Metrohm

Determination of copper in water with the scTRACE Gold

Summary

Copper is one of the few metals which is available in nature also in its metallic form. This and the fact that it is rather easy to smelt lead to intense use of this metal already in pre-Christian times, in the so-called Copper and Bronze Age. Nowadays it is more important than ever, due to its good electrical conductivity and its other physical properties.

For plants and animals it is an essential trace element, for bacteria in contras it is highly toxic.

This Application Bulletin describes the determination of copper by anodic stripping voltammetry using the scTRACE Gold electrode. With a deposition time of 30 s, the limit of detection is about 0.5 µg/L.

Samples

Surface water, ground water

Instrument 946 Portable VA Analyzer

946 Portable VA Analyzer	2.946.0010

or

Instrument 884 Professional VA

884 Professional VA	2.884.0110
Accessories	
viva 2.0	
Electrode equipment with scTRACE Gold for 884 Professional VA	6.5339.050
Containing:	
Electrode shaft	6.1241.080
Stirrer for 884	6.1204.500
Measuring vessel 5 mL	6.1415.150
SGJ Stopper B-14	6.1446.000
Threaded stopper	6.1446.040
Connection bushing M6	6.1808.000
Cap	6.2753.210

or

Instrument 797 VA Computrace

797 VA Computrace	2.797.0020
Accessories	

Electrode equipment with scTRACE Gold for 797 VA Computrace	6.5340.000
Containing:	
Electrode shaft	6.1241.080
Stirrer	6.1204.200
Driving belt	6.1244.020
Measuring vessel 5 mL	6.1415.150
SGJ Stopper B-14	6.1446.000
Cover	6.2753.210

Electrodes

scTRACE Gold	6.1258.000

The scTRACE Gold

The scTRACE Gold sensor holds all three electrodes required for a voltammetric determination. Together with the electrode shaft it makes a complete electrode system which can be used in any Metrohm voltammetric measuring stand. No further electrodes are required. The working electrode is a gold microwire. Reference and auxiliary electrode, on the rear side of the sensor are screen printed electrodes.

Different from other solid state electrodes the scTRACE Gold does not need extensive conditioning before it can be used. A new sensor only needs to be activated as described in paragraph «Activation of the scTRACE Gold with … » of the respective instrument. This takes about 10 minutes and the sensor is ready for the first determination.

Due to its construction the scTRACE Gold is maintenance-free. It can be electrochemically cleaned as described in paragraph «Cleaning of the scTRACE Gold with …» of the

respective instrument, but mechanical cleaning is neither necessary nor possible. As any electrode the performance of the scTRACE Gold will deteriorate with the number of determinations. Signals will get smaller and curves are less reproducible. Then it is time to replace the sensor.

Overview

The Application Bulletin describes the following methods:

Activation of scTRACE Gold

A new sensor needs to be activated. The activation only has to be carried out prior to the first use. If the electrode needs to be cleaned before, in between or after determinations the procedure described in the respective subchapters of the instruments «Cleaning of the scTRACE Gold with …» should be used.

Determination of copper

Copper is determined by anodic stripping voltammetry. In an acidic electrolyte, containing chloride, free Cu^{2+} ions are reduced and deposited as metallic Cu on the gold working electrode. In the subsequent stripping step the copper is re-oxidized giving the analytical signal.

Cleaning of the scTRACE Gold

To maintain the scTRACE Gold the sensor can be electrochemically cleaned. The cleaning can be performed before, after, but also in between a series of determinations. But it should only be carried out when necessary, e.g. when the background current is unusually high or peaks show an unusual shape, since it reduces the lifetime of the electrode.

