 ml, fill up with H_2O

Standard Solutions:
Cu^{2+} (0.1 g/l): 0.039 g Cu_2SO_4, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O
Se(IV) (1 g/l): 0.1405 g SeO_2, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

Method

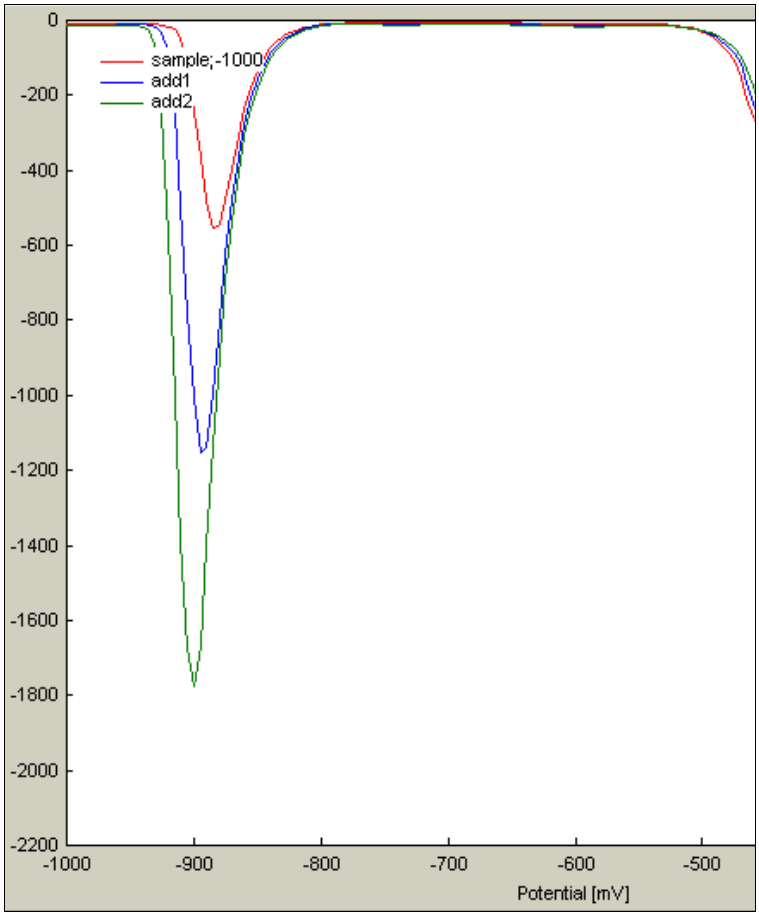
DP stripping-HMDE

Solution

- 25 ml sample
- 6.6 g $(NH_4)_2SO_4$
- 2 ml Na_2EDTA
- 0.5 ml Cu^{2+}- standard solution
- adjust the pH to 2.2 with sulfuric acid

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-200		Inert gas [s]	300-600
Final E_{fin} [mV]	-900		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-200
			Accumulation time [s]	15-300
			Rest [s]	15-20
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential for the determination of selenium is at -0.80 V.
- If the pH is not adjusted to 2.2, the peak potential shifts to -0.9 V.
- Standard addition is used for evaluation.
- At very low concentrations a blank experiment is advisable.
- Detection limit 0.63 µg/l

5.10. Determination of selenium in biological samples

Principle Selenium is determined by cathodic stripping voltammetry (CSV) (cf. 5.9.).

Reagents **Supporting Electrolyte:**
0.05 M HCl

10^{-5} M EDTA:
0.29 g EDTA/ 100 ml, fill up with H_2O

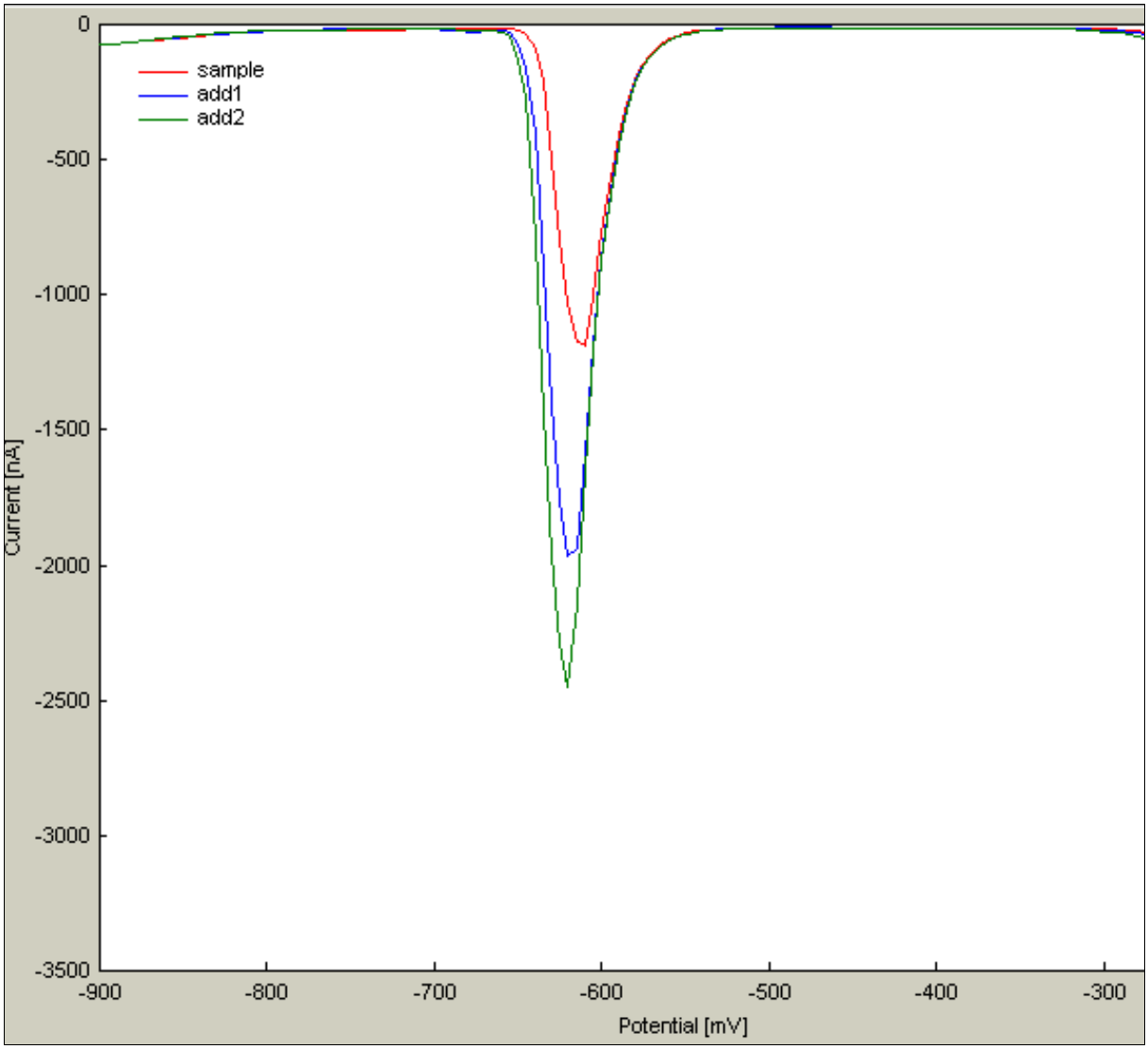
Se(IV)-Standard Solution (1 g/l):
0.1405 g SeO_2, 0.6 ml conc. -HNO_3/ 100 ml, fill up with H_2O

Method DP stripping-HMDE

Solution
- digestion of the sample as described in section A
- 1 ml sample solution
- 20 ml 0.05 M HCl
- purge with nitrogen for 10 minutes

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-200		Inert gas [s]	300-600
Final E_{fin} [mV]	-900		Number of scans [1]	1-3
Scan rate [mV.s^{-1}]	20		Accumulation potential [mV]	-200
			Accumulation time [s]	15-150
			Rest [s]	15
			Pulse height [mV]	-50
			Pulse width [ms]	80



- Two peaks appear, the potentials are -0.62 V (this peak is used for evaluation) and -0.22 V (smaller peak)
- Standard addition is used for evaluation.
- At very low concentrations a blank experiment is advisable.
- If the sample contains no copper ions, it is necessary to add some in a slight excess over the assumend selenium content.
- If the sample contains lead and copper ions in higher concentrations, it can interfere with the selenium determination. Then, 1 ml 10^{-5} M EDTA solution is added and the accumulation time increased (up to 300 s).
- Detection limit 5.7 µg/l.

5.11. Determination of total chromium content

Principle Chromium is determined as the sum of Cr(III)- and Cr(IV) ions by the method of AdSV (adsorptive stripping voltammetry) after accumulation on the surface of the hanging mercury drop electrode of a chelate with the diethylentriaminopentaacetic acid. In the cathodic determination step, the catalytic effect of nitrate ions is utilized.

Reagents

Supporting Electrolyte:
1.96 g **diethylenetriaminepentaacetic acid**
1.64 g **sodium acetate**
21.3 g **sodium nitrate**
1 ml NaOH solution (30%)
fill up to 100 ml with H_2O

Cr(III)-Standard Solution (1 g/l):
0.2828 g $K_2Cr_2O_4$/ 100 ml, fill up with H_2O

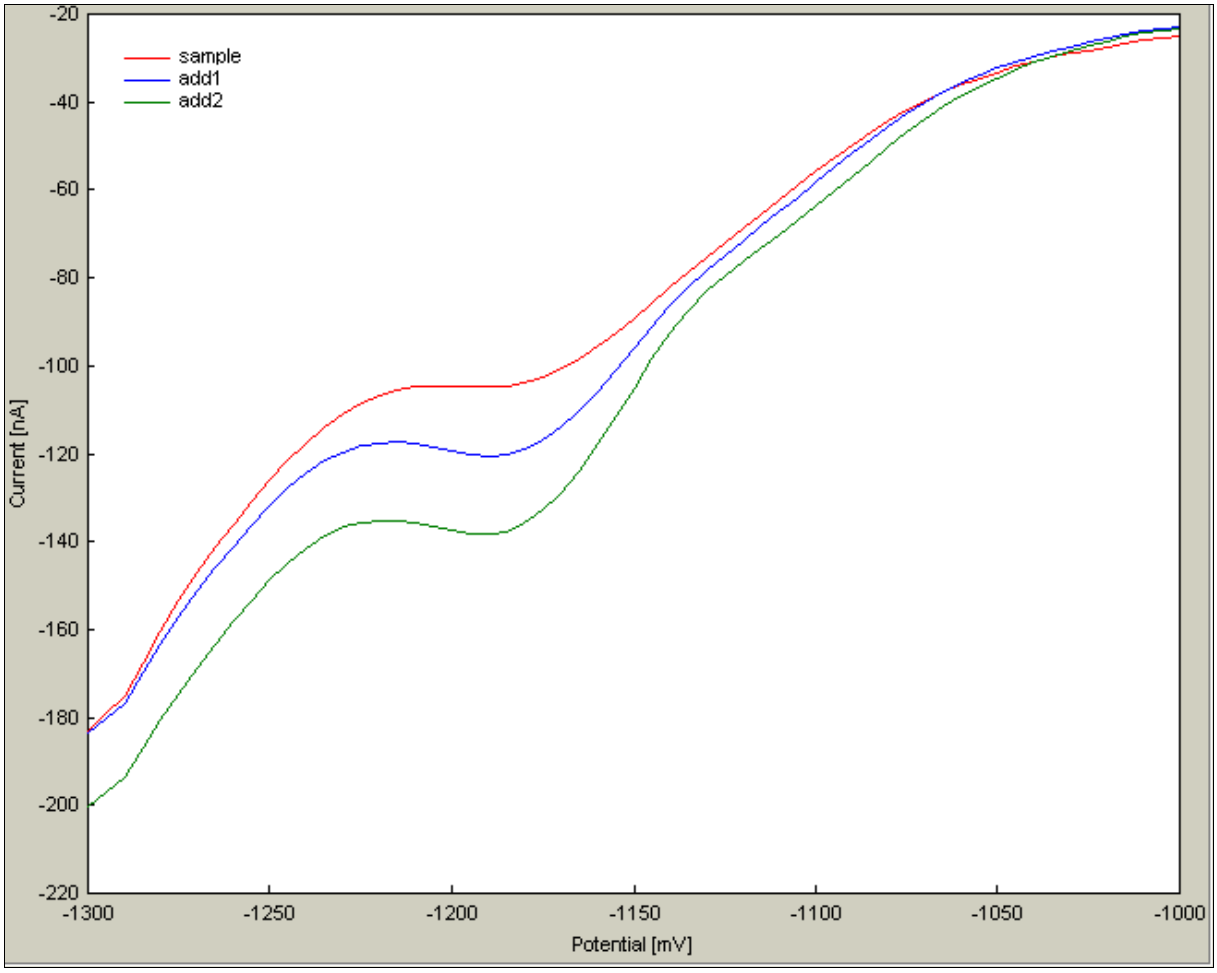
The standard solution is diluted 1:10.

Method DP stripping-HMDE

Solution
- digestion of the sample as described in section A
- 20 ml sample solution
- 1 ml supporting electrolyte
- adjust the pH to 6.2

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1000		Inert gas [s]	300-600
Final E_{fin} [mV]	-1300		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-1000
			Accumulation time [s]	100
			Rest [s]	15
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential is –1.2 V.
- Standard addition is used for evaluation.
- The adjustment of the pH plays an important role. In strong acidic solutions, the peaks are influenced by the beginning of the hydrogen evolution. In case of strong alkaline solutions, the background current is very high and no peaks are obtainable.
- Detection limit 5.5 µg/l

5.12. Determination of higher chromium contents in water

Principle Higher chromium concentrations in water are determined by CSV (cathodic stripping voltammetry).

Reagents **HCl (1:1)**

hydrogen peroxide 30 %

NaOH 1 M:
0.4 g NaOH/ 100 ml, fill up with H_2O

KCN 0.25 M:
1.63 g KCN/ 100 ml, fill up with H_2O

Cr(III)-Standard Solution (1 g/l):
0.2828 g $K_2Cr_2O_4$/ 100 ml, fill up with H_2O

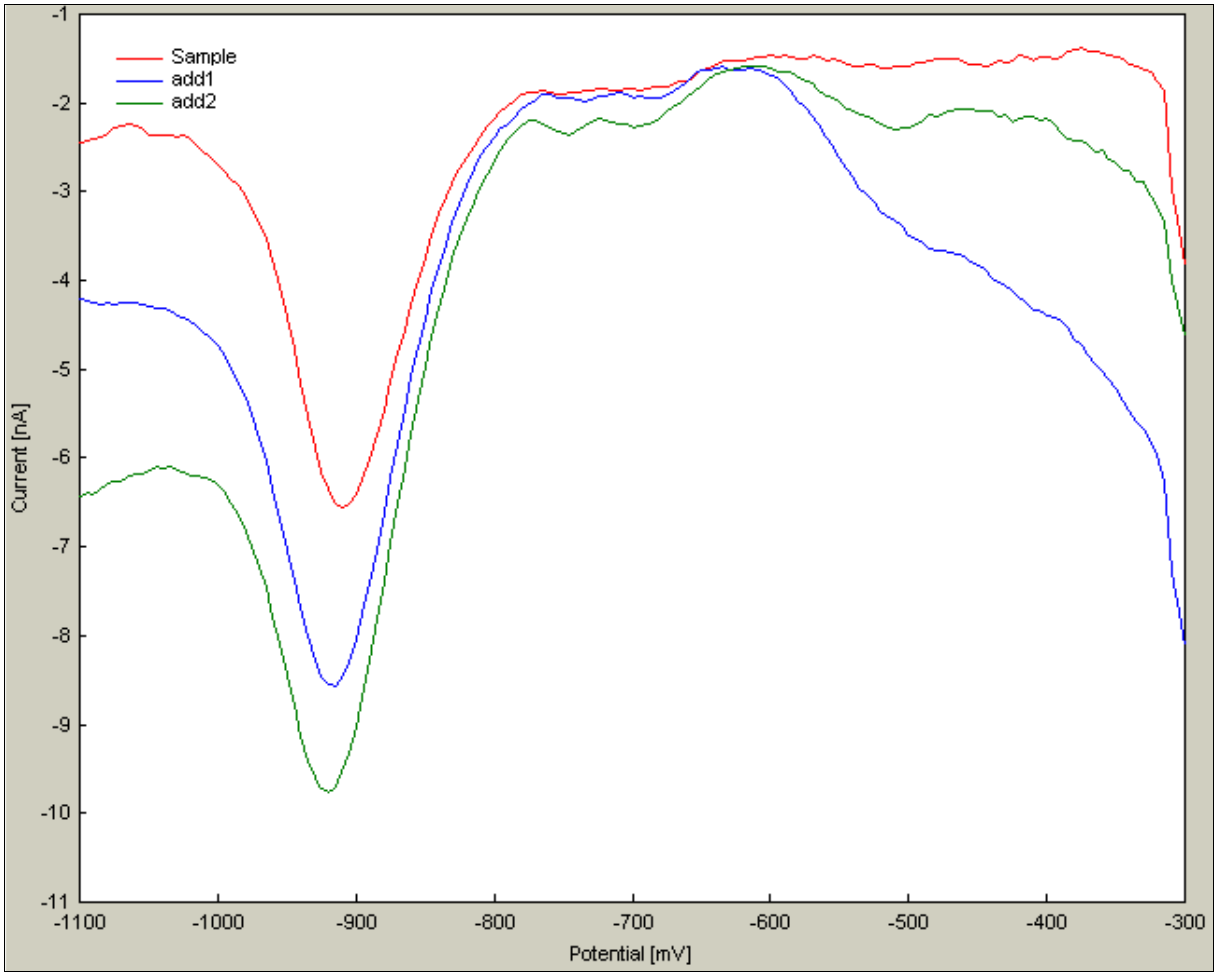
The standard solution is diluted 1:10.

Method DP stripping-HMDE

Solution
- 20 ml sample solution
- 3 drops of HCl (1:1)
- 100 µl hydrogen peroxide (1:1)
- boiling for about 10 minutes, cooling down
- 2 ml 1 M NaOH
- 50 µl 0.25 M KCN

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-300		Inert gas [s]	300-600
Final E_{fin} [mV]	-1100		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-300
			Accumulation time [s]	100
			Rest [s]	10
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential is - 900 mV.
- Standard addition is used for evaluation.
- Cyanide is added for suppressing the disturbing effect of copper if present.
- Detection limit 0.1 µg/l.

5.13. Determination of vanadium

Principle Vanadium is determined by adsorptive stripping voltammetry (AdSV). Vanadium forms with pyrocatechin a complex and can be accumulated in this form at the mercury surface (HMDE).

Reagents

Pyrocatechin $C_6H_4(OH)_2$
0.22 g/ 100 ml, fill up with H_2O,
must be prepared fresh every day

0.1 M KCl:
0.75 g KCl/ 100 ml, fill up with H_2O

0.1 % HCl

0.1 % KOH

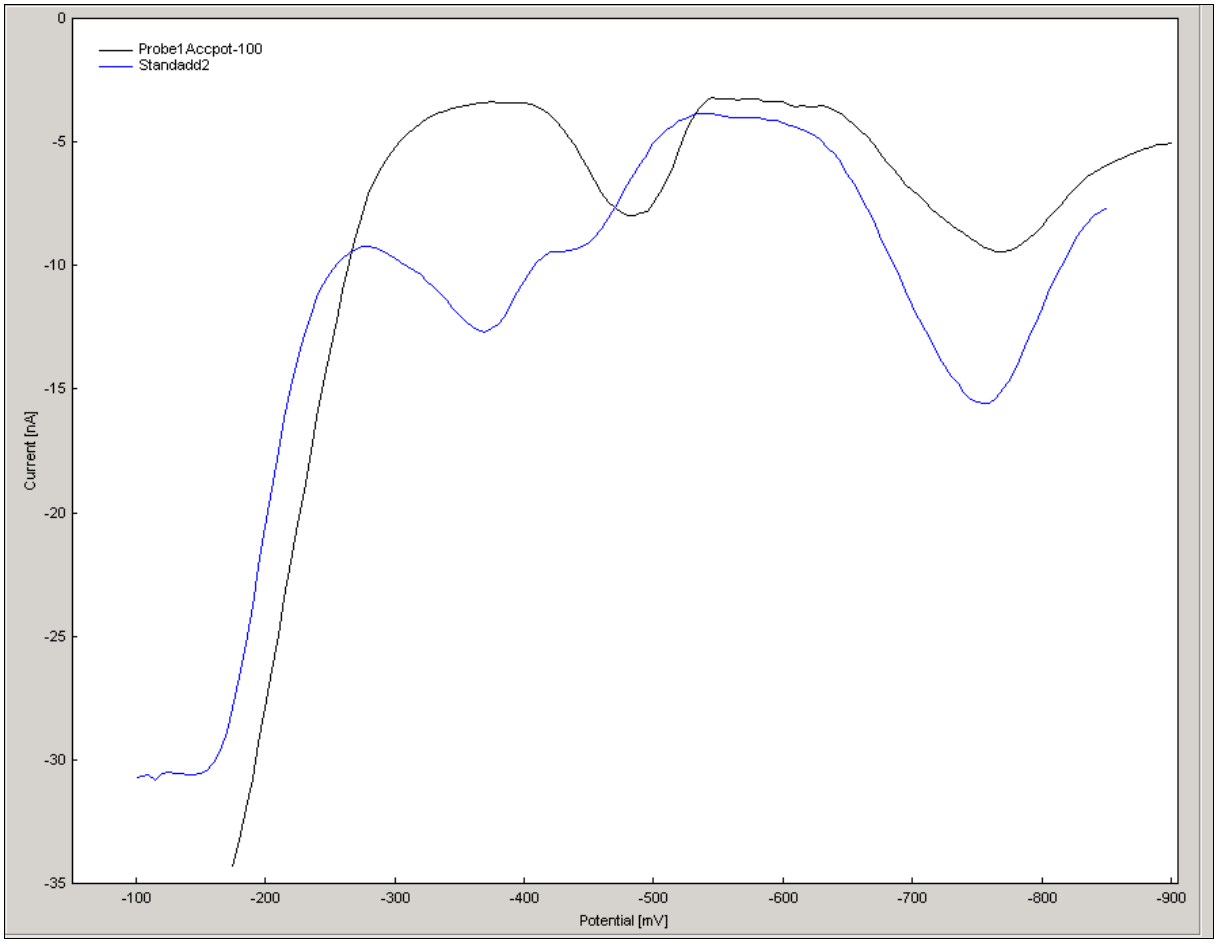
V(V)-Standard Solution (1 g/l):
0.2296 g NH_4VO_3, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

Method DP stripping-HMDE

Solution
- 20 ml sample
- 1 ml 0.1 M KCl
- adjust the pH to 6.9 with KOH and HCl
- 100 µl pyrocatechin solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-400		Inert gas [s]	300-600
Final E_{fin} [mV]	-900		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-100
			Accumulation time [s]	1-60
			Rest [s]	15
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential is - 770 mV.
- Standard addition is used for evaluation.
- The presence of surface-active compounds interferes the determination of vanadium. They must be removed as described in section A.
- For adjusting the pH value it is advantageous to use a 1 M PISES buffer [piperazin - N, N -bis (2 – ethanesulfonic) acid]: 30.2 g PISES, 3.2 ml NH_4OH/ 100 ml, fill up with H_2O.
- The natural waters often contain a small amount of uranium, the latter element in the given method yields a peak at -500 mV. Hence, small amounts of uranium do not disturb the determination of vanadium.
- Detection limit 0.02 µg/l.

5.14. Determination of molybdenum in the presence of low concentration of disturbing metals

Principle

In solution containing NO_3^- ions and 8-hydroxyquinoline molydenum(VI) gives a catalytic current advantageous for its determination by DP voltammetry.

Reagents

conc. HNO_3 and 0.01 M HNO_3:
0.4 ml conc. HNO_3/ 100 ml, fill up with H_2O

1 M KNO_3:
10.11 g KNO_3/ 100 ml, fill up with H_2O

conc. H_2SO_4

H_2O_2 30%

0.1 mM 8-Hydroxychinoline Solution:
0.145 g/ 100 ml, fill up with H_2O and dilute 1:100

Supporting Electrolyte:
50 ml 1 M KNO_3 and 50 ml 0.01 M HNO_3

Mo-Standard solution (1 g/l):
0.522 g Na_2MoO_4, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O **or**
0.1840 g $(NH_4)_6Mo_7O_{24}$ $4H_2O$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

Method

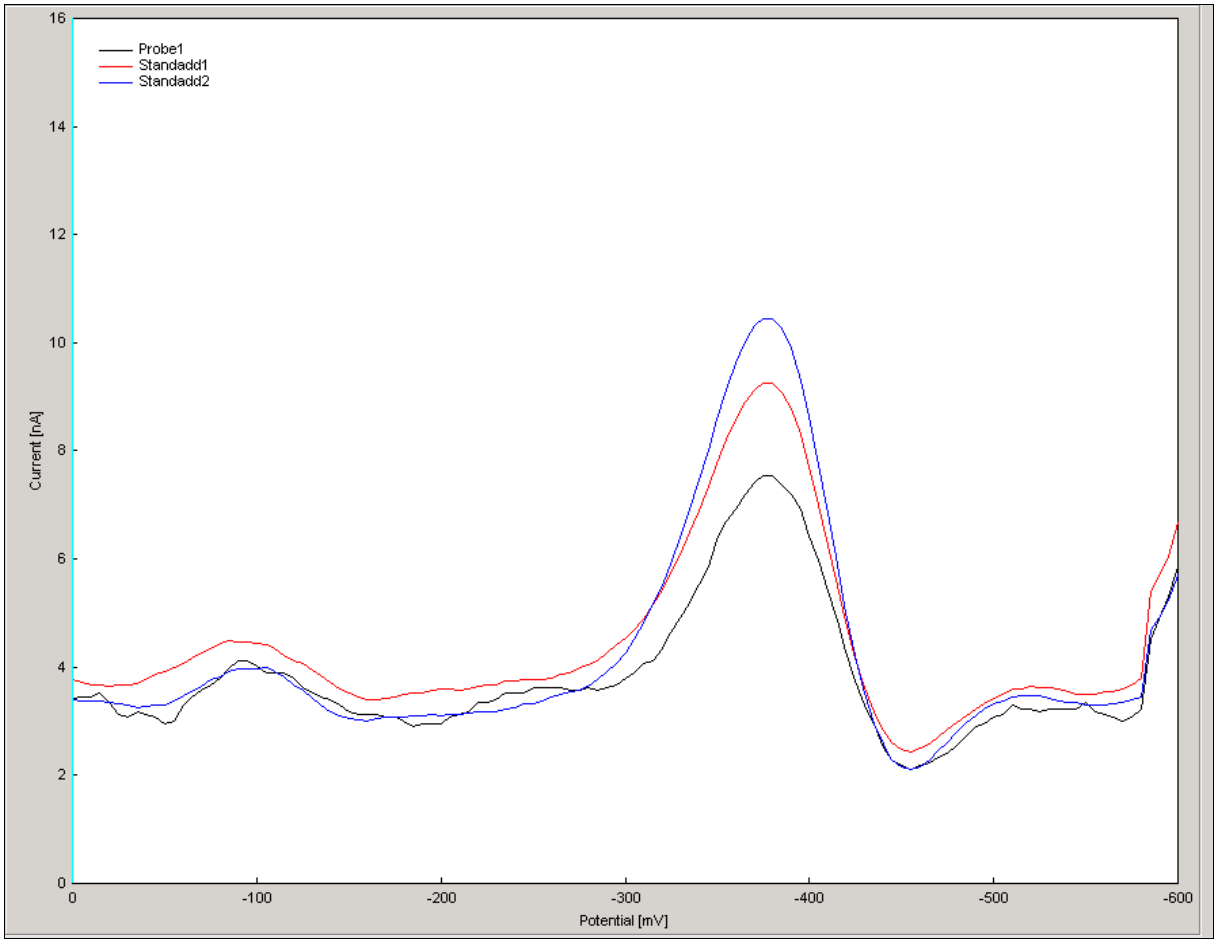
DP-Voltammetry

Solution

- stabilization of the water sample by adding 2.5 ml conc. H_2SO_4 per 250 ml sample.
- 100 ml of the acidified sample are mixed with 10ml conc. HNO_3 and 5ml H_2O_2
- 10 ml of the mixture are slowly evaporated almost to dryness
- almost dry rest is dissolved in 50 ml of the supporting electrolyte
- 20 ml of that solution is filled into the electrolytic cell
- addition of 4 ml 8-hydroxychinoline solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-600		Inert gas [s]	300-600
Final E_{fin} [mV]	0		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Pulse height [mV]	50
			Pulse width [ms]	80



- The peak potential is - 370 mV.
- Standard addition is used for evaluation.
- The method described here is even suitable for the determination of molybdenum in plant material after mineralization of the sample as given in section A.
- Detection limit 0.1 µg/l.
- Cr(VI), Cu(II), Cd(II) and Pb(II) decrease the height of the molybdenum peaks in concentrations higher than that of Mo.

5.15. Determination of lower concentrations of manganese (<0,1mg/l)

Principle

Manganese is deposited with other metals electrochemically on the surface of the mercury drop electrode. Then, manganese is selectively electrochemically dissolved at a potential, at which the other metal ions are not yet dissolved.

Hence, the solution in the close distance from the electrode surface is enriched by Mn^{2+} ions, which can be determined by a cathodic polarization.

Reagents

20 % KCl solution

2 % NaOH solution

Mn^{2+}-Standard Solution (1 g/l):
0.3602 $MnCl_2$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

The standard solution is diluted 1:10, 1:100 and 1:200.

Method

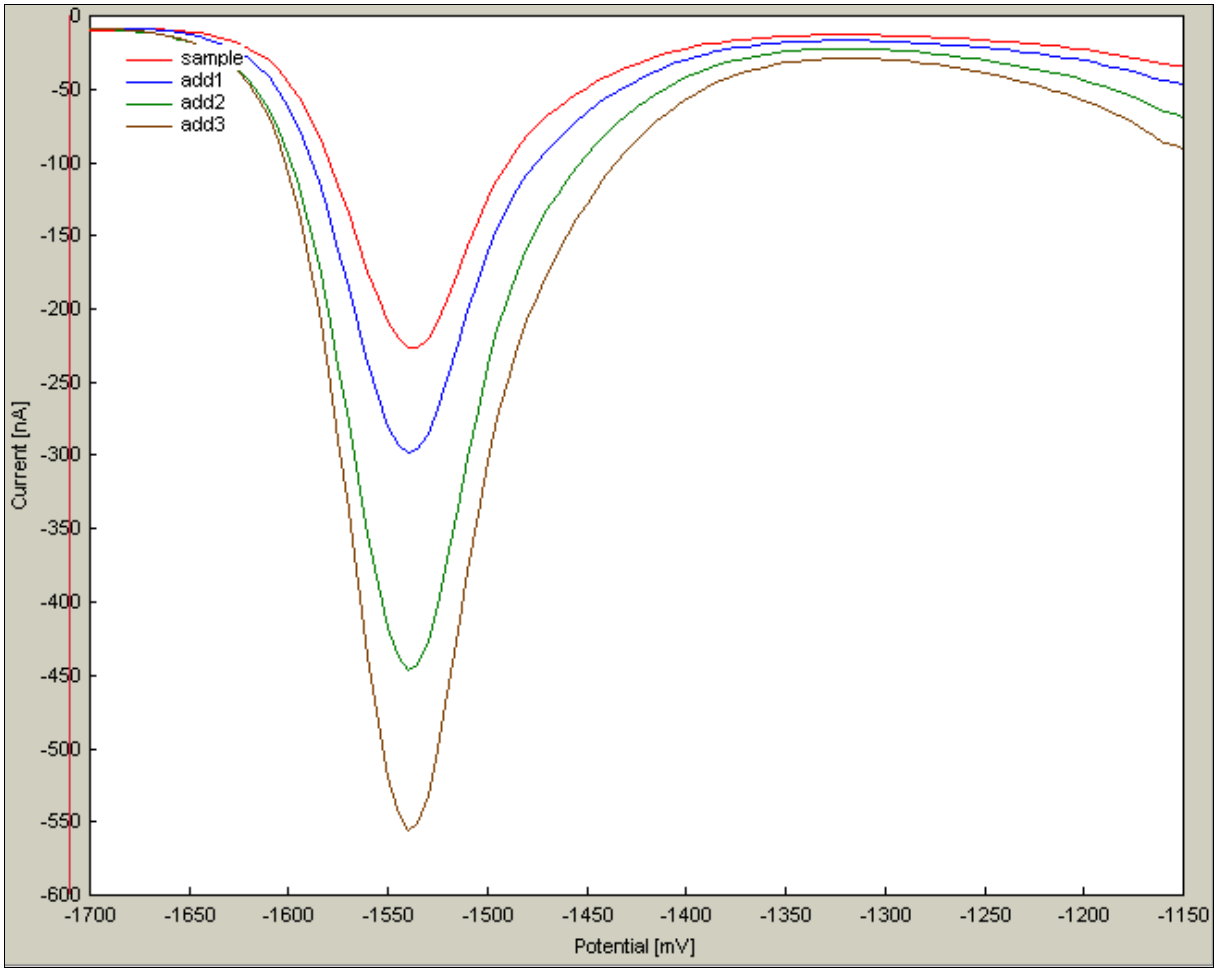
DP stripping–HMDE + Ox

Solution

- 10 ml acidified sample solution
- 10 ml bidistilled water
- 2 ml KCl solution
- adjust the pH to 6.5 by dropwise adding of the NaOH solution.

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1150		Inert gas [s]	300-600
Final E_{fin} [mV]	-1700		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-1700
			Accumulation time [s]	60
			Rest [s]	15
			Oxidation potential [mV]	-1150
			Oxidation time [s]	3
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential appears at -1.50 V.
- Standard addition is used for evaluation.
- A blank experiment is advisable.
- In case of higher concentrations of zinc ions, it must be separated before the determination.
- In case the sample contains higher amount of iron...

  ...Ferric hydroxide is precipitated while the sample solution is being brought to pH 6.5.

  ...manganese ions get adsorbed at the surface of the precipitated hydroxid.

  ...it is necessary to reduce the sample amount to 2.5 ml, or else to prolong the time of electrolysis.
- Detection limit 3 µg/l

5.16. Determination of manganese by ASV

Principle Manganese is determined by ASV (anodic stripping voltammetry)

Reagents **20 % KCl solution**

2 % NaOH solution

Mn^{2+}-Standard Solution (1 g/l):
0.3602 $MnCl_2$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

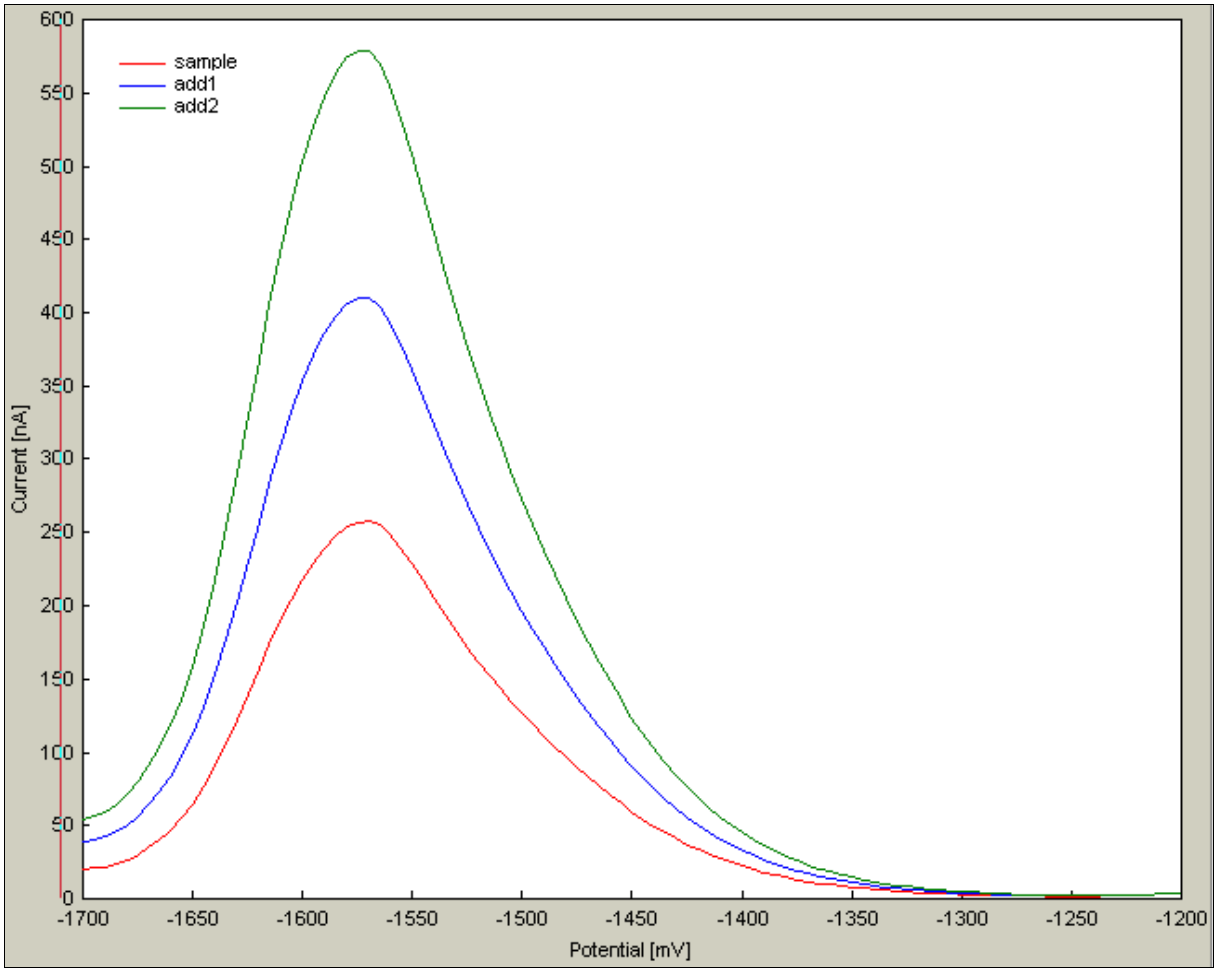
The standard solution is diluted 1:10, 1:100 and 1:200.