Detailed information on the specifics of measuring solution and voltammetric parameters for the different instruments can be found in the respective chapters «Determination with the 946 Portable VA analyzer», «Determination with the 884 Professional VA» or «Determination with the 797 VA Computrace»

Reagents

- Cu standard stock solution, $\beta(Cu)$ = 1 g/L

- Sulfuric acid, $w(H_2SO_4)$ = 96%, for trace analysis*, CAS 7664-93-9

- Hydrochloric acid, $w(HCl)$ = 30%, for trace analysis*, CAS 7647-01-0

- Nitric acid, $w(HNO_3)$ = 65%, for trace analysis*, CAS 7697-37-2

- Potassium chloride, KCl, for trace analysis*, CAS 7447-40-7

- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Honeywell/Fluka TraceSelect® or equivalent

Solutions

Cleaning solution	$c(H_2SO_4)$ = 0.5 mol/L $c(KCl)$ = 0.05 mol/L In a 100 mL volumetric flask 0.373 g KCl are dissolved in approx. 80 mL ultrapure water. 2.78 mL $w(H_2SO_4)$ = 96% are carefully added. Attention! Solution gets very hot. After cooling down to room temperature the solution is made up to the mark with ultrapure water.
Electrolyte	$c(KCl)$ = 0.3 mol/L $c(HCl)$ = 0.1 mol/L In a 100 mL volumetric flask 2.236 g KCl are dissolved in approx. 80 mL ultrapure water. 1 mL $w(HCl)$ = 30% is added. The solution is made up to the mark with ultrapure water.

Standard solutions

Cu standard	$\beta(Cu)$ = 1 mg/L Approx. 40 mL ultrapure water are filled into a 50 mL volumetric flask. 0.05 mL $w(HNO_3)$ = 65% and 0.05 mL Cu standard stock solution are added. The solution is made up to the mark with ultrapure water.

Sample preparation

Ground, drinking, and mineral water can usually be analyzed directly.

Water with a low to medium degree of contamination by organic substances is digested in the 909 UV Digester: 10 mL acidified water sample (pH = 2) are mixed with 10 µL $w(HNO_3)$ = 65% and 50 µL $w(H_2O_2)$ = 30% and irradiated for 90 min at 90 °C.

Determination with the 946 Portable VA analyzer

Activation of the scTRACE Gold with the 946 Portable VA Analyzer

Analysis

18 mL cleaning solution are pipetted into the measuring vessel. The activation is carried out using the parameters «Parameters for activation with 946 Portable VA Analyzer».

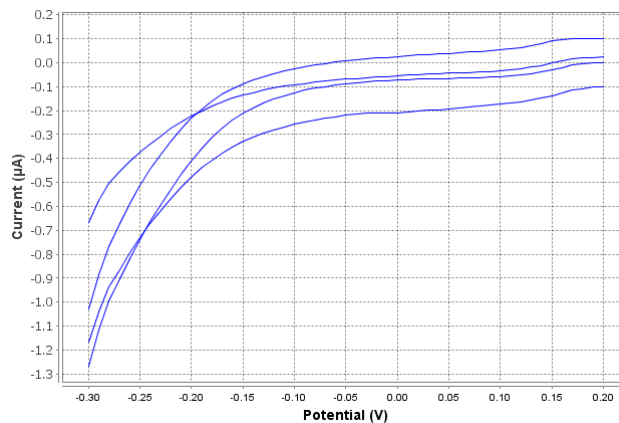### *Activation solution for 946 Portable VA Analyzer*

18 mL cleaning solution

Parameters for activation with 946 Portable VA Analyzer

Voltammetric	
Measuring mode	LSV – Linear sweep
Stirring rate	2000 min^{-1}
Cyclovoltammetric pretreatment	
Start potential	-1.5 V
Vertex potential	1.0 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	-1.0 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	10 s
Equilibration time	5 s
Sweep	
Start potential	-0.3 V
End potential	0.2 V
Potential step	0.01 V
Sweep rate	0.4 V/s

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the curves obtained during activation with 946 Portable VA Analyzer

Comments

The lifetime of the sensor will significantly be reduced if the activation is repeated or carried out more than once.

For more comments see chapter «Comments» at the end of the document.

Determination of copper with the 946 Portable VA Analyzer

Analysis

15 mL sample and 3 mL electrolyte are pipetted into the measuring vessel. If the concentration in the sample is too high, less sample or a diluted sample has to be used. The determination is carried out using the parameters «Parameters for determination of copper with 946 Portable VA Analyzer».

The concentration of Cu is quantified by two additions of Cu standard solution.

Measuring solution for 946 Portable VA Analyzer

15 mL (diluted) sample

3 mL electrolyte

Parameters for determination of copper with 946 Portable VA Analyzer

Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	3000 min^{-1}
Cyclovoltammetric pretreatment	
Start potential	0 V
Vertex potential	0.75 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	0.75 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	30 s
Equilibration time	10 s
Sweep	
Start potential	-0.1 V
End potential	0.6 V
Potential step	0.006 V
Sweep rate	0.1 V/s
Pulse amplitude	0.05 V
Pulse time	0.02 s
Potentiostat	
Current measuring range	± 1 µA
Substance	
Name	Cu

Characteristic potential	0.25 V

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the determination of copper with 946 Portable VA Analyzer
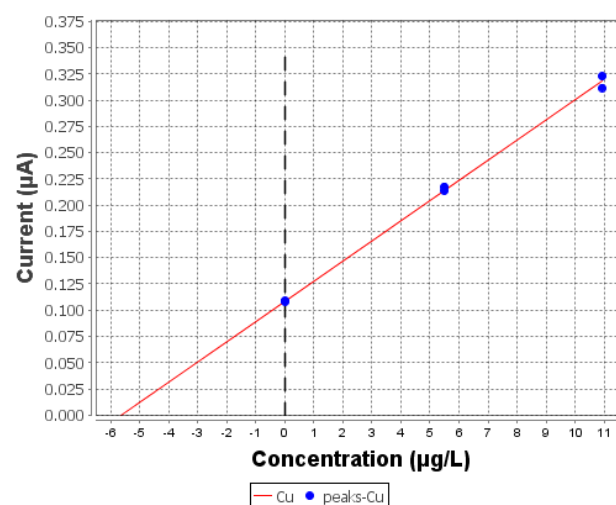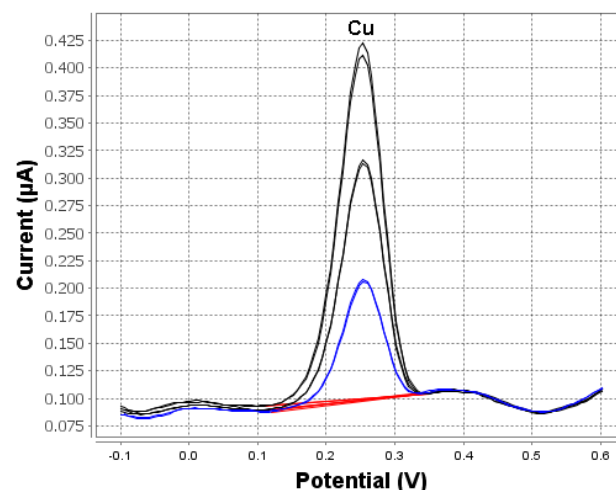
Result

Sample	Tap water
Sample size	2.0 mL
β(Cu)	50.9 µg/L

Comments

See chapter «Comments» at the end of the document.

Cleaning of the scTRACE Gold with the 946 Portable VA Analyzer

Analysis

15 mL ultrapure water and 3 mL electrolyte are pipetted into the measuring vessel. The cleaning is carried out using the parameters «Parameters for cleaning with 946 Portable VA Analyzer».