Method DP stripping-HMDE

Solution
- 10 ml acidified sample solution
- 10 ml bidistilled water
- 2 ml KCl solution
- adjust the pH of the solution to 6.5 by dropwise adding of NaOH

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1700		Inert gas [s]	300-600
Final E_{fin} [mV]	-1200		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	1-2		Accumulation potential [mV]	1700
			Accumulation time [s]	60
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80



- The peak potential of the manganese oxidation appears at -1.56V.
- Standard addition is used for evaluation.
- In case of higher concentrations of zinc ions, these must be separated.
- The application of a low scan rate is necessary (1-2 mV/sec).
- Detection limit 2µg/l

5.17. Determination of manganese and iron

Principle Manganese and iron are determined voltammetrically in an alkaline solution of triethanolamine.

Reagents

Triethanolamine solution:
7.5 g/ 100 ml, fill up with H_2O

5 M HCl:
45 ml conc. HCl/ 100 ml, fill up with H_2O

5 M NaOH:
20 g NaOH/ 100 ml, fill up with H_2O

Zn powder

Standard Solutions (1 g/l):
Mn^{2+}: 0.3602 $MnCl_2$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O
Fe^{3+}: 0.7234 g $Fe(NO_3)_3$ $9H_2O$, 0.9 ml conc. HCl/100ml, fill up with H_2O **or**
0.4978 g $FeSO_4$ $7H_2O$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

The standard solutions are diluted 1:10, 1:100 and 1:200.

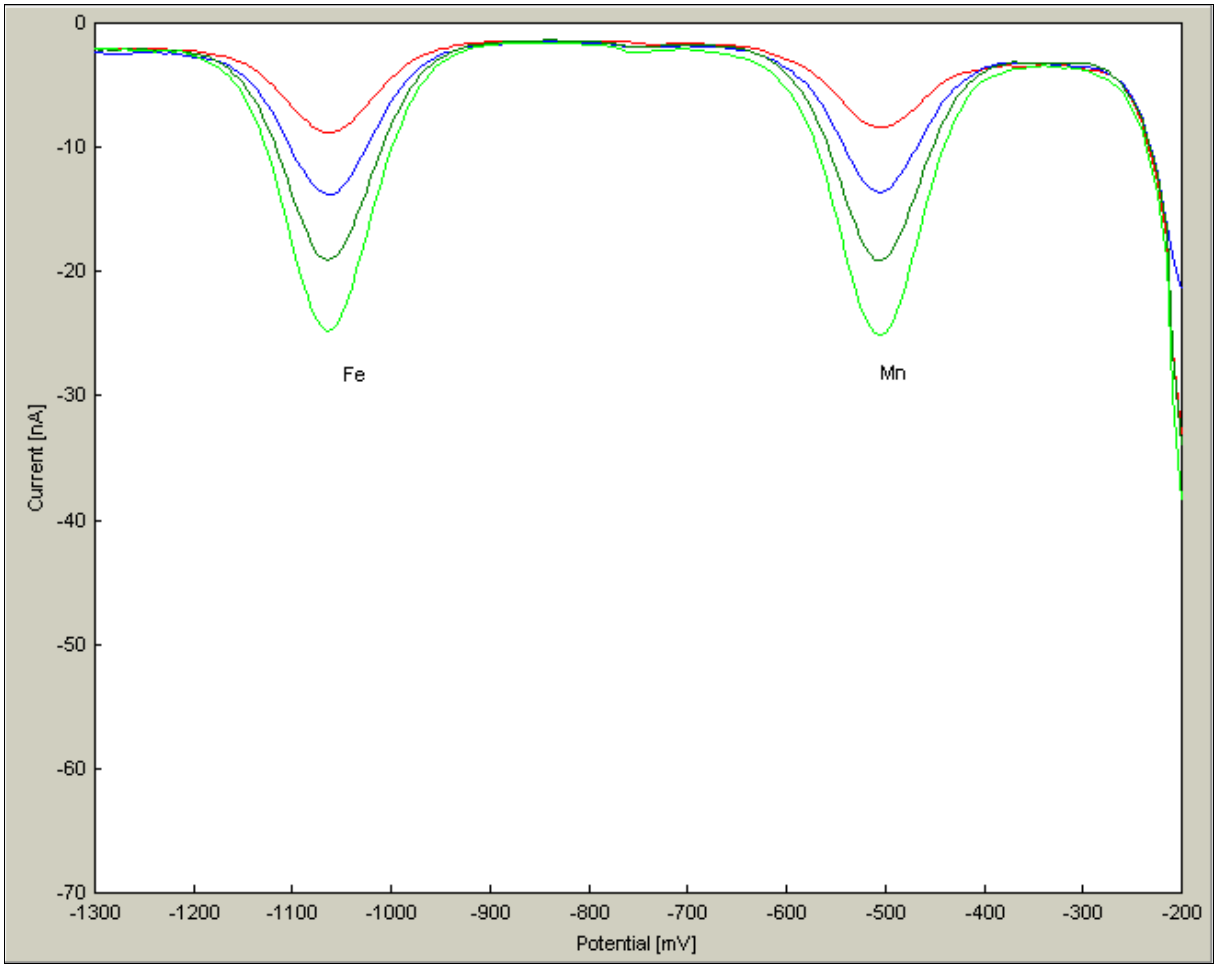
Method DP stripping-HMDE

Solution
- 20 ml aqueous solution
- 4 ml 5 M HCl
- 4 ml triethanolamine solution
- 4 ml 5 M NaOH

The solution is then to be made slowly alkaline by adding dropwise 2 ml of NaOH under intensive stirring of the solution so that the triethanolamine complex of manganese gets oxidized by air.

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-200		Inert gas [s]	300-600
Final E_{fin} [mV]	-1300		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-200
			Accumulation time [s]	0-60
			Rest [s]	0-10
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potentials of manganese and iron are -0.50 V and -1.1V.
- Standard addition is used for evaluation.
- In case the manganese and iron content is less than 1 mg/l the sample has to be made thicker by partial evaporation.
- If the sample contains Cu and Pb in amounts exceeding manganese it is necessary to separate these disturbing elements by reduction with zinc powder in the following way:
    - 20 ml sample solution
    - 0.8 ml HCl
    - 50-100 mg zinc powder
    - stirr the solution intensively for 10 s
    - filter it over a dry filter
    - filtrate is further treated as given above.
- Detection limit 0.3 mg/l

6. Determination of phosphates

Principle The phosphate is transferred into phospho-12-tungstic acid. The acid is extracted into amyl alcohol and after addition of electrolyte the concentration of the pholarographically reducible phosphotungstic acid is measured.

Reagents

0.1 M tungstate solution:
3.3 g 0 Na_2WO_4 $2H_2O$ / 100 ml, fill up with H_2O

1 M $HClO_4$:
86 ml conc. $HClO_4$/ 1 l, fill up with H_2O

Amylalcohol

2.5 % $NaClO_4$ ethanolic solution

Ethanol

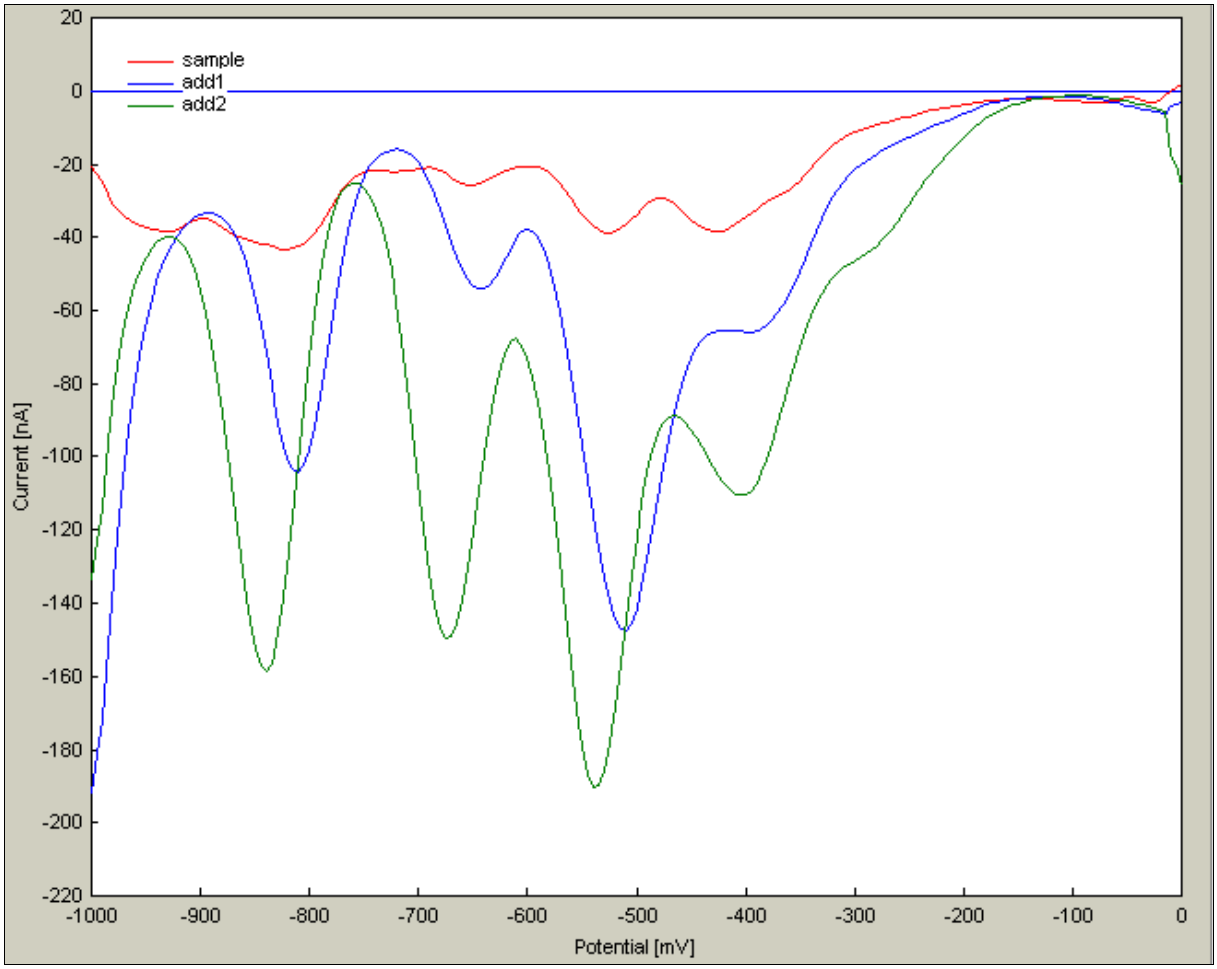
PO_4^{3-}-Standard Solution (1 g/l):
0.14329 g KH_2PO_4/ 100 ml, fill up with H_2O

Method DP voltammetry

Solution
- 5 ml sample solution
- 0.5 ml 1 M $HClO_4$
- 5 ml bidistilled water
- 1.5 ml 0.1 M Na_2WO_4 solution
- After mixing the solution is warmed in a beaker at a boiling water bath. The cooled down solution is transferred into a 100 ml separatory funnel.
- Add 10 ml amylalcohol and extract for 5 min.
- separate the organic phase and fill it into the electrolytic cell
- add 10 ml 2.5 % $NaClO_4$ solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	0		Inert gas [s]	300-600
Final E_{fin} [mV]	-1000		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Pulse height [mV]	-50
			Pulse width [ms]	80



- Because of different reduction steps, in minimum three peaks appear in the voltammogram. The peak at –800 mV is used for evaluation.
- Standard addition is used for evaluation, the sample with standard addition are prepared in the same way as the individual sample.
- Detection limit 7 µg/l

7. Determination of sulfates in water

7.1. Determination of sulfates in water I

Principle Sulfates are gradually precipitated by lead ions and their increasing excess is measured by anodic stripping voltammetry.

Reagents

Supporting Electrolyte:
0.2 M acetate buffer with pH 4.4:
11.4 ml **conc. acetic acid**
16.407 g **CH_3COONa**
fill up to 1 l mit H_2O

Methanol

Standard solution (1 g/l):
Pb^{2+}: 0.1599 g $Pb(NO_3)$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O **or**
0.1831 g $Pb(CH_3COO)_2$ $3H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

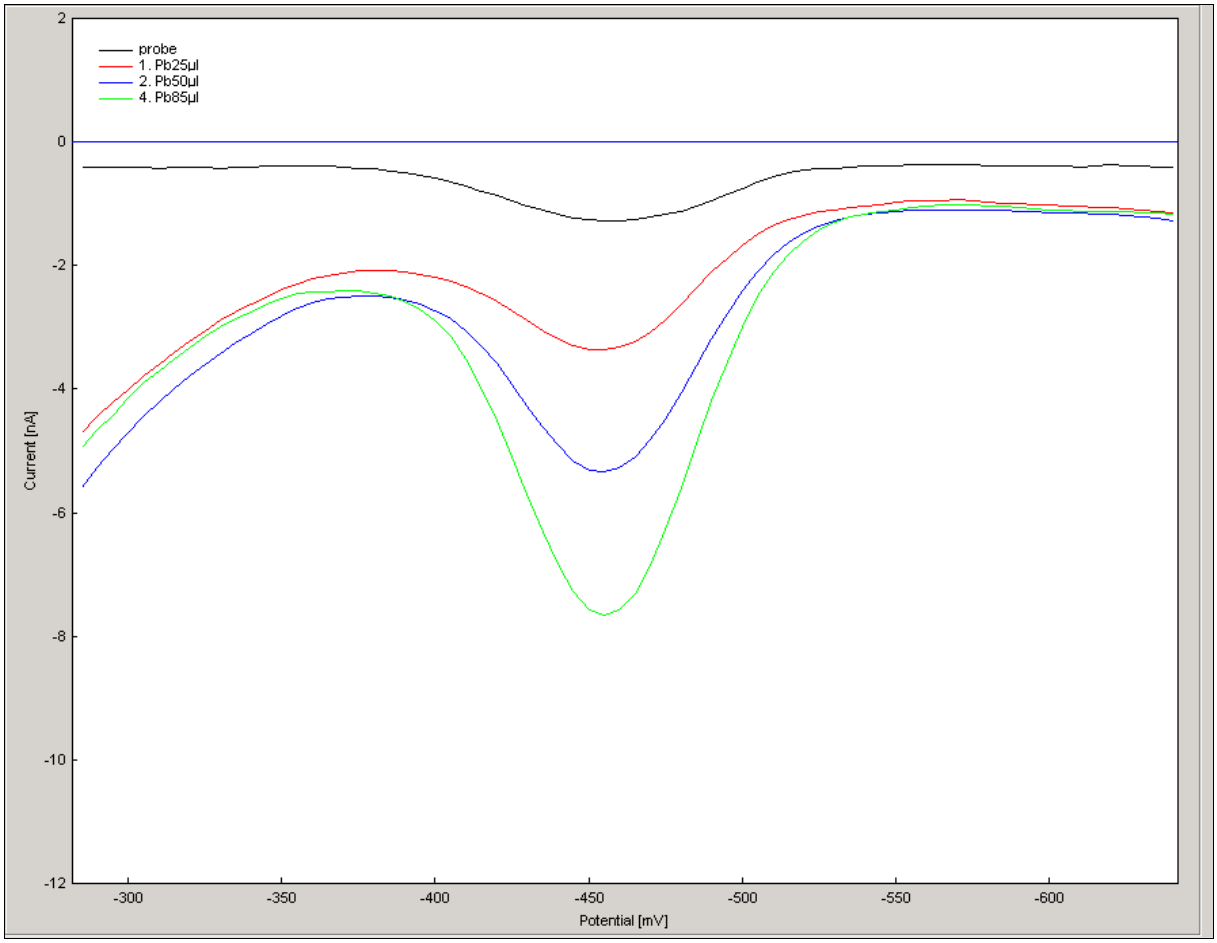
The standard solution is diluted 1:10 and 1:100.

Method DP-voltammetry

Solution
- 5 ml sample solution
- 5 ml acetate buffer
- 10 ml methanol

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-100		Inert gas [s]	300-600
Final E_{fin} [mV]	-700		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential of the lead reduction appears at -450 mV.
- On the first measurement when the sample contains only sulfate no peak of lead reduction appears.
- After measuring the sample known amounts of lead are added and this continuous until the peak due to lead starts appearing.
- The peak height of the lead reduction is plotted in a separate graphic depending on the added amount of lead ions. Two linear data sets are obtainable with different slopes: one group of points near the x axis (sulfate ions are precipitated with lead, no lead is detectable), and one group of points representing increasing amounts of lead in the solution (excess of lead ions). The abscissa of the intersection of the two straight lines determines the amount of lead ions necessary for precipitation of the sulfate ions in the solution. From stoichiometry it follows that 1 mg of Pb(II) corresponds to 0.4636 mg of sulfate ions.
- Detection limit 20 µg/l

7.2. Determination of sulfates in water II

Principle Sulfate ions are precipitated by an excess of Pb ions. The excess of lead ions is determined by anodic stripping voltammetry (ASV).

Reagents

Supporting Electrolyte:
0.2 M acetate buffer with pH 4.4:
11.4 ml **conc. acetic acid**
16.407 g **CH_3COONa**
fill up to 1 l with H_2O

Methanol

Standard solution (1 g/l):
Pb^{2+}: 0.1599 g $Pb(NO_3)$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O **or**
0.1831 g $Pb(CH_3COO)_2$ $3H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

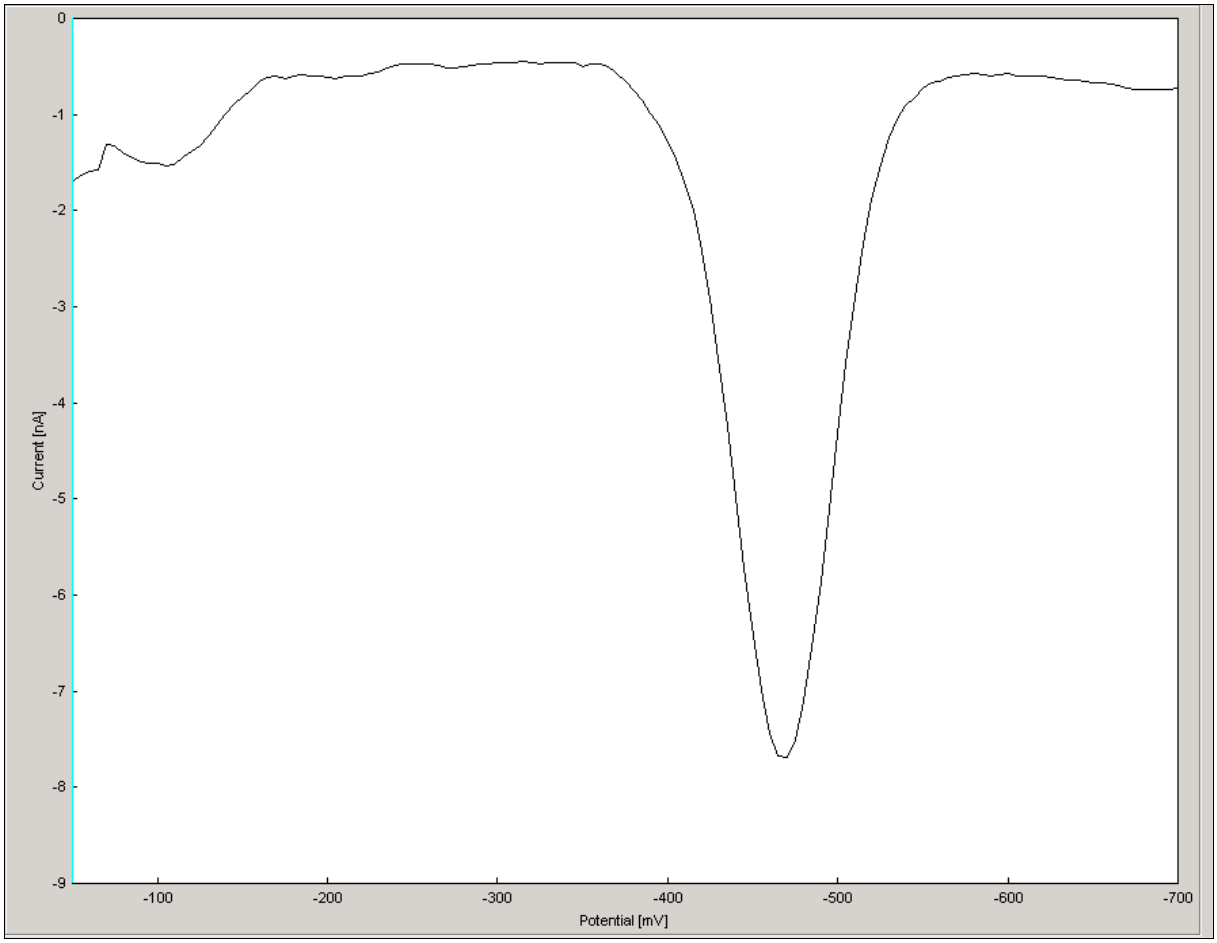
The standard solution is diluted 1:10 and 1:100.