Cleaning solution for 946 Portable VA Analyzer

15 mL ultrapure water
3 mL electrolyte

Parameters for cleaning with 946 Portable VA Analyzer

Voltammetric	
Measuring mode	LSV – Linear sweep
Stirring rate	2000 min^-1
Cyclovoltammetric pretreatment	
Start potential	-1.0 V
Vertex potential	0.8 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	-0.8 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	5 s
Equilibration time	5 s
Sweep	
Start potential	-0.2 V
End potential	0.6 V
Potential step	0.01 V
Sweep rate	0.1 V/s

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the curves obtained during cleaning with 946 Portable VA Analyzer
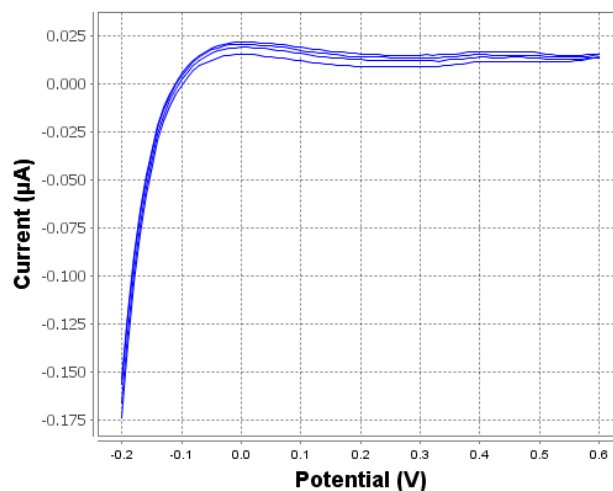
Comments

Before the sensor is stored, it should be thoroughly rinsed with ultrapure water.

For more comments see chapter «Comments» at the end of the document.

Determination with the 884 Professional VA

Activation of the scTRACE Gold with the 884 Professional VA

Analysis

12 mL cleaning solution are pipetted into the measuring vessel. The activation is carried out using the parameters «Parameters for activation with 884 Professional VA».

Measuring solution for 884 Professional VA

12 mL cleaning solution

Parameters for activation with 884 Professional VA

Voltammetric	
Measuring mode	CVS – Cyclic voltammetric stripping
Stirring rate	2000 min^{-1}
Hydrodynamic measurement	No
Cyclovoltammetric pretreatment	
Start potential	-1.5 V
Vertex potential	1.0 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	-1.0 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	10 s
Equilibration time	5 s
Sweep	
Start potential	-0.3 V
First vertex potential	0.2 V
Second vertex potential	-0.3 V
Potential step	0.01 V
Sweep rate	0.4 V/s

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the curves obtained during activation with 884 Professional VA
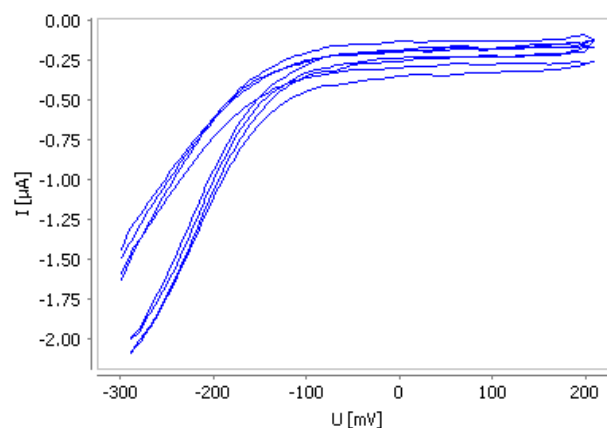
Comments

The lifetime of the sensor will significantly be reduced if the activation is repeated or carried out more than once.

For more comments see chapter «Comments» at the end of the document.

Determination of copper with the 884 Professional VA

Analysis

10 mL sample and 2 mL electrolyte are pipetted into the measuring vessel. If the concentration in the sample is too high, less sample or a diluted sample has to be used. The determination is carried out using the parameters «Parameters for determination of copper with 884 Professional VA».

The concentration of Cu is quantified by two additions of Cu standard solution.

Measuring solution for 884 Professional VA

10 mL (diluted) sample

2 mL electrolyte

Parameters for determination of copper with 884 Professional VA

Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Cyclovoltammetric pretreatment	
Start potential	0 V
Vertex potential	0.75 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	0.75 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	30 s
Equilibration time	10 s
Sweep	
Start potential	-0.1 V
End potential	0.6 V
Potential step	0.006 V
Potential step time	0.1 s
Pulse amplitude	0.05 V
Pulse time	0.04 s
Measuring time	0.01 s
Potentiostat – current measuring range	
Highest range	2 mA
Lowest range	20 µA

Substance

Name	Cu
Characteristic potential	0.25 V

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the determination of copper with 884 Professional VA
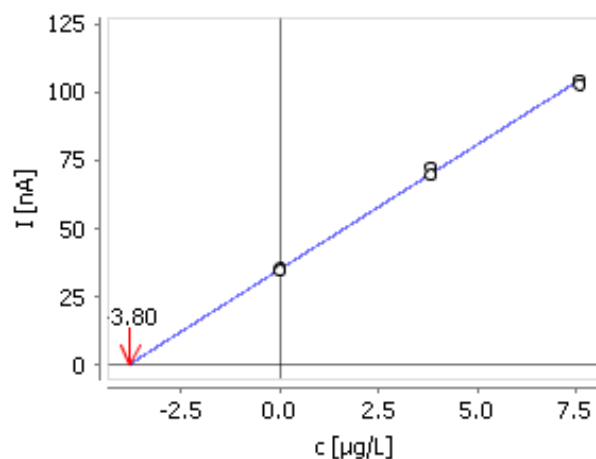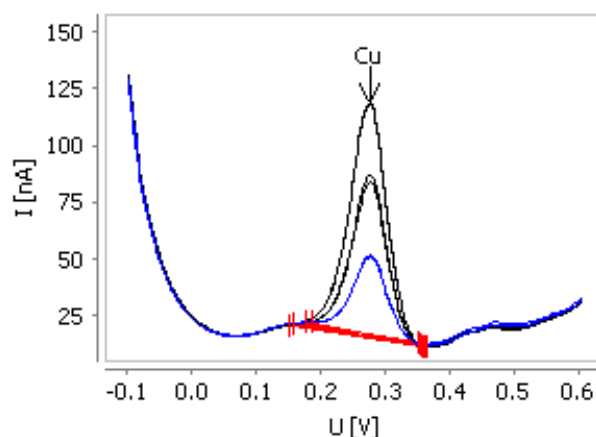
Result

Sample	Tap water
Sample size	1.0 mL
β(Cu)	49.4 µg/L

Comments

See chapter «Comments» at the end of the document.

Cleaning of the scTRACE Gold with the 884 Professional VA

Analysis

10 mL ultrapure water and 2 mL electrolyte are pipetted into the measuring vessel. The cleaning is carried out using the parameters «Parameters for cleaning with 884 Professional VA».

### *Cleaning solution for 884 Professional VA*

10 mL ultrapure water
2 mL electrolyte

Parameters for cleaning with 884 Professional VA

Voltammetric	
Measuring mode	CVS – Cyclic voltammetric stripping
Stirring rate	2000 min^{-1}
Hydrodynamic measurement	No
Cyclovoltammetric pretreatment	
Start potential	-1.0 V
Vertex potential	0.8 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	0.8 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	10 s
Equilibration time	5 s
Sweep	
Start potential	-0.2 V
First vertex potential	0.6 V
Second vertex potential	-0.2 V
Potential step	0.01 V
Sweep rate	0.4 V/s

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the curves obtained during cleaning with 884 Professional VA
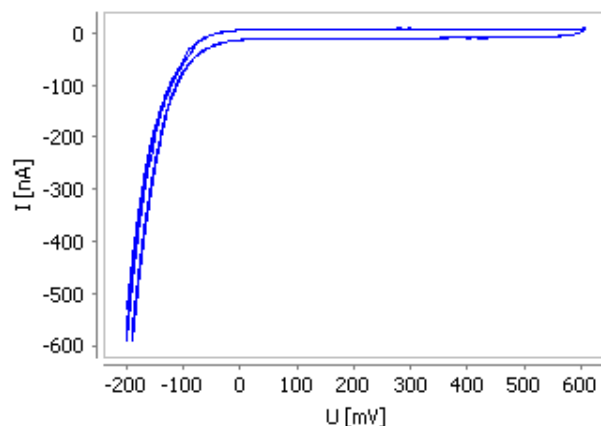
Comments

Before the sensor is stored, it should be thoroughly rinsed with ultrapure water.