Method DP stripping-HMDE

Solution
- 5 ml sample solution
- 5 ml acetate buffer
- 10 ml methanol
- excess of lead ion standard solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-100		Inert gas [s]	300-600
Final E_{fin} [mV]	-700		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential of the lead reduction is -450 mV.
- Standard addition is used for evaluation.
- The found amount of lead is subtracted from the amount contained in the standard solution added at the beginning of the measurement. The result gives the amount of lead necesarry for the quantitative precipitation of sulfate ions.
- From stoichiometry is follows that 1 mg of Pb(II) corresponds to 0.4636 mg sulfate ions.
- Detection limit 20 µg/l

C. Measurements with the mercury film electrode (MFE)

1. The mercury film electrode (MFE)

The hanging mercury drop electrode (HMDE) in voltammetric analysis can be in certain cases replaced by the so-called mercury film electrode (MFE). In consists in a thin layer of mercury electrolytically deposited on the surface of a graphite electrode.

The mercury film electrodes are used for the determination of traces of amalgam-forming heavy metals. The essential difference between the mercury film and the mercury drop electrodes is in the extremely small volume of the film electrode. With the mercury film thickness of $5x10^{-5}$ cm the total volume of the film electrode is about 1000 times less than that of a mercury drop of diameter equal to the diameter of the graphite disc on which the film electrode is deposited.

The film electrodes are prepared by electrolytic deposition of mercury on appropriate inert material as carbon or noble metals. It has to be borne in mind that the deposition of mercury on noble metals is accompanied by formation of amalgams the disadvantage of which is lower overvoltage of hydrogen evolution, narrowing the accessible potential span. When mercury is deposited on the surface of graphite it does not form a continuous layer but an array of microscopic spheres. The actual quality of the mercury film surface depends on the potential of electrolysis. At low potentials mercury deposits only on active centers of the graphite surface and the result is larger droplets of mercury distant from each other. It is more advantageous to use highly negative potential for the mercury deposition which leads to almost homogeneous surface film, formed by a layer of microdrops of practically equal size.

The main advantage of MFE, given by its small volume, is the possibility to determine traces of amalgam-forming heavy metals with detection limits as low as 0.1 ng/L. The anodic peaks are very narrow and better measurable than the peaks recorded with the mercury drop electrodes. The fact that it does not involve handling with metallic mercury can be regarded as a favorable feature of the MFE. The main disadvantage is the nontrivial way of renewing the electrode surface unlike with the mercury drop electrodes, and the stronger tendency toward forming intermetallic compounds due to the small volume of MFEs.

At present it is recommended to use glassy carbon (GC) as support for deposition of the mercury film. For that purpose a GC disk electrode 1-3 mm in diameter is prepared and its surface is ground and polished to mirror lusture. Alumina with grain size of 0.1 to 0.01 µm has to be used for the polishing.

The mercury deposition is done “in situ”, it means that to the solution in electrolytic cell an appropriate amount of of solution containing mercuric ions is added (the concentration of mercuric ions should be 1 - $5x10^{-5}$ M) and the deposition of the mercury film takes place simultaneously with deposition of the metallic ions to be determined. A separate formation of MFE by deposition of mercury from a solution containing only mercuric ions before electrolytic deposition of the metals to be determined from the sample solution is not recommended.

During the voltammetric measurement proper when the electrode is positively polarized, it is important to stop the voltage scan when the electrode potential reaches 0 V, especially in cases when the sample contains chloride ions. Under such conditions calomel is formed at the surface of the MFE in the region of positive potentials which disturbs the electrode surface.
An intermetallic compound is formed, e. g., during simultaneous determination of zinc and copper. The formation of the interfering intermetallic compound can be eliminated by addition of gallium ions.

The formation of Cu-Zn-Hg compounds takes place in the mercuy electrode in course of the electrolytic accumulation in the first step of the analytical determination. Under such conditions, the results are usually lower for zinc and higher for copper than expected. This is due to the fact that the electrochemical dissolution of the Cu-Zn-Hg compound occurs at a potential close to the potential of dissolution of copper itself so that the two anodic signals cannot be distinguished.

The considerable effects caused by such reasons on the precision of analytical determinations are demonstrated by the data in Table 1. They are characteristic for any type of mercury electrode; however, they appear more markedly with the MFEs in which the concentration of metals in mercury is higher than with the HMDE. When gallium ions are added to the sample solution, intermetallic Cu-Ga compound is formed which is more stable than the Cu-Zn-Hg one. It has been confirmed experimentally that after addition of Ga(III) ions to an acetate buffer containing ions of zinc, cadmium, lead and copper the anodic peak of zinc dissolution increases and that of copper decreases which markedly improves the precision of the analysis, as shown by data in Table 1. In the case of gallium it is advantageous the the metal is dissolved anodically at a potential of -0.97 V, i.e. in a potential region sufficiently remote from the anodic potentials of zinc and cadmium.

Cu [ng/ml]	Zn [ng/ml]		error [%]
	given	found	
2.4	6.3	6.3	0
	16.3	15.8	-3.1
	26.3	25.1	-4.6
12.4	8.9	7.6	-14.6
	12.3	6.9	-44.0
42.4	8.9	2.4	-73.0
	18.9	12.6	-33.5
42.4 + 400 ng/ml Ga	16.4	16.4	0
	36.4	36.1	-0.8
	46.4	45.8	-1.3

Table:
Effect of copper on the determination of zinc by method of standard addition. The data were obtained in a measurement with MFE.

2. Determination of Zn, Cd, Pb and Cu in water at a MFE

Principle The metals are determined by anodic stripping voltammetry (ASV) at a MFE.

Reagents **conc. HNO_3, suprapur**

1 M Sodium Acetate Solution:
8.2 g/ 100 ml, fill up with H_2O

Standard Solutions (1 g/l):
Cd^{2+}: 0.2282 g $CdSO_4$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O
Pb^{2+}: 0.1599g $Pb(NO_3)_3$, 0.6 ml conc. HNO_3/ 100ml, fill up with H_2O **or**
0.1831 g Pb $(CH_3COO)_2$ $3H_2O$, 0.6ml conc. HNO_3/ 100ml, fill up with H_2O
Cu^{2+}: 0.3929 g $CuSO_4$ $5H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O
Zn^{2+}: 0.4399 g $ZnSO_4$ $7H_2O$, 0.9 ml conc. HCl/ 100ml, fill up with H_2O
Ga^{3+}: 0.2525 g $GaCl_3$, 0.9 ml conc. HCl/ 100ml, fill up with H_2O
Hg^{2+}: 0.1354 g $HgCl_2$, 2.6 ml conc. H_2SO_4/ 100ml, fill up with H_2O

The standard solutions are diluted 1:10 and 1:100.

Method DP-stripping solid

Solution
- 50 ml sample + 0,5 ml conc. HNO_3 + 1 ml acetate solution
fill up with water to 100 ml
- 20 ml sample
- 200 µl Hg standard solution
- 200 µl of the 1:100 Ga standard solution

Waters containing minimum amount of dissolved organic substances can be measured directly; water samples containing dissolved organic compounds are first treated according to procedure given in section A.

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1250		Inert gas [s]	600-900
Final E_{fin} [mV]	150		Number of scans [1]	1
Scan rate [$mV.s^{-1}$]	20		Cleaning potential [mV]	200
			Cleaning time [s]	2-5
			Accumulation potential [mV]	-1300
			Accumulation time [s]	1-600
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80

- The peak potentials are:
  Zn -1080 mV, Cd -650 mV, Pb -450 mV, Cu -10 mV, Ga -830 mV.
- Standard addition is used for evaluation.
- At very low concentrations a blank experiment is advisable.
- In the case that zinc content is not to be determined, it is not necessary to add Ga salt and the parameter are adjusted in the sence that the accumulation and also the initial potential change to -850 mV, The other parameters remain unchanged.
- Detection limit for Zn, Cd, Pb and Kupfer is 0.05 µg/l

D. Further applications

1. Determination of vitamin C in fruit juices and jams

Principle Vitamin C – ascorbic acid – is electrooxidized at a mercury electrode and hence can be determined directly by voltammetric measurement.

Reagents

Supporting Electrolyte:
0.1 M acetat buffer:
5.7 ml **conc. acetic acid**
8.2034 g **$NaCH_3COO$**
fill up to 1 l mit H_2O

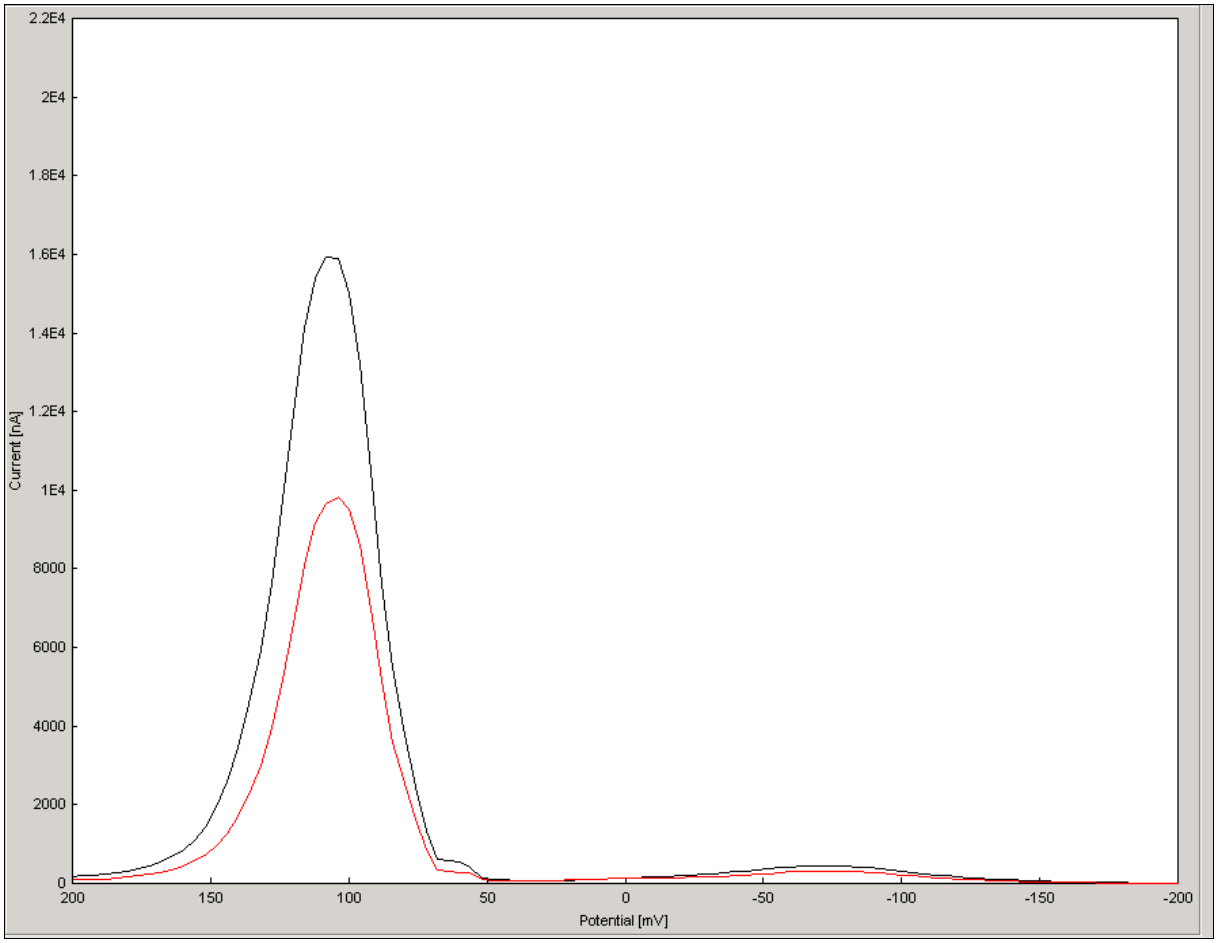
Standard Solution of ascorbic acid (1 g/l)
has to be prepared fresh each day

Method DP voltammetry

Solution
- 20 ml buffer, purge for 10 min
- 0.2 ml fruit juice or 1-5 g jam, purge again for at least 1 min

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-200		Inert gas [s]	300-600
Final E_{fin} [mV]	+250		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Pulse height [mV]	50
			Pulse width [ms]	80



- The peak potential of the oxidation of ascorbic acid appears at 100 mV.
- Standard addition is used for evaluation.
- Detection limit 0.1 mg/l.

2. Determination of riboflavine

Principle Riboflavine can be reduced directly at the surface of the mercury electrode.

Reagents

Supporting Electrolyte:
0.05 M KCl:
3.728 g KCl/ 100 ml, fill up with H_2O
0.1 M K_2CO_3:
1.382 g K_2CO_3/ 100 ml, fill up with H_2O
0.3 M KOH:
1.683 g KOH/ 100 ml, fill up with H_2O

Sample:
Multivitamin tablets: 1 tablet is dissolved in 50 ml 0.03 M KOH

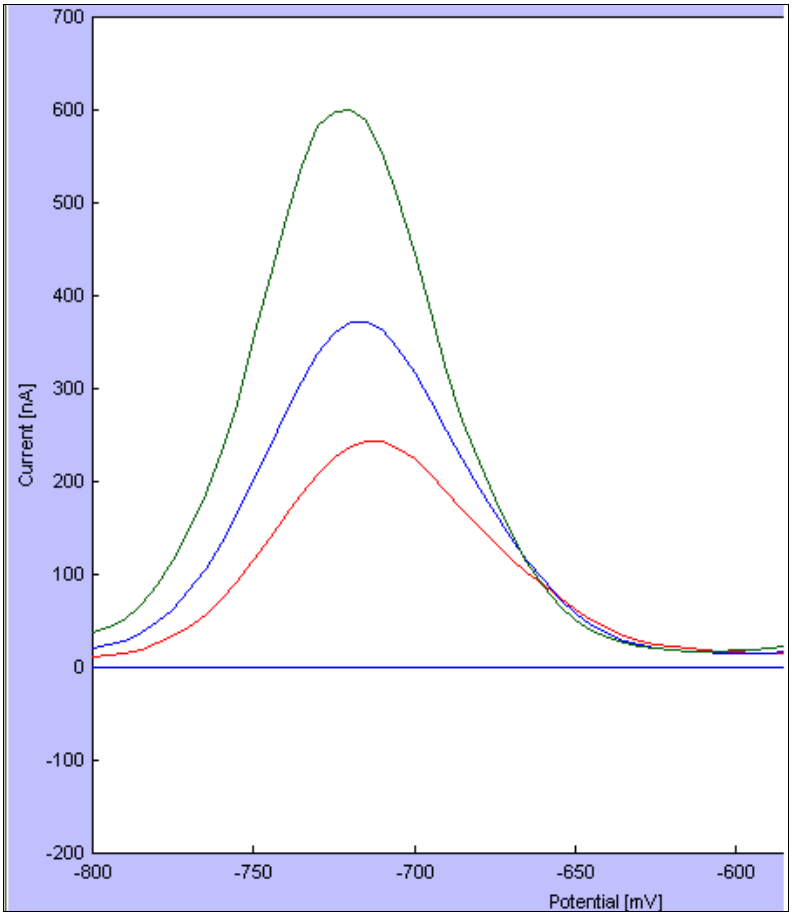
Riboflavine Standard Solution (1 g/l)

Method DP voltammetry

Solution
- 3 ml sample solution
- 17 ml supporting electrolyte

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-550		Inert gas [s]	300-600
Final E_{fin} [mV]	-800		Number of scans [1]	1-3
Scan rate [mV.s^{-1}]	3		Pulse height [mV]	50
			Puls width [ms]	80



- The peak potential is –720 mV.
- Standard addition is used for evaluation.
- Detection limit 0.26 mg/l.

3. Determination of pyridoxine (vitamin B_6) in multivitamin tablets

Principle Pyridoxine is oxidized with active mangan dioxide to give pyridoxal. This can be reduced at the surface of the mercury electrode.