For more comments see chapter «Comments» at the end of the document.

Determination with the 797 VA Computrace

Activation of the scTRACE Gold with the 797 VA Computrace

Analysis

12 mL of the cleaning solution are pipetted into the measuring vessel. The activation is carried out using the parameters given under «Parameters for activation with 797 VA Computrace».

Measuring solution

12 mL cleaning solution

Parameters for activation with 797 VA Computrace

Voltammetric	
Measuring mode	DC – Sampled direct current
Stirring rate	2400 min⁻¹
Cyclovoltammetric pretreatment	
Start potential	-1.5 V
Vertex potential	1.0 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	0.1 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	10 s
Equilibration time	5 s
Sweep	
Start potential	-0.3 V
End potential	0.2 V
Potential step	0.6 V
Potential step time	0.025 s

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the curves obtained during activation with 797 VA Computrace
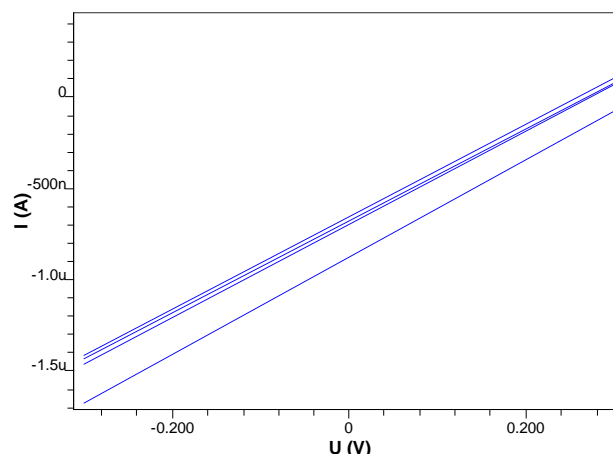
Comments

The lifetime of the sensor will significantly be reduced if the activation is repeated or carried out more than once.

For more comments see chapter «Comments» at the end of the document.

Determination of copper with the 797 VA Computrace

Analysis

10 mL (diluted) sample and 2 mL electrolyte are pipetted into the measuring vessel. If the concentration in the sample is too high, less sample or a diluted sample has to be used. The determination is carried out using the parameters «Parameters for determination of copper with 797 VA Computrace».

The concentration of Cu is quantified by two additions of Cu standard solution.

Measuring solution for 797 VA Computrace

10 mL (diluted) sample

2 mL electrolyte

**Parameters for determination of copper with 797 VA Computrace**

Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Cyclovoltammetric pretreatment	
Start potential	0 V
Vertex potential	0.75 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	0.75 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	30 s
Equilibration time	10 s
Sweep	
Start potential	-0.1 V
End potential	0.6 V
Potential step	0.006 V
Potential step time	0.06 s
Pulse amplitude	0.05 V
Pulse time	0.02 s
Substance	
Name	Cu
Characteristic potential	0.25 V