Reagents

2.5 M NaOH:
10 g NaOH/ 100 ml, fill up with H_2O

MnO_2

Phosphate buffer pH 6.8:
7.16 g Na_2HPO_4, 2.8 g KH_2PO_4/ 1 l, fill up with H_2O

Sample:
multivitamin tablets, 1 tablet is dissolved in 40 ml phosphate buffer
add 1 g of MnO_2
shake for 1 h
excess of MnO_2 is separated by centrifugation

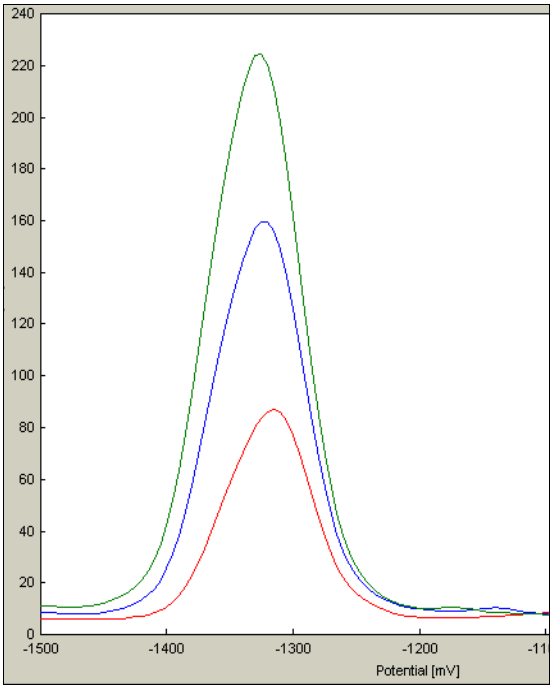
Pyridoxine Standard Solution (1 g/l)

Method DP voltammetry

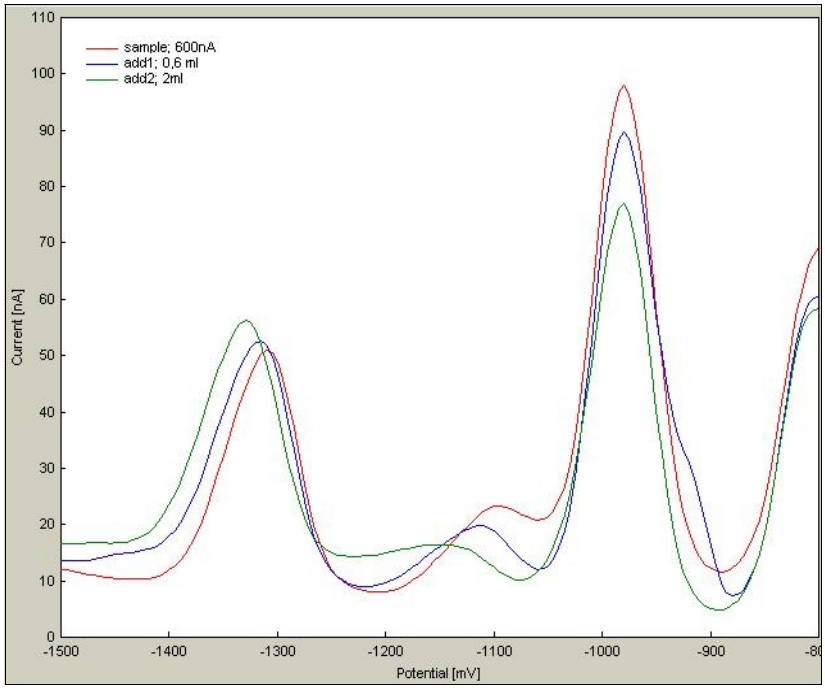
Solution
- 15 ml sample solution
- 5 ml NaOH

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-800		Inert gas [s]	300-600
Final E_{fin} [mV]	-1500		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	5		Pulse height [mV]	50
			Puls width [ms]	80



A.) Pyridoxin Standard Solution



B.) Pyridoxine in a multivitamin tablet.
The peak at -1 V is caused by nicotinamide.

- The peak potential of pyridoxine is –1320 mV.
- There is no interference with other vitamins.
  The peak caused by nicotinamide is sufficiently remote from the pyridoxine peak to allow the determination of both compounds, simultaneously.
- Standard addition is used for evaluation.
- The quality of the determination depends strongly on the kind of the vitamin tablets.
  The method is not applicable to tablets containing surface-active colloids because of the strong adsorption of these compounds at the electrode surface.
- It is very important to separate the excess of MnO_2 very carefully, because otherwise the peaks are broardened (interfering side reaction: reduction of manganese in many steps)
- Pyridoxal is not stable in aqueous alkaline solutions. The polarograms have to be reported immediatly after sample preparation (less than 30 min).
- Detection limit 68.82 mg/l

4. Determination of coumarin in vodka

Principle Coumarin is reduced at the hanging mercury electrode.

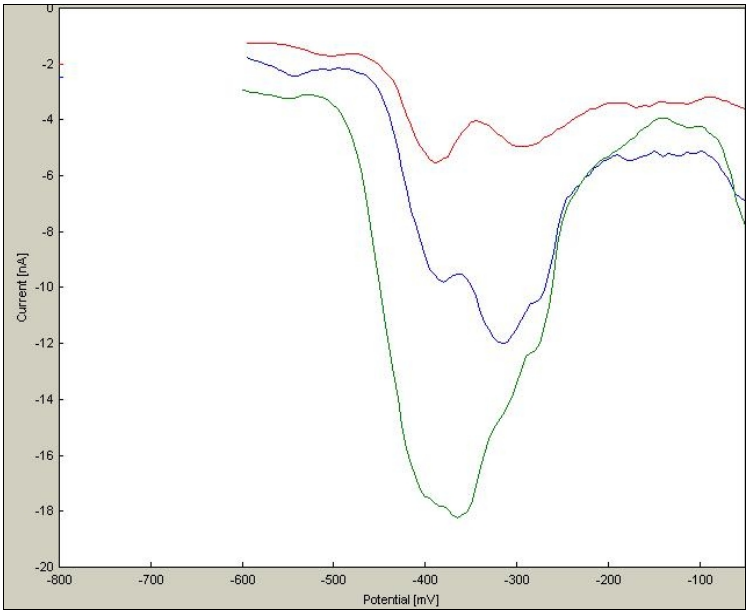
Reagents **Supporting Electrolyte:**
0.1 M NH_4Cl/NH_3 Puffer, pH 9,5:
- 5.349 g NH_4Cl, 7.6 ml NH_3 25 %ig/ 1 l, fill up with H_2O
Coumarin Standard Solution (1 g/l) in Ethanol

Method DP-stripping HMDE

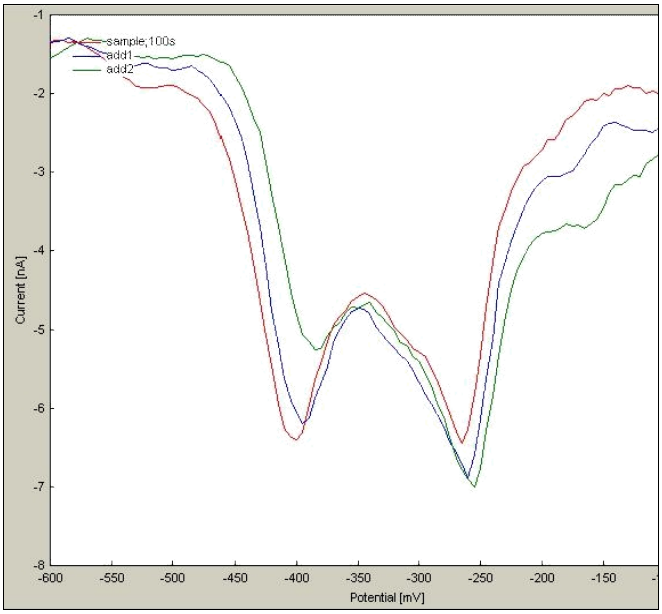
Solution
- 20 ml buffer
- 100 µl sample solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-50		Inert gas [s]	300-600
Final E_{fin} [mV]	-800		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	5		Accumulation potential [mV]	-50
			Accumulation time [s]	50
			Rest [s]	10
			Pulse height [mV]	-50
			Pulse width [ms]	80



A.) Coumarin standard solution



B.) Vodka sample

- The peak potential of coumarin is –350 mV.
- At lower concentrations two peaks can appear.
- In neutral solutions the peak heights decrease. Best results are obtainable in solutions with pH values between 9 and 10.
- Standard addition is used for evaluation.
- Detection limit 0.57 g/l

5. Determination of tartrazine

Principle Tartrazine is reduced at the hanging mercury drop electrode.

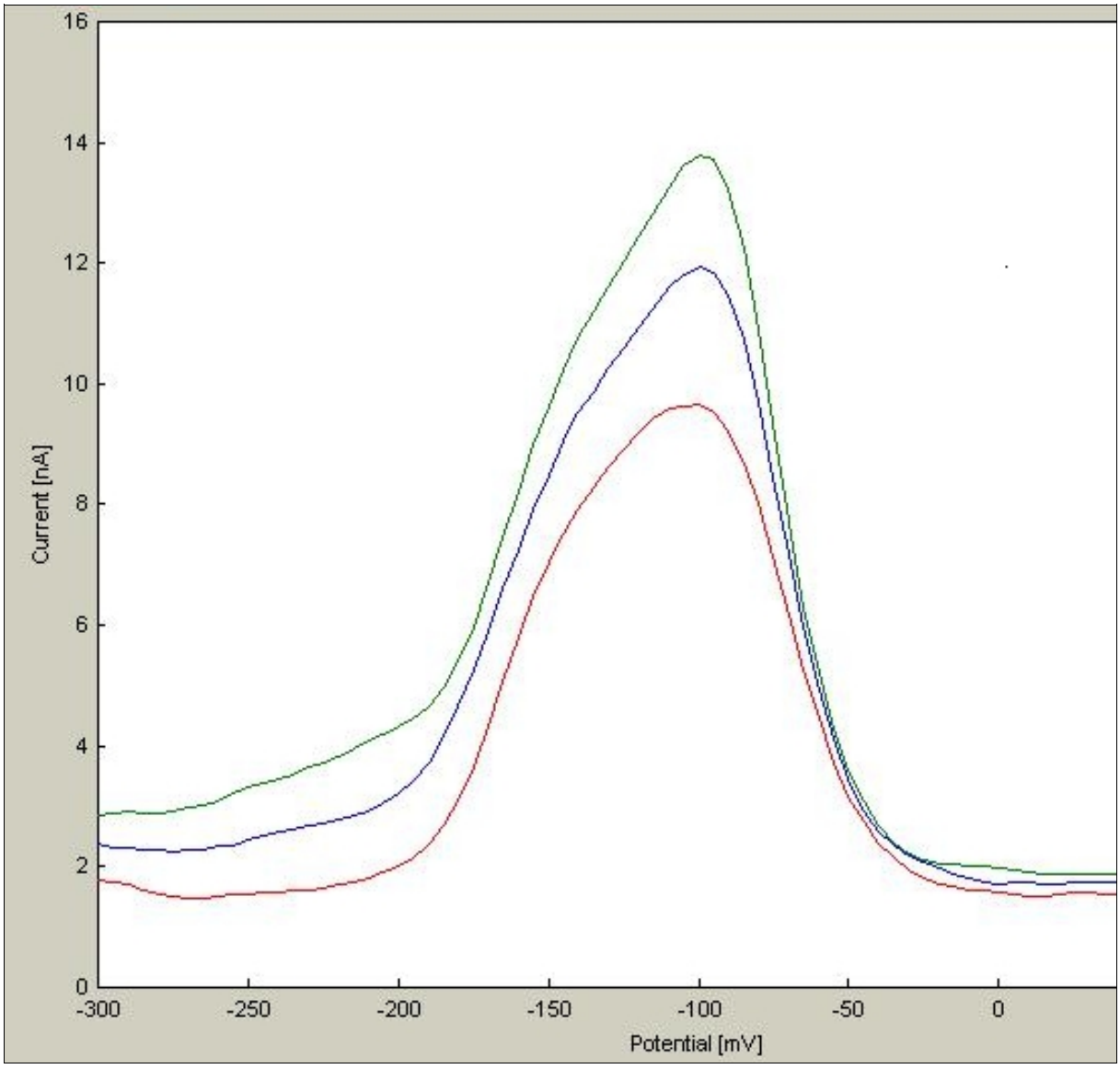
Reagents **Supporting Electrolyte:**
0.1 M H_2SO4:
- 5.6 ml conc. H_2SO_4/ 1 l, fill up with H_2O
Tartrazine Standard Solution (1 g/l) H_2O

Method DP stripping-HMDE

Solution
- 20 ml supporting electrolyte
- 20 µl aqueous sample

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	100		Inert gas [s]	300-600
Final E_{fin} [mV]	-300		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	5		Accumulation potential [mV]	100
			Accumulation time [s]	50
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80



- The peak potential is – 110 mV.
- Standard addition is used for evaluation.
- Detection limit 0.67 mg/l

6. Determination of Zn, Cd, Pb, Cu, Tl, Ni and Co in water (according to DIN)

Methods with electrochemical accumulation are used for the determination of the metal ions, because a high sensitivity can be obtained with such an accumulation at the surface of the mercury electrode. Because not all metal ions can be determined simultaniously, separate methods have to be applied:

6.1. Determination of Zn, Cd, Pb and Cu

Principle Zn, Cd, Pb and Cu are determined by andodic stripping voltammetry (ASV) at the hanging mercury electrode.

Reagents
Supporting Electrolyte:
0.1 M acetate buffer:
- 5.7 ml acetic acid
- 8.2034 g $NaCH_3COO$
- fill up to 1 l with H_2O

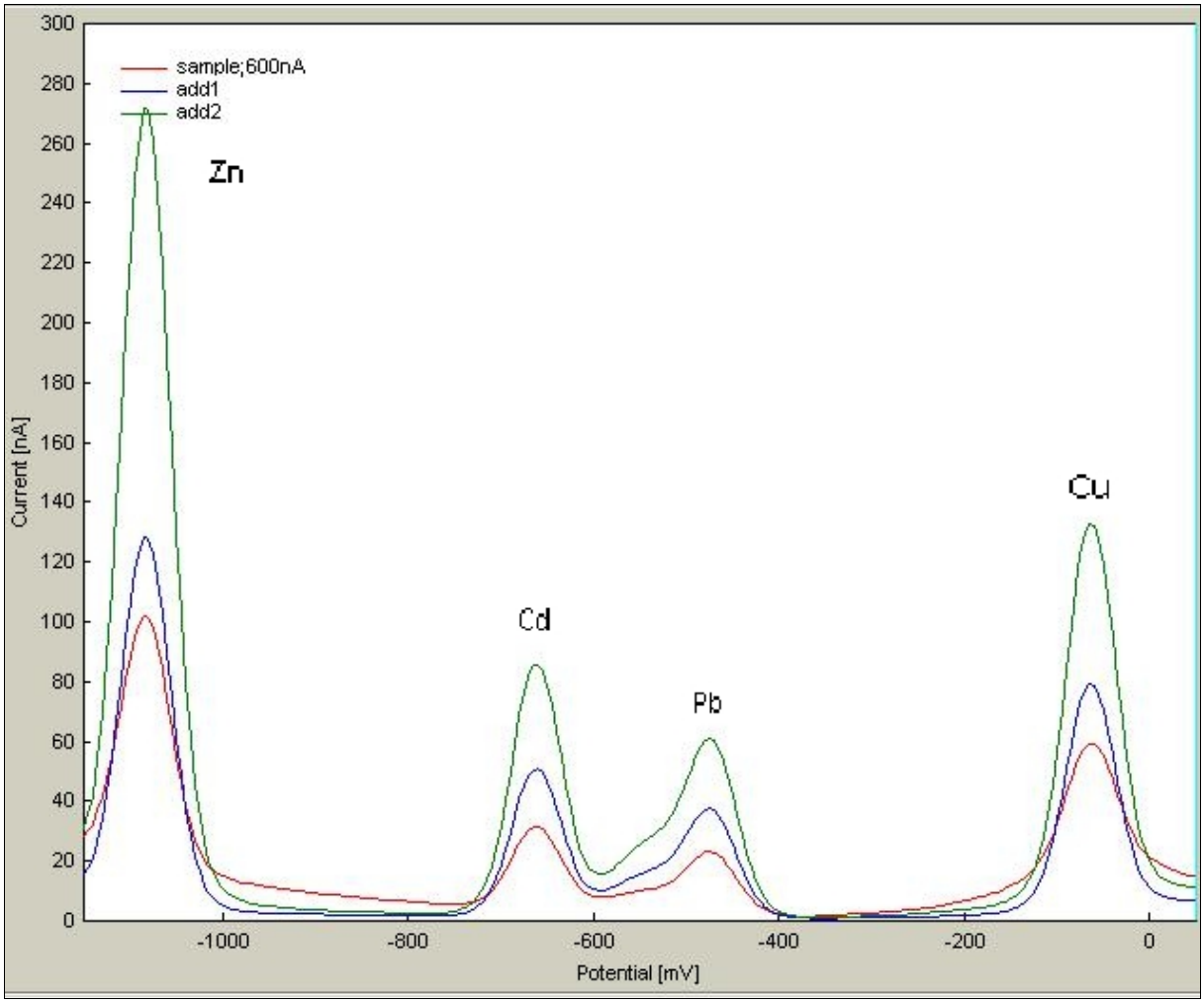
Standard Solutions:
ß (Zn^{2+}) = 10 mg/l
ß (Cd^{2+}) = 0.1 mg/l
ß (Pb^{2+}) = 0.5 mg/l
ß (Cu^{2+}) = 2.5 mg/l

Method DP stripping-HMDE

Solution
- 20 ml water sample
- 2 ml supporting electrolyte

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1150		Inert gas [s]	300-600
Final E_{fin} [mV]	50		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	5		Accumulation potential [mV]	-1150
			Accumulation time [s]	90
			Rest [s]	10
			Pulse height [mV]	50
			Pulse width [ms]	80



- The peak potentials are:
  Zn –1000 mV, Cd -690 mV, Pb -500 mV, Cu -70 mV
- Standard addition is used for evaluation.
- In case of aqueous solutions containg high amounts of zinc, this metal should be determined separatly with decreasing accumulation time or increasing dilution.

6.2. Determination of thallium

Principle The peak potential of the determination of thallium is very closed to that caused by lead (by using acetate buffer as supporting electrolyte the peak separation is 50 mV). Hence, both metals must be determined separatly. First, the sum of both metals is determined. Lead ions can be masked by adding EDTA anions. In that way, thallium ions are determined. The amount of lead ions can be calculated from the difference of both determinations.

Reagents

Supporting Electrolyte:
0.1 M acetate buffer:
- 5.7 ml conc. acetic acid
- 8.2034 g $NaCH_3COO$
- fill up to 1 l with H_2O

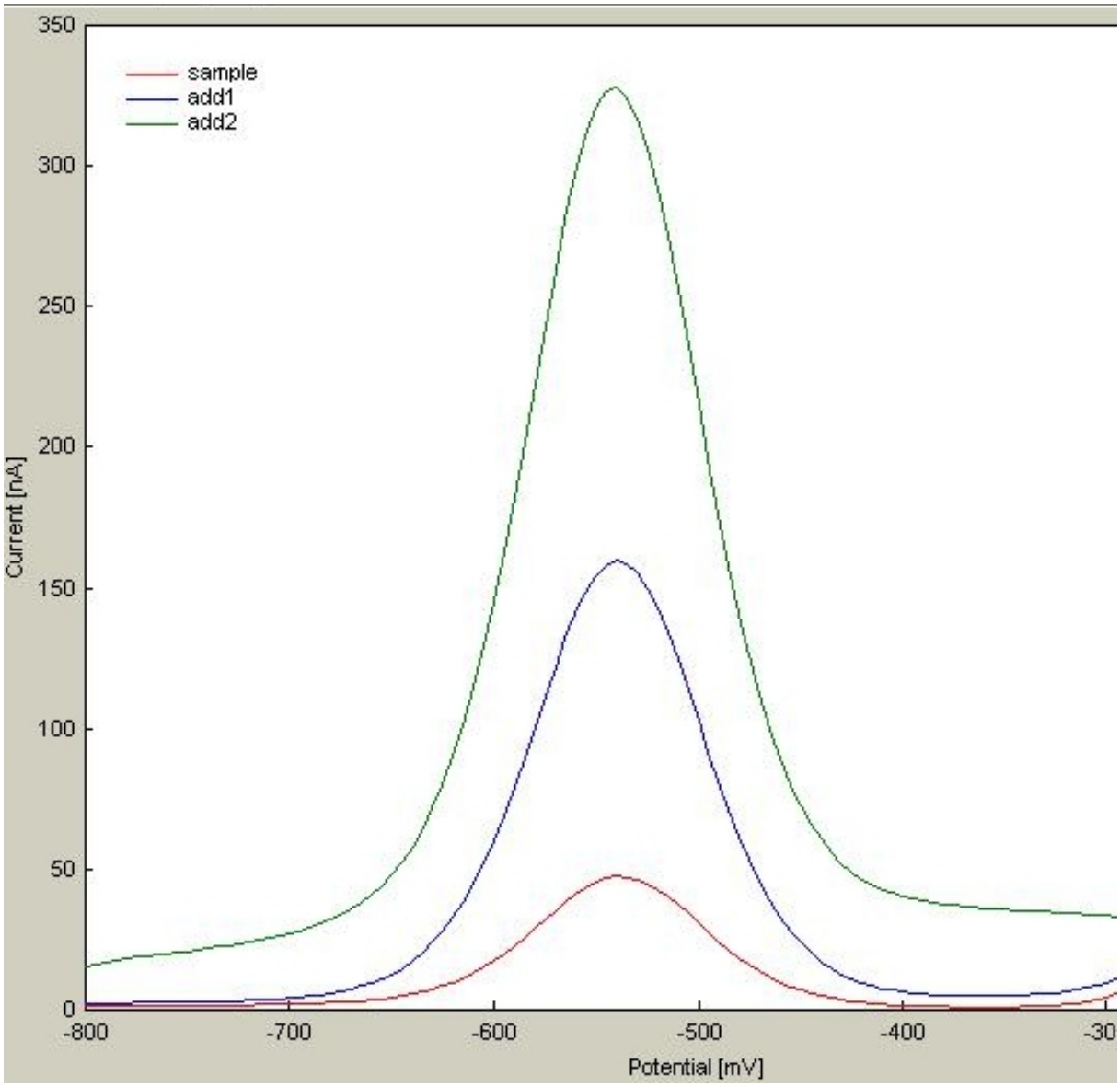
Standard Solution:
- ß(Tl) = 0.5 mg/l
- 0.1 M EDTA solution

Method DP stripping-HMDE

Solution
- solution of determination 6.1
- 200 µl EDTA

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-800		Inert gas [s]	300-600
Final E_{fin} [mV]	-200		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	5		Accumulation potential [mV]	-800
			Accumulation time [s]	180
			Rest [s]	10
			Pulse height [mV]	50
			Pulse width [ms]	80



- The peak potential is –550 mV.
- Standard addition is used for evaluation.
- Detection limit 0.89 µg/l

6.3. Determination of Ni and Co

Principle Cobalt and Nickel are determined by adsorptive stripping voltammetry (AdSV). Both metals form stable complexes with DMG. These complexes are accumulated at the surface of the mercury electrode. Nickel and cobalt can be reduced in the cathodic scan.

Reagents ***Supporting Electrolyte:***
0.1 M NH_4Cl/NH_3 buffer pH 9.5:
- 5.349 g NH_4Cl, 7.6 ml NH_3 25 %ig/ 1 l, fill up with H_2O
- 0.1 M DMG solution: 116 mg / 100ml ethanol
- 0.01 M HNO_3: 0.7 ml conc. HNO_3/ 1 l, fill up with H_2O

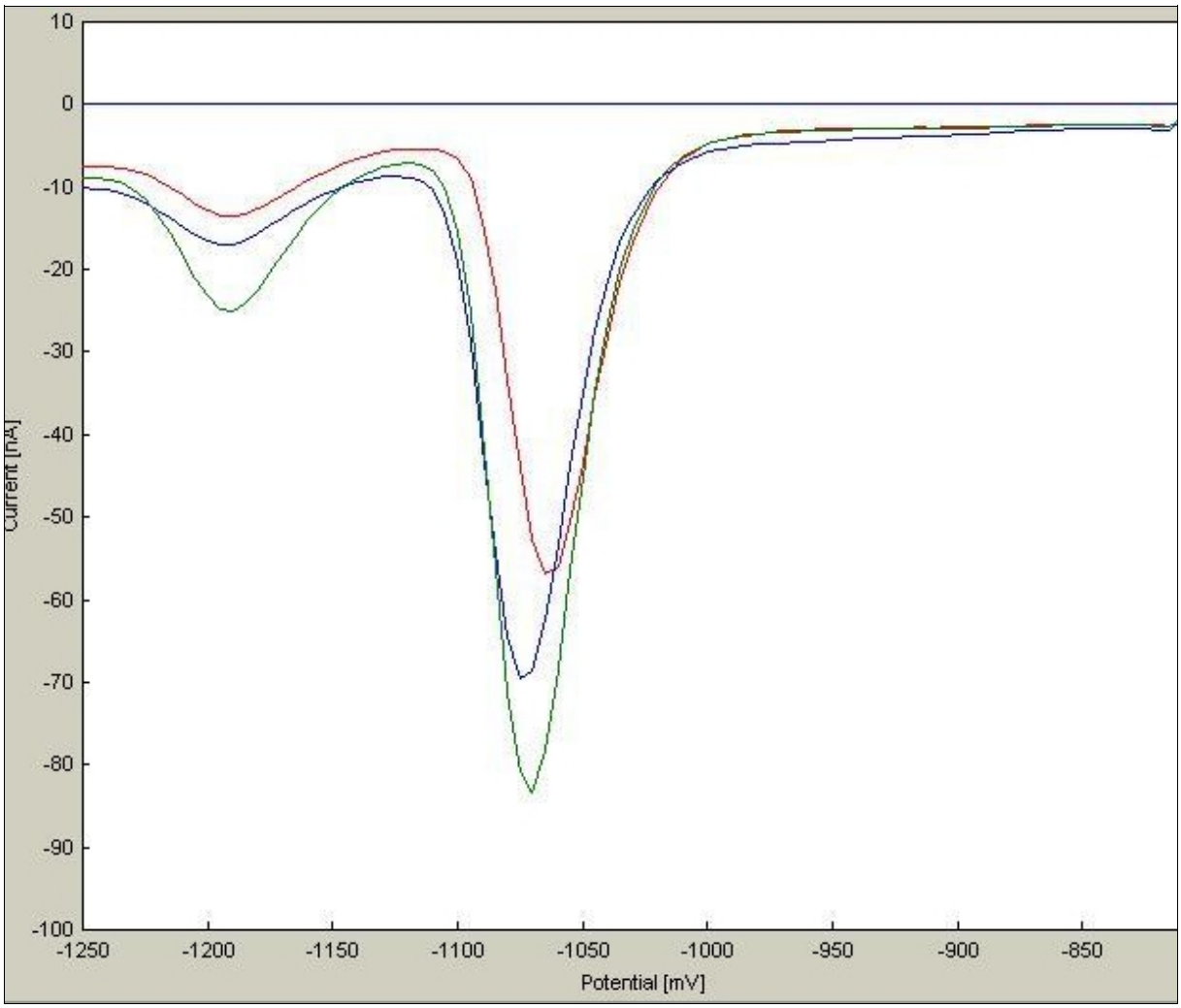
Standard Solutions:
- ß (Ni^{2+}) = 1 mg/l
- ß ($C0^{2+}$) = 0.1 mg/l

Method DP stripping-HMDE

Solution
- 20 ml diluted sample (dilute with 0.01M HNO_3)
- 1 ml 0.1 M NH_4Cl/NH_3 buffer
- 0.2 ml DMG solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-800		Inert gas [s]	300-600
Final E_{fin} [mV]	-1250		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	13		Accumulation potential [mV]	-700
			Accumulation time [s]	90
			Rest [s]	10
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak potential of Ni is –1075 mV and that of Cobalt is -1200 mV.
- Standard addition is used for evaluation.

7. Determination of Cu and Pb in vine

Principle Copper and lead are determined by anodic stripping voltammetry (ASV)

Reagents **1 M HCl:** 83 ml conc. HCl/ 1 l, fill up with H_2O
Standard Solutions (1 g/l):
- Pb^{2+}: 0.1599g $Pb(NO_3)_3$, 0.6 ml conc. HNO_3/ 100ml, fill up with H_2O **or**
0.1831 g Pb $(CH_3COO)_2$ $3H_2O$, 0.6ml conc. HNO_3/ 100ml, fill up with H_2O
- Cu^{2+}: 0.3929 g $CuSO_4$ $5H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O

Solution
- 10 ml vine
- 10 ml 1 M HCl

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-800		Inert gas [s]	300-600
Final E_{fin} [mV]	+150		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-800
			Accumulation time [s]	0-300
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80

- The peak potential of lead is -400 mV, that of copper is -100 mV
- Standard addition is used for evaluation.
- A blank experiment is advisable; in that case water is used instead of vine.

8. Determination of Zn, Pb and Cu in suggar, chilli powder and chilli sauce

Principle The metals are determined by anodic stripping voltammetry (ASV). It is important that an acid digestion is combined with a UV radiation (cf. section A).

Reagents **Supporting Electrolyte:**
0.1 M acetate buffer, 0.25 M NaCl:
- 5.7 ml conc. acetic acid
- 8.2034 g $NaCH_3COO$
- 14.611 g NaCl
- fill up to 1 l with H_2O

Standard Solutions (1 g/l):
- Pb^{2+}: 0.1599 g $Pb(NO_3)$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O **or**
0.1831 g $Pb(CH_3COO)_2$ $3H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O
- Cu: 0.3929 g $CuSO_4$ $5H_2O$, 0.6 ml conc. HNO_3/ 100 ml, fill up with H_2O
- Zn^{2+}: 0.4399 g $ZnSO_4$ $7H_2O$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

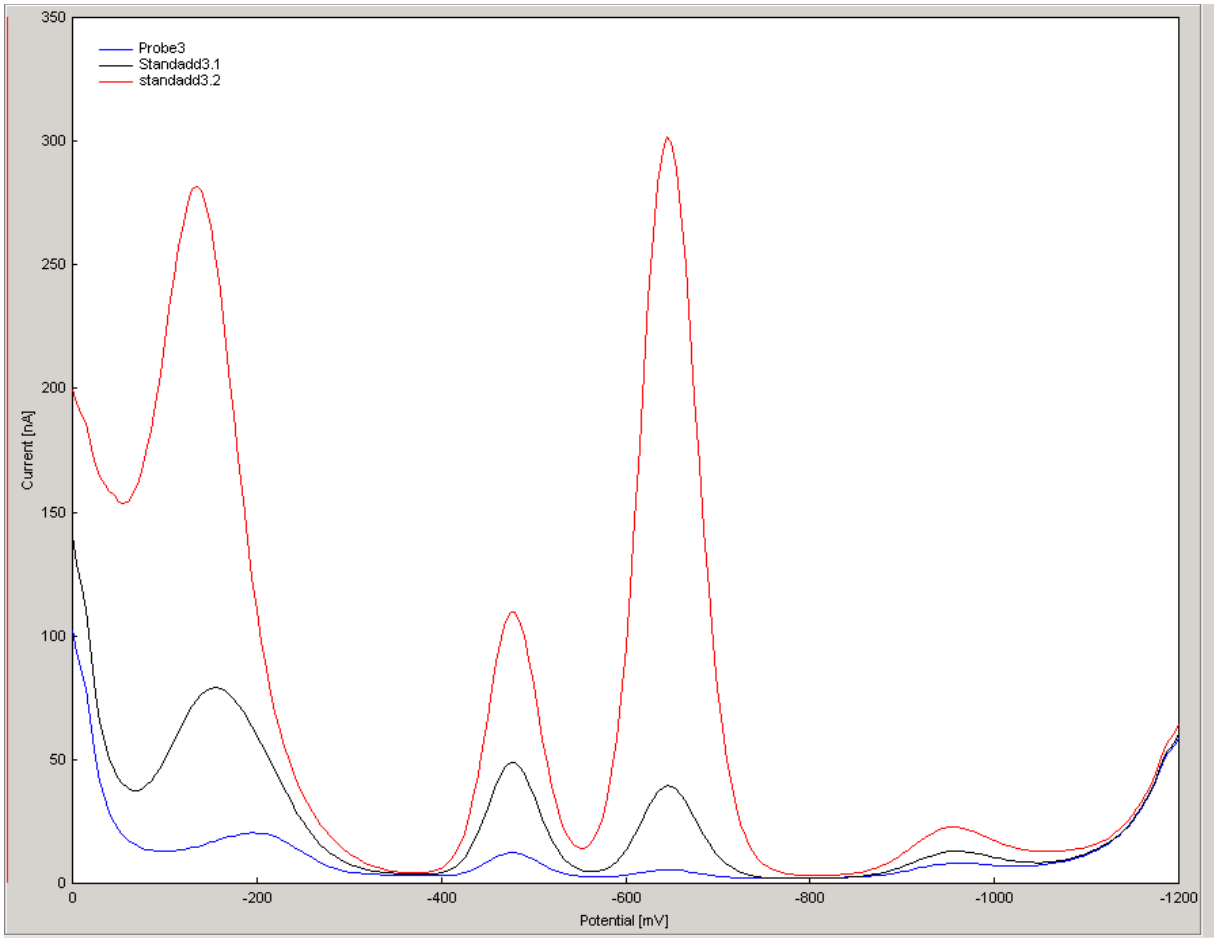
The standard solutions are diluted 1:10 and 1:100.

Method DP stripping-HMDE

Solution
- 9 ml aqueous sample
- 9 ml supporting electrolyte

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1200		Inert gas [s]	300-600
Final E_{fin} [mV]	50		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	10		Accumulation potential [mV]	-1200
			Accumulation time [s]	0-300
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80



Example Chilli sauce

- The peak potentials are: Zn -980 mV, Pb -500 mV, Cu -100 mV.
- Standard addition is used for evaluation.
- At very low concentrations a blank experiment is advisable. In that case, a water sample should be treated in the same manner (digestion and determination).

9. Determination of iron in suggar

Principle Iron can form complexes with triethanolamine in alkaline solution. The complex is accumulated at the mercury surface. In the determination step the complex is determined by cathodic reduction. It is important that the mineralization of the suggar sample is combined with UV radiation.

Reagents **Triethanolamine Solution:** (7.5 g/ 100 ml, fill up with H_2O)
- 3 M KOH (16.831 g KOH/ 100 ml, fill up with H_2O)

Fe^{3+} Standard Solution (1 g/l):
- 0.7234 g $Fe(NO_3)_3$ $9H_2O$,
- 0.9 ml conc. HCl/100 ml, fill up with H_2O **or**

0.4978 g $FeSO_4$ $7H_2O$, 0.9 ml conc. HCl/ 100 ml, fill up with H_2O

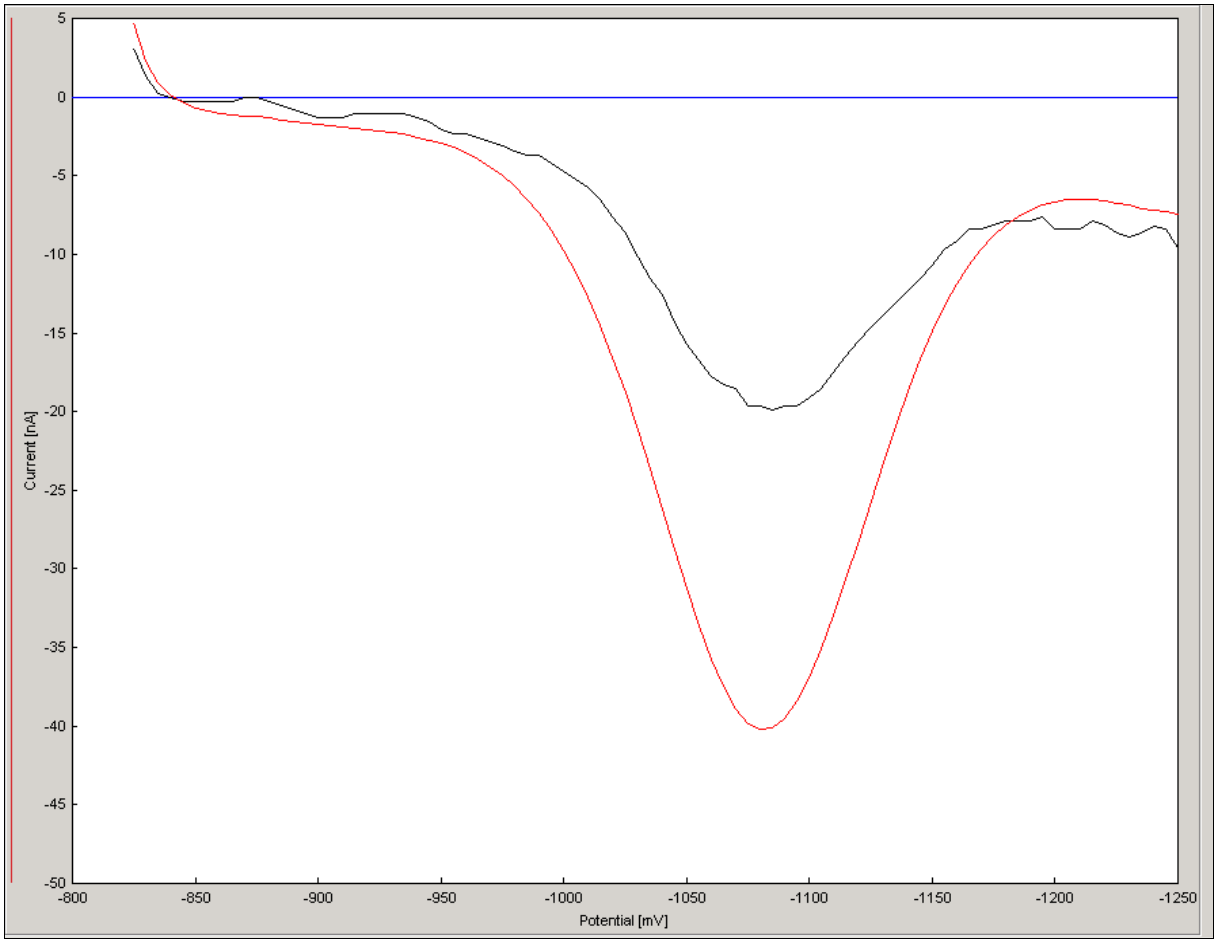
The standard solution is diluted 1:10, 1:100 and 1:200.

Method DP stripping-HMDE

Solution
- 9 ml aqeuous sample
- 9 ml 3 M KOH
- 12 ml triethanolamine solution

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-800		Inert gas [s]	300-600
Final E_{fin} [mV]	-1250		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-800
			Accumulation time [s]	0-60
			Rest [s]	0-10
			Pulse height [mV]	-50
			Pulse width [ms]	80



- The peak appears at -1085 mV.
- Standard addition is used for evaluation.

10. Determination of fructose in fruits and fruit juices

Principle Fructose is determined by linear sweep voltammetry (LSV) in strongly alkaline electrolyte solution.

Reagents
- LiOH/LiCl
- 0.5 %ige gelatine solution, must prepared fresh each day

Fructose Standard Solution (1g/l)

Method DC voltammetry

Solution
- 20 ml LiOH/LiCl
- 0.5 ml fruit juice
- 0.2 ml gelatine

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1600		Inert gas [s]	300-600
Final E_{fin} [mV]	-2300		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Pulse height [mV]	-50
			Pulse width [ms]	80

- The peak caused by the reduction of fructose appears at -1700 mV.
- Standard addition is used for evaluation.

11. Determination of antimony

Principle Antimony is determined by the method of anodic stripping voltammetry.

Reagents
- 1 M KCNS
- 0.3 M H_2SO_4

Sb Standard Solution (1g/l)

Method DP stripping - HMDE

Solution
- 10 ml of the sample
- add 0.25 ml KCNS and 0.5 ml H_2SO_4

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-300		Inert gas [s]	600-900
Final E_{fin} [mV]	100		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-300
			Accumulation time [s]	15-300
			Rest [s]	10-15
			Pulse height [mV]	50
			Pulse width [ms]	80

- The peak of antimony is at the potential -0.07 V.
- Standard addition is used for evaluation.
- At low Sb concentrations the blank experiment is advisable.

12. Determination of arsenic

12.1. Determination of arsenic I

Principle Arsenic is determined by the cathodic stripping technique with the hanging mercury drop electrode.

Reagents
- High purity HCl
- fresh solution of 1 g hydrazine hydrochloride in 100 ml H_2O
- **solution of a copper salt containing 0.6 mg Cu in 1 ml (1g/l)**
- **Standard solution: Standard As solution, 1ml =1 mg As,**

Standard solution is diluted 1:10 and 1:100.

Method DP stripping - HMDE

Solution
- 20 ml of sample in the electrolytic cell
- add 1 ml of conc. HCl
- add 0.5 ml of the hydrazine solution
- add 0.2 ml of the Cu solution.

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-100		Inert gas [s]	600-900
Final E_{fin} [mV]	-850		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-500
			Accumulation time [s]	100-400
			Rest [s]	30
			Pulse height [mV]	-50
			Pulse width [ms]	80

- The peak of arsenic(III) appears at -0.75 V.
- Standard addition is used for evaluation.
- At low arsenic concentrations a blank experiment is advisable.
- Note: By the given method only As(III) can be determined.
- To the water sample, immediately after it has been taken, hydrazine hydrochloride has to be added (0.25 g/500 ml) and the water has to be kept at the temperature of – 4°C.
- For determining the total arsenic a chemical reduction has to be carried out:
  to 50 ml of water in a beaker 1 g of NaCl and 0.2 g of hydrazine hydrochloride are added. The solution is then acidified by 4 ml of concentrated HCl and subjected to reduction by 1 ml of 48% HBr for 45 min at the temperature of 90 °C in a beaker covered by a watch glass.
- When determining arsenic in biological material the mineralization must be carried out in a way excluding any losses of arsenic. During dry decomposition it is absolutely necessary to heat the sample together with an auxiliary agent (MgO, $MgNO_3$).

12.2. Determination of arsenic II

Principle From the analysed material arsenic gets separated in the form of AsH_3 which is then oxidized to AsO_2^-. The late form is finally determined by the method of differential pulse voltammetry.

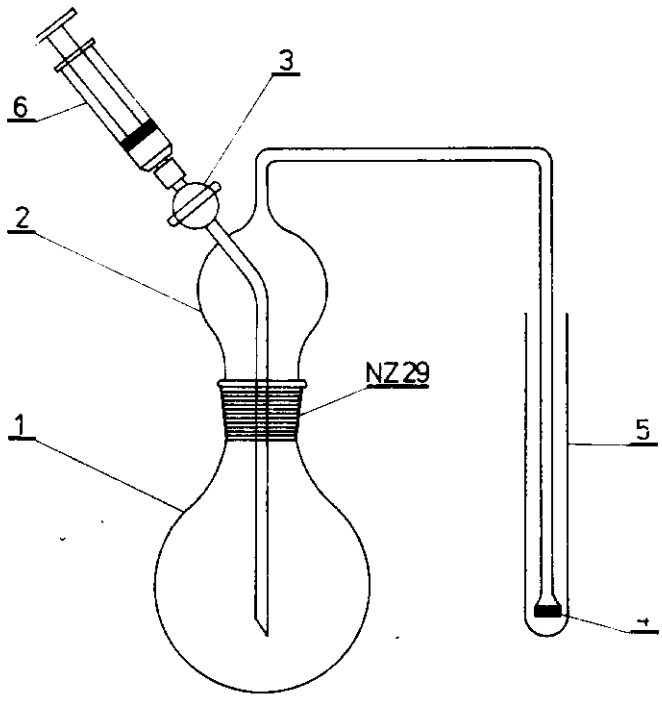
Reagents
- HNO_3 conc.
- HCl conc.
- saturated $SnCl_2$ solution in HCl conc.
- 30% solution of KI
- 0.01 M $AgNO_3$
- metallic zinc (p.a., arsenic free)

Method DP voltammetry

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-150		Inert gas [s]	300-600
Final E_{fin} [mV]	-900		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Pulse height [mV]	-50
			Pulse width [ms]	80

Glass apparatus



1 – reaction flask
2 – gas evolution adapter
3 – stopcock
4 – thin glass frit
5 – test tube
6 - syringe (10 ml) connected to (2) by a rubber tube

Procedure:

100 to 300 ml of water sample (according to the arsenic content) after addition of 5 ml HNO_3 conc. Is evaporated down to the volume of about 30 ml. The resulting solution is transferred to the reaction flask, 0.5 ml of saturated solution of $SnCl_2$ in HCl conc. and 2-4 ml of 30 % solution of KCl are added, the flask gets stoppered and the contents stirred. After a couple of minutes about 5 g of metallic zinc are introduced to the mixture and to the reaction flask is connected the gas evolution adapter whose end provided with a frit dips into a test tube containing 10 ml of 0.01 M $AgNO_3$. The syringe joined to the adapter is to be filled with HCl conc.; after opening the stopcock 5 ml of HCl are added to the solution; the stopcock is then closed. The generated mixture of gases containing AsH_3 should form a small stream of minute bubbles in the $AgNO_3$ solution in the test tube. The presence of arsenic is indicated by gradual darkening of the solution (reduction of Ag^+ ions). The evolution of arsine is over in about 50 minutes; when the reaction slows down it is possible to add to the mixture in the cell some more hydrochloric acid. After 50 minutes it is possible to remove the syringe from the adapter and use an inert gas for complete transfer of AsH_3 from the apparatus to the $AgNO_3$ solution. However, if the procedure was followed correctly this step is not necessary.
In the $AgNO_3$ solution arsine is oxidized to arsenite. The solution from the test tube is prepared for measurement by adding 1 ml of HCl conc. which precipitates excess Ag^+ ions. After shaking the precipitate is removed by centrifugation and the clear solution is analyzed by the “DP voltammetry” method with **parameters**.

- Peak corresponding to arsenite is measured at –450 mV
- evaluation is done by the standard addition or the calibration curve method.
- Note: Antimony which reacts in a way similar to arsenic (by reaction it turns to stibine) gives also a peak, but at a different potential (E_p = -150 mV) so that both peaks can be clearly distinguished. However, the above method cannot be used for determination of antimony because the yield of the separation technique for antimony is merely 20%.
- Due to possible presence of arsenic in the reagents it is advisable to try a blank experiment.

When determining arsenic in biological material it is necessary to carry out the digestion in a way preventing losses of arsenic. For dry decomposition the sample must be heated together with an auxiliary reagent (MgO, $MgNO_3$).

12.3. Determination of arsenic III

Principle Arsenic(III) is determined by anodic stripping voltammetry using a gold working electrode after preceding preparation and activation of the electrode surface.

Reagents
- H_2SO_4 conc.
- H_2SO_4 1 M, HCl conc.
- HCl 1 M
- Triton X-100 0.2 % aqueous solution, toluene, formic acid, reducing solution:
6 g KBr + 1 g $N_2H_4.H_2SO_4$ to 100 ml water
- for electrode polish alpha alumina (Al_2O_3) with particle size 0.3 μm or less.

Method anodic stripping voltammetry

Preparation of gold electrode for measurement

If the surface of the gold electrode does not have a mirror lustre, it has to be polished in wet way by alumina until mirror lustre is attained. Afterwards the electrode has to be dipped for several minutes in 1 M H_2SO_4 and then rinsed with distilled water. In this way the electrode is prepared for measurement.

Activation of the gold electrode surface

To 20 ml water in the electrolytic cell 1 ml of concentrated H_2SO_4 is added and after cooling to ambient temperature the solution is deaerated for 10 minutes by a stream of nitrogen. The surface activation is carried out by the Prep-SE with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	200		Inert gas [s]	300-600
Final E_{fin} [mV]	1900		Number of scans [1]	50
Scan rate [$mV.s^{-1}$]	700		Pause Tin [s]	0
			Pause Tfin [s]	0
			Number of scans M [1]	2
			Pause Tin M [s]	0
			Pause Tfin M[s]	0

In course of the measurement it is displayed on the monitor how the current response of the electrode is gradually stabilized. During measurement with the above parameters the first, the one but last and the last curves are automatically saved. The courses of the last two curves is identical what shows that the electrode surface has been correctly activated.

Method DP stripping – SE

Procedure To 20 ml of the water sample to be analyzed 1 ml of concentrated H_2SO_4 is added and the solution is deaerated for 10 minutes by stream of nitrogen. Further are added 0.1 ml of concentrated HCl and 0.1 ml of 0.2 % of Triton X-100. After further short passage of nitrogen the solution is analyzed by means of the “DP stripping – SE” program with the following parameters:

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-300		Inert gas [s]	300-600
Final E_{fin} [mV]	400		Number of scans [1]	3
Scan rate [$mV.s^{-1}$]	20		Cleaning potential [mV]	2500
			Cleaning time [s]	10-15
			Accumulation potential [mV]	-300
			Accumulation time [s]	20-180
			Rest [s]	30
			Pulse height [mV]	50
			Pulse width [ms]	80

The anodic peak of arsenic appears in potential region between +160 and +30 mV. The evaluation is carried out by means of the calibration curve or the standard addition methods. The time of electrolysis (accumulation) is taken 20s for samples with arsenic content between 30 and 300 ppb, for samples with arsenic between 2 and 25 ppb the time of electrolysis is taken 120 to 180 s. The time of cleaning is taken between 1 and 3 s.

Notes 1:

- Electrochemically active is only As(III). As(V) does not give any electrochemical response.
- When taking samples of waters it is important to make sure that arsenic (III) does not get oxidized to As(V); this can be reached e.g. by additions of ascorbic acid or hydrazine.

An advantageous method of As(V) reduction is based on reaction with potassium bromide and hydrazine combined with extraction of As(III) to toluene. In that case the sample is evaporated to a small volume to which is added sulfuric acid so that the final volume is about 20 ml and the resulting concentration of H_2SO_4 about 80 %, and 1 ml of formic acid. (The latter is added to prevent possible nitration of toluene). The solution thus prepared is warmed up until first fumes of SO_3 appear, after cooling down it is transferred into a 25 ml measuring flask. To the flask is added 1 ml of the reducing solution, the volume is filled up to the mark by water, then exactly 1 ml of toluene is added and in a 50 ml flask extraction goes on for 5 minutes. Another 25 ml measuring flask is filled to the mark by 0.5 M HCl and after separation of phases in the first flask o.5 ml of toluene is transferred from it into the second flask with 0.5 M HCl. There the reextraction of As(III) from toluene into hydrochloric acid takes place for 3 minutes. After separation of phases the layer of toluene is sucked away (e.g. by a piece of cotton) and 2.5 ml of the aqueous solution is transferred to an electrolytic cell containing 20 ml water and 1 ml of concentrated H_2SO_4. The ensuing voltammetric measurement is carried out with the parameters given above.

Notes 2:

- Electrochemically active is only arsenic (III); As(V) does not yield any electrochemical response.
- Introduction of the positive cleaning potential (2 500 mV) for 1 to 10s after each measurement is necessary for the results to be reproducible. It is recommended ro repeat each measurement three times (number of cycles 3) and for calculating the concentration to take mean values of the second and third measurements.
- Addition of hydrochloric acid is essential, otherwise the sensitivity of determination is considerably reduced. In case the sample contains a higher concentration of chloride ions is sufficient to add 0.05 ml of HCl conc.
- The addition of surface active agents affects positively the shape of the anodic peak of arsenic, its potential and the corresponding current. For that reason in analysis of natural waters it is not necessary to remove organic compounds; on the contrary, it is advisable to add the given amount of Triton-X 100.
- If total arsenic content has to be determined, first the above determination of As(III) is carried out and then in the second part of the sample the As(V) present is reduced, best by gaseous SO_2, and the total content of arsenic is determined by the method described.
- When taking samples of waters it is necessary to prevent spontaneous oxidation of As(III) which can be achieved, e.g., by addition of ascorbic acid or hydrazine.

When determining arsenic in biological material care must be taken to carry out mineralisation in a way avoiding losses of arsenic. In dry mineralisation the sample must be heated together with an auxiliary reagent (MgO, $MgNO_3$).

12.4. Determination of arsenic in phosphoric acid – determination of lower As content

Principle Determination is carried out by differential pulse stripping voltammetric method with gold electrode.

Reagents Mixed solution containing:
1 M HCl and 1 M H_2SO_4, solid NaOH, hydrazine hydrochloride

Method DP – stripping SE

Procedure 10 ml of the phosphoric acid sample are neutralized by 7.4 g NaOH dissolved in 10 ml water; to the mixture are added 7 ml water and 3 ml of the 1 M HCl – 1 M H_2SO_4 mixture. On further addition of several mg hydrazine the solution is boiled for a few minutes; after cooling it is transferred to electrolytic cell and measured by the DP – stripping SE program with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-150		Inert gas [s]	300-600
Final E_{fin} [mV]	500		Number of scans [1]	3
Scan rate [$mV.s^{-1}$]	20		Cleaning potential [mV]	1600
			Cleaning time [s]	60
			Accumulation potential [mV]	-350
			Accumulation time [s]	20-240
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80

- The arsenic peak is measured at the potential of 130 mV.
- The evaluation is done by the method of standard addition.
- The method has been worked out for low contents of arsenic – of the order of ppb.

13. Determination of beryllium

13.1. Determination of beryllium I

Principle Beryllium is determined in the form of its complex by the adsorptive stripping voltammetry.

Reagents EDTA (ethylenediaminetetraacetic acid) - 10^{-5} M aqueous solution
beryllon II:
[disodium salt of 2-(8-hydroxy-3,6-disulfonaphtyle-1-azo)-1,8-dihydroxynaphtalene-3,6-disulfonic acid] - 3.10^{-4} M aqueous solution
0.1 M borate buffer of pH 7.0

Method DP stripping - HMDE

Procedure
- 10 ml of the sample to be mixed with 0.25 ml of the 10^{-5} M EDTA
- 0.25 ml of 3.10^{-4} M beryllon II and 10 ml of the borate buffer and distilled water to be added to the total volume of 25 ml.
- From the thus prepared solution 10 ml to be transferred to the polarographic cell, stirred and allowed to stand for 15 min at rest.
- Then the technique of „DP stripping - HMDE“ is to be applied with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-400		Inert gas [s]	600-900
Final E_{fin} [mV]	-900		Number of scans [1]	1-3
Scan rate [mV.s^{-1}]	20		Accumulation potential [mV]	-400
			Accumulation time [s]	0-180
			Rest [s]	15
			Pulse height [mV]	-50
			Pulse width [ms]	80

- The peak due to beryllium appears at -600 mV.
- For the evaluation either the method of standard addition or
  that of the calibration curve is used.

Note:
Before and after each measurement it is necessary to wash the cell by the dichromate - sulfuric acid solution, because the complex of beryllium ions is strongly adsorbed on its walls. It is advisable to make the blank experiment.

13.2. Determination of beryllium II

Principle Beryllium is determined in form of its complex with thorin by differential pulse adsorptive stripping voltammetry

Reagents thorin (disodium salt of o-[3,6-disulfo-2-hydroxy-1-naphtyl-azo]benzenearsonic acid) 10^{-5} M solution, 0.5 M ammonia buffer of pH 9.1

Method DP stripping - HMDE

Procedure to 10 ml of the water sample 0.1 ml of the 10^{-5} M thorin solution and 2.5 ml of 0.5 M ammonia buffer of pH 9.1 are added and fill up to the volume of 25 ml. From that solution 10 ml are transferred to the polarographic cell where it is deaerated for 10 min. The measurement is done by the method “DP stripping – HMDE” with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-480		Inert gas [s]	300-900
Final E_{fin} [mV]	-900		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-480
			Accumulation time [s]	0-180
			Rest [s]	15
			Pulse height [mV]	-50
			Pulse width [ms]	80

- The peak appears around –650 mV.
- Quantitative evaluation is carried out by the method of standard addition or of calibration curve.

Note:
Before each measurement it is necessary to wash the polarographic cell with dichromate-sulfuric acid solution, as the beryllium complex adsorbs strongly on glass. It is advisable to start with a blank experiment.

14. Determination of aluminium

Principle Aluminium is determined voltammetrically or by the method of adsorptive stripping voltammetry in the form of its complex with the alizarin red - S.

Reagents Alizarin red S (1,2 - dihydroxyanthraquinone - 3 - sulfonic acid) 10^{-3} M (75 mg to 250 ml of distilled water); buffer (N,N - bis (2 - hydroxyethyl) - 2 - aminoethanesulfonic acid 0.04 M pH = 7.1; NaOH 0.04 M; solution of the complex of EDTA with Ca (Ca - EDTA 0.001 M is prepared by dissolving 0.328 g of $Ca(NO_3)_2$ and of 0.7421 g of disodium salt of EDTA in 100 ml of distilled water). Standard solution of Al: 1 mg/1 ml.

Method DP stripping - HMDE

Procedure To 10 ml of the sample in the electrolytic cell add 100 µl of Ca EDTA and 200 µl of the buffer (the pH - value to be controlled by means of a pH - meter). Further add 200 µl of the alizarin red S. The measurement is carried out by the “DP stripping – HMDE” technique with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-800		Inert gas [s]	600-900
Final E_{fin} [mV]	-1300		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-800
			Accumulation time [s]	10-60
			Rest [s]	10-15
			Pulse height [mV]	50
			Pulse width [ms]	80

- In the case of a low Al content (µg/l) the accumulation of the aluminium complex on the electrode surface takes place for 10 - 50 sec in an unstirred or in a stirred solution (at the lowest concentrations - ppb - the solution has to be stirred).
- The peak potential appears at - 1.10 V
- for the evaluation either of the two methods, the "standard addition" or the "calibration curve" method, are used.

As the complex formation of Al with the alizarin red - S takes place only slowly, it is advantageous in the evaluation procedure (the "standard addition" method) to add aluminium already in form of the complex with the agent.

With a higher aluminium content (mg/l) the determination takes place without accumulation, that means that the voltammetric curve is recorded from the potential - 0.80 V immediately after the new drop has been generated.

The reason for the addition of the Ca EDTA complex is the elimination of the disturbing effect of zinc, which is often present in waters. In the case the recommended buffer is not available, it is possible to use e.g. the phosphate buffer the exact setting of which to pH 7.1 must be checked by a pH-meter.

15. Determination of iron(III) and of total iron

Principle Fe(III) is determined, even in the presence of Fe(II), by the adsorptive stripping voltammetric method using the Solochrome Violet RS as complexing agent. The total iron is determined by the same technique with catechol.

Reagents 0.1 M acetate buffer (pH 5.1) containing 1.10^{-4} mol/l Solochrome Violet RS; 0.1 M 1,4-piperazinediethanesulfonic acid buffer (pH 6.8) containing 1.10^{-4} mol/l catechol.

Method DP stripping - HMDE

Procedure 10 ml of the acetate buffer containing Solochrome Violet to be pipetted to the electrolytic cell and the technique of „DP stripping - HMDE“ to be applied with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	0		Inert gas [s]	600-900
Final E_{fin} [mV]	-1000		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-450
			Accumulation time [s]	0-30
			Rest [s]	15
			Pulse height [mV]	-50
			Pulse width [ms]	80

- The thus obtained curve corresponds to the blank current. The measured solution is then purged for 3 more minutes by the inert gas, a small volume of the sample is added (maximum 1 ml), and after a short further purging the curve of iron is recorded under the same conditions as above.
- The height of the peak at the potential -50 mV corresponds to the concentration of Fe(III) in the sample.
- For evaluation the method of standard addition is used.

The total concentration of iron, often determined by the AAS method, can be also measured by the adsorptive stripping voltammetry. The determination is carried out in the way as outlined above with the difference that instead of the acetate buffer with Solochrome Violet the given buffer with catechol is used; the procedure and the parameters remain the same, only the potential of electrolysis is changed to -0.10 V. In the present case it is not necessary to pre-purge the buffer solution before the addition of the sample.

16. Determination of mercury in waters

16.1. Determination of mercury in waters (gold electrode)

Principle Hg is determined by the anodic stripping voltammetry using the gold working electrode

Reagents $HClO_4$ 1 M and 0.1 M, H_2O_2 30 %

Method DP stripping - HMDE

Procedure In the case when the electrode surface is not smooth and shining, it has to be polished by means of a fine emery paper (e.g. Papier Corindon 500, SIA, Switzerland) or by a grinding paste (e.g. alumina 0.5 µm) and well rinsed by distilled water. Thus prepared electrode has to be inserted into the central conical hole in the cell head and its lead has to be connected to the connector marked "WORK". Into the other holes have to be introduced the auxiliary platinum electrode (connected to "AUX W") and the reference electrode (connected to "REF"). The switch "ELECTRODES" on the base of the stand is to be turned to "3" (the corresponding green control lights on).
The electrolytic cell is then to be filled with about 10 ml of 0.1 M $HClO_4$ and the gold electrode is activated by cyclic polarization at the rate of 10 V/s between the potentials +1.60 V and -0.20 V about 20 times, ending at +1.60 V. For this purpose the technique of Prep-SE is used with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-200		Inert gas [s]	150-300
Final E_{fin} [mV]	1600		Number of scans [1]	20
Scan rate [$mV.s^{-1}$]	10000		Pause Tin [s]	0
			Pause Tfin [s]	0
			Number of scans M [1]	2
			Pause Tin M [s]	0
			Pause Tfin M[s]	0

The corresponding current - voltage curves are not saved in the memory, the polarization serves merely for activation of the electrode surface. After the above treatment the electrode is prepared for measurement; when not in use it has to be kept in a closed space for protection from dust and mechanical damage.

Sample preparation Immediately after the taking the sample has to be filtered (convenient are, e.g., the cellulose filters Sartorius with the pore size 0.45 μm) and the filtrate to be acidified to pH 2. With the samples of natural waters before the actual measurement it is necessary to decompose the potentially present organic compounds which could form stable complexes with mercury. For that purpose to each 10 ml of the sample 50 μl of the 30 % H_2O_2 are added and the solution is irradiated for 2 hours in a closed quartz vessel by a 400-500 W UV lamp; during the fotolysis the vessel should be cooled by a stream of air not to allow the solution temperature to exceed 70^{o} C.

Method DP stripping - Solid electrode

Procedure After the fotolysis the solution has to be cooled to room temperature, 20 ml of the sample solution are to be transferred to the electrolytic cell and 2 ml of 1 M $HClO_4$ added. The measurement is carried out by the technique of DP stripping - Solid electrode with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	200		Inert gas [s]	600-900
Final E_{fin} [mV]	900		Number of scans [1]	2-3
Scan rate [mV.s^{-1}]	20		Cleaning potential [mV]	1600
			Cleaning time [s]	150
			Accumulation potential [mV]	-200
			Accumulation time [s]	30-600
			Rest [s]	30
			Pulse height [mV]	50
			Pulse width [ms]	80

In this measurement the mercury electrode is not used, therefore the parameters of HMDE are not given, also the time for purging is 0 as it is not necessary this time to remove oxygen from the solution. The peak of mercury is measured at the potential +700 mV, for evaluation the method of standard addition is used. The lowest concentration that can be determined is 0.03 μg/l.

Notes: Gold with mercury form amalgams of various compositions, however, on the pre-treated gold surface (as described above) during electrodeposition of mercury from dilute solutions only one kind of amalgam is formed which yields only one peak on anodic stripping; the height of this peak is directly proportional to the concentration of mercury ions in the solution. After the irradiation of the solution by UV light this method includes besides the inorganic mercury also the organomercury compounds; methylmercury is decomposed at pH 2 and hence gets also determined. The determination is disturbed by a high excess of Cu^{2+} and Cl^{-} ions. Under the given conditions copper yields a peak at +0.30 V and can be determined together with mercury. The disturbing effect of chlorides can be eliminated by the exchange of electrolytes, i.e., after the electrolysis has ended, during the 30 seconds of the "rest" period, the cell with the measured solution is replaced by another cell containing only pure 0.1 M $HClO_4$ solution; the anodic dissolution of mercury then takes place in the pure perchloric acid solution without any interference by chloride ions.

16.2. Determination of mercury in waters (glassy carbon electrode)

Principle Mercury is determined by anodic stripping voltammetry using glassy carbon as working electrode

Reagents **0.1M KCNS**

Supporting Electrolyte:
9.7 g of KCNS dissolved in about 200 ml water
added 2 ml of HCl conc. and
200 μl of the standard solution of mercury, which contains 0.1 mg of Hg in 1 ml, and all in a measuring flask filled up to 1000 ml.

Electrode Preperation The surface of the graphite electrode must be smooth and shining which can be achieved e.g. by polishing with a fine abrasive powder (alumina 1 micron), or by an equally efficient means. Before the measurement the carbon electrode is dipped into the electrolytic cell filled with 0.1 M solution of KCNS and is polarized under stirring for 2 minutes at potential of +0.40 V.

Method DP stripping – SE

Procedure 5 ml of the water sample is mixed with 5 ml of the supporting electrolyte and the measurement is carried out by the “DP stripping – SE” method with the parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1000		Inert gas [s]	300-900
Final E_{fin} [mV]	300		Number of scans [1]	3
Scan rate [$mV.s^{-1}$]	20		Cleaning potential [mV]	-1000
			Cleaning time [s]	0
			Accumulation potential [mV]	-1000
			Accumulation time [s]	30-600
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80

- The potential of the mercury peak is +0.03 V.
- The quantitative evaluation of the curves is done by either of the usual analytical methods.

Depending on the type (dimensions) of the carbon electrode used with respect to the cell construction and dimensions it might be necessary to replace the glass shaft stirrer by a magnetic stir bar.

17. Determination of silver in water

Principle Differential pulse anodic stripping voltammetry with the use of the composite carbon electrode PS C/S190/12

Reagents **1M NH_4OH and 1M NH_4NO_3 buffer solution**

0.1 M EDTA

H_2O_2 30 %

Standard silver solution diluted 1:10 and 1:100

Method DC polarography

Pretreatment of the carbon electrode Before measurement the surface of the electrode is slightly polished using hard paper card (punched card). The electrode is then polarized in 0.1M ammoniacal buffer solution using the method DC polarography and the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-600		Inert gas [s]	600-900
Final E_{fin} [mV]	400		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	500			

Cathodic and anodic scans (cyclic voltammetry) are repeated approx. ten times and thus the electrode is prepared for measurement. When not used the electrode is kept in closed space to prevent a mechanical damage of the active surface.

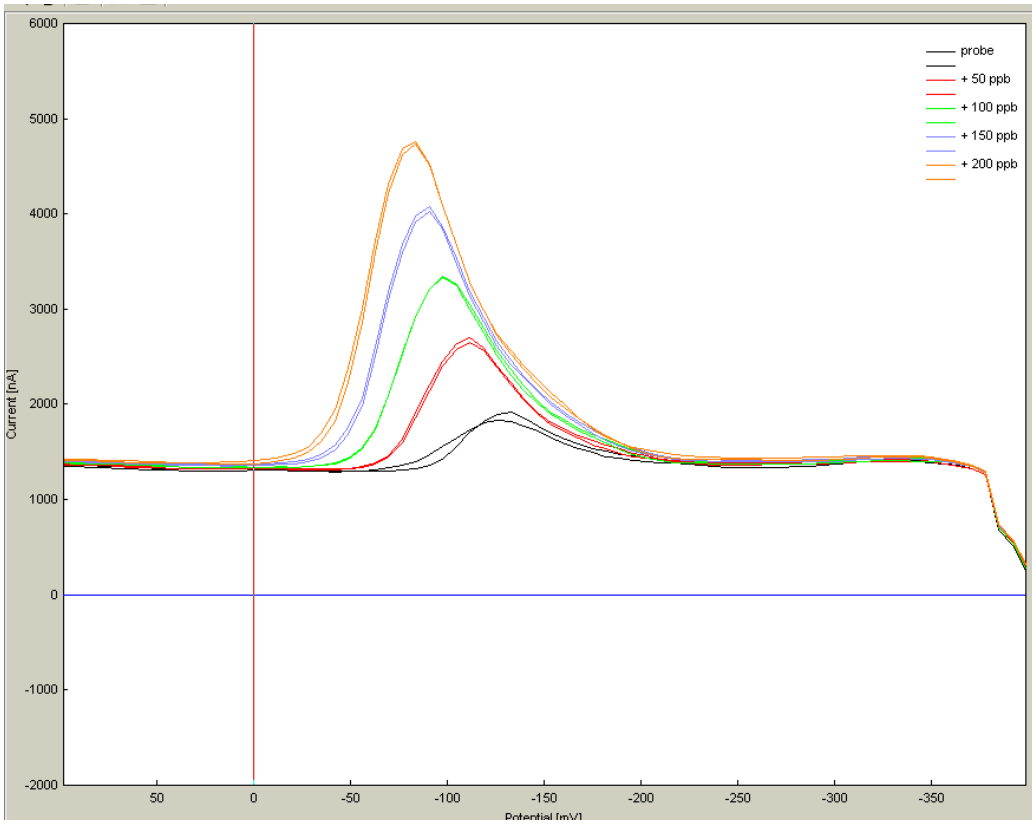
Sample treatment After sampling the water samples are usually filtered (filter pore size 0.45m) and the filtrate is acidified to the pH value 2. In samples, where silver is to be determined, do not use hydrochloric acid for acidification.
The samples of natural waters may contain organic compounds. The elimination of these compounds is carried out by irradiation with UV lamp (400 - 500 W) in the presence of H_2O_2 (50 µl of 30% H_2O_2 per each 10 ml of the sample) for two hours in closed quartz vessel cooled by a stream of air, the solution temperature must not exceed 90 °C.

Method DP stripping – SE

Procedure To 10 ml of the sample in the electrolytic cell add 1 ml of ammoniacal buffer solution and 100 µl of EDTA solution. After mixing the measurement is carried out using the method DP stripping – SE and the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-600		Inert gas [s]	600-900
Final E_{fin} [mV]	400		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Cleaning potential [mV]	400
			Cleaning time [s]	60
			Accumulation potential [mV]	-600
			Accumulation time [s]	50-200
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80



- The peak of silver is situated at the potential 25 mV.
- For the evaluation use the method of standard addition or calibration line (linear approximation).

Note:
When calomel or Ag/AgCl electrode is used as the reference electrode, it has to be separated from the measured solution by a salt bridge filled with ammoniacal buffer solution or NH_4NO_3 solution (0.1 M). If a $Hg/HgSO_4$ reference electrode is used a salt bridge is not needed, but all potentials mentioned above to be increased by 400 mV.

E. Tribodiagnostics of motors and lubricants

18. Determination of Cu, Cd, Pb, Zn and Fe in lubricating oils

Principle

The determination of abrasive metals in lubricating oils is carried out in two phases:

- extraction of metals from the oil into the aqueous acidic solution (by means of an extractor from the TRIBO II - 2 set),
- polarographic determination of:
  - a) Cu, Cd, Pb and Zn
  - b) Fe

Reagents

Pure ethanol

HCl 37%, p. a.
for the concentrations of metals in the oils less than 10 ppm the "suprapur" purity HCl is essential

Trichloroethylene or chloroform, p. a.

H_2O_2 30%

Standard Solution of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} containing 0.5 mg/ml.

Method

DC polarography

Procedure

Before measurement the surface of the electrode is slightly polished using hard paper card (punched card). The electrode is then polarized in 0.1M ammoniacal buffer solution using the method DC polarography and the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-600		Inert gas [s]	600-900
Final E_{fin} [mV]	400		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	500			

Cathodic and anodic scans (cyclic voltammetry) are repeated approx. ten times and thus the electrode is prepared for measurement. When not used the electrode is kept in closed space to prevent a mechanical damage of the active surface.

Extraction

In the case the oil contains a high percentage of additives, part of them has to be first removed. The oil sample is therefore first to be shaken with an equal volume of pure ethanol. 1 ml of the oil has then to be introduced into the extraction vessel, 3 ml of the organic solvent added and the mixture to be stirred for 5 minutes. 4 ml of conc. HCl are to be transferred into the upper vessel of the extractor. During the stirring the acid is to be added into the extraction vessel at the rate which brings the whole volume down in 5 minutes. Then to the upper vessel 21 ml of distilled water are added and let flow slowly down into the extraction vessel where the mixture is being stirred. In the meantime the solution is being spontaneously transferred through a side-arm into a collecting vessel. A part of the aqueous extract is then to be boiled for 3 minutes with 2 drops of 30 % H_2O_2, filled up to a known volume by distilled water and used for the polarographic determination.

18.1. Determination of Cu, Pb, Cd and Zn

Method DP stripping - HMDE

Procedure 2 ml of the adjusted extract to be mixed with 8 ml of distilled water in the polarographic cell and to apply the technique of „DP stripping - HMDE“ with the parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-1100		Inert gas [s]	600-900
Final E_{fin} [mV]	100		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-1100
			Accumulation time [s]	0-180
			Rest [s]	15
			Pulse height [mV]	50
			Pulse width [ms]	80

The accumulation time has to be tried each time. If the peak of Zn appears too high in comparison with those of other metals, first the record with the above parameters has to be carried out and then the same measurement to be repeated for Pb, Cd and Cu with the initial potential of - 800 mV.

The evaluation has to be carried out by the method of standard addition, for each metal with the same measurement accuracy, same size of the mercury drop and same accumulation time as in the original solution. However, the "calibration curve" method can also be applied.

18.2. Determination of Fe

Reagents **3 M KOH, p. a. in H_2O**

3 M triethanolamine, p. a. in H_2O

Standard Solution of Fe (III) ions containing 0.4 mg Fe in 1l

Method DP stripping - HMDE

Procedure Into the polarographic cell to be introduced 3 ml of the extract (after the H_2O_2 treatment), 3 ml of 3 M KOH and 4 ml of the 0.2 M triethanolamine, and the „DP stripping - HMDE“ technique to be applied with the following parameters:

Parameters

POTENTIAL			METHOD PARAMETERS	
Initial E_{in} [mV]	-800		Inert gas [s]	600-900
Final E_{fin} [mV]	-1250		Number of scans [1]	1-3
Scan rate [$mV.s^{-1}$]	20		Accumulation potential [mV]	-800
			Accumulation time [s]	0
			Rest [s]	0
			Pulse height [mV]	-50
			Pulse width [ms]	80

Note:
Do not forget that the result obtained must be recalculated with respect to the dilutions and the treatment to which the sample was subjected before the analysis.

Appendix A: Solutions

A1: The Standard Solutions

The results of polarographic and voltammetric analyses are evaluated by comparing the polarographic or the voltammetric curve of the sample, obtained according to the procedures given below, with the curve obtained with a solution which contains an exactly known amount of the followed species. For that purpose it is necessary to have prepared a stock of solutions containing the known amounts of the species to be measured – these are the standard solutions. The standard solutions are prepared by dissolving an exactly weighed amount of the followed substance of highest purity (e.g., a 99.99% metallic lead) in an appropriate solvent, usually acid (most frequently HNO_3), again of the highest purity grade. The weighed amount of the metal is taken so that the resulting solution contains 1 mg of the metal in 1 ml. The solutions of metals prone to hydrolysis (Al^{3+}, Fe^{3+}) must be acidified. Such stock standard solutions are best stored in bottles made of polyethylene. Once prepared they can be used over the period of up to 6 months.

In the case that no pure metal is available the standard solutions can be prepared from a soluble salt of the required metal. In Table 1 are listed the appropriate salts and the corresponding weights for preparing 100 ml of a standard solution containing 1 mg of the metal in 1 ml.

On the following site you will find an overview of several standard solutions.

metal	compound	weighed g	solvent
aluminium	$AlCl_3.6H_2O$	0.8948	0.1 M HCl
arsenic	$Na_2HasO_4.7H_2O$	0.4165	0.1 M HCl
cadmium	$CdSO_4.8/3\ H_2O$	0.2282	“
cobalt	$Co(NO_3)_2.6H_2O$	0.4938	“
chromium	$K_2Cr_2O_7$	0.2829	
copper	$CuSO_4.5H_2O$	0.3929	0.1 M HNO_3
iron	$Fe(NO_3)_3.9\ H_2O$	0.7234	0.1 M HCl
	$FeSO_4.7\ H_2O$	0.4978	“
lead	$Pb(CH_3COO)_2 3\ H_2O$	0.1831	0.1 M HNO_3
	$Pb(NO_3)_2$	0.1599	“
manganese	$MnCl_2.4\ H_2O$	0.3602	0.1 M HCl
mercury	$HgCl_2$	0.1354	0.5 M H_2SO_4
molybdenum	$Na_2MoO_4.2\ H_2O$	0.2522	0.1 M HCl
	$(NH_4)_6Mo_7O_{24}.4\ H_2O$	0.1840	“
nickel	$NiSO_4.7H_2O$	0.4784	„
selenium	SeO_2	0.1405	0.1 M HNO_3
silver	$AgNO_3$	0.1575	0.1 M HNO_3
tin	$SnCl_2.2\ H_2O$	0.1901	1 M HCl
uranium	$UO_2(NO_3).6\ H_2O$	0.2110	0.1 M HNO_3
zinc	$ZnSO_4.7\ H_2O$	0.4399	0.1 M HCl
Chlorides	NaCl	0.1648	
	KCl	0.2103	
Bromides	NaBr	0.1288	
Nitrites	$NaNO_2$	0.1500	
Sulfides	$Na_2S.9H_2O$	0.7490	0.2 M NaOH
Sulfite	Na_2SO_3	0.1574	
Thiosulfate	$Na_2S_2O_3.5H_2O$	0.2213	
Cyanides	KCN	0.2503	0.01 M KOH
Antimony	Sb_20_3	0.1197	conc. HCl
Vanadium	NH_4VO_3	0.2296	0.1 M HCl
Ammonium	NH_4Cl	0.2965	
Beryllium	$Be(NO_3)_2.3\ H_2O$	2.0757	0.1 M HCl
Thallium	$TlNO_3$	0.1303	0.1 M HNO_3
Phosphates	KH_2PO_4	0.14329	
Iodine	KIO_3	0.1686	

Appendix B: Contact Details

B1: Contact Details

If you have any questions or if you need further assistant with specific methods please feel free to contact your local distributor or us directly.

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