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the determination of copper with 797 VA Computrace
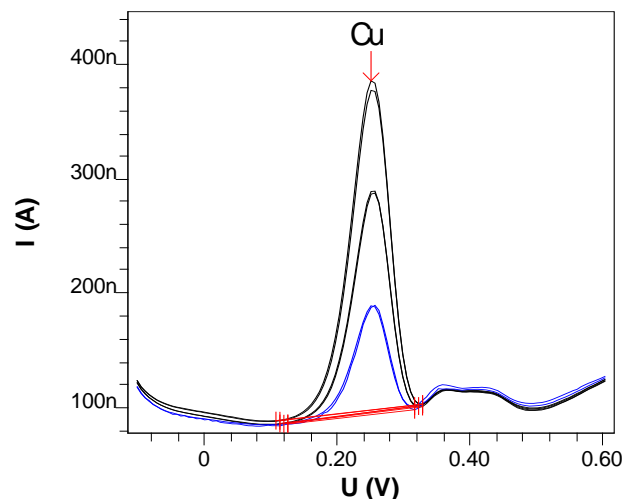

```
Cu
c =    48.593 ug/L
+/-     1.277 ug/L (2.63%)
```
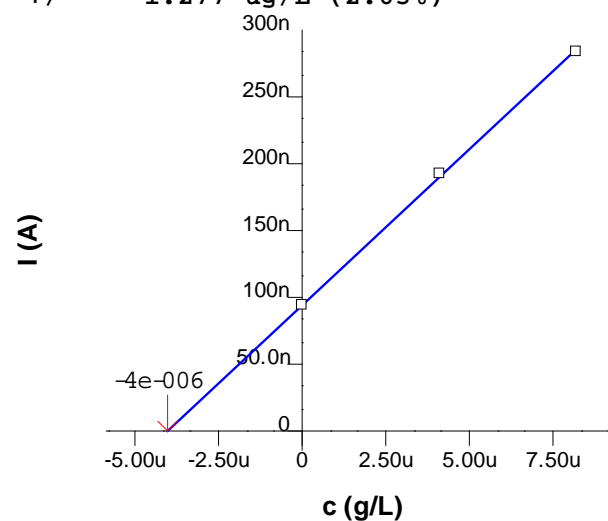

Result

Sample	Tap water
Sample size	1.0 mL
β(Cu)	48.6 µg/L

Comments

See chapter «Comments» at the end of the document.

Cleaning of the scTRACE Gold with the 797 VA Computrace

Analysis

10 mL ultrapure water and 2 mL electrolyte are pipetted into the measuring vessel. The cleaning is carried out using the parameters «Parameters for cleaning with 797 VA Computrace».

Cleaning solution for 797 VA Computrace

10 mL ultrapure water
2 mL electrolyte

Parameters for cleaning with 797 VA Computrace

Voltammetric	
Measuring mode	DC – Sampled direct current
Stirring rate	2000 min^{-1}
Cyclovoltammetric pretreatment	
Start potential	-1.0 V
Vertex potential	0.8 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	0.8 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	10 s
Equilibration time	5 s
Sweep	
Start potential	-0.2 V
End potential	0.6 V
Potential step	0.01 V
Potential step time	0.1 s

More detailed method parameters can be found in the method printout which is available as a separate document.

Example for the curves obtained during cleaning with 797 VA Computrace
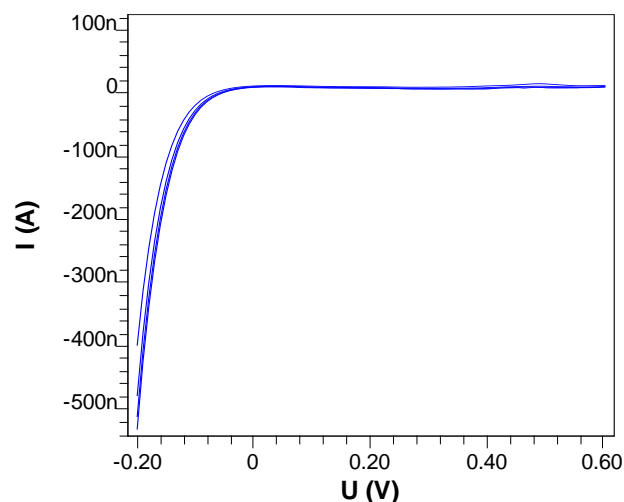
Comments

Before the sensor is stored, it should be thoroughly rinsed with ultrapure water.

For more comments see chapter «Comments» at the end of the document.

Comments

Putting a new scTRACE Gold into operation

After the activation of a new scTRACE Gold electrode it is possible that a few determinations have to be carried out before the electrode shows good results. Best performance was obtained when the following steps were carried out before the first sample determination:

1) Activation of scTRACE Gold
2) Cleaning of scTRACE Gold
3) Determination of reagent blank

Limit of detection

The limit of detection was determined using the «regression approach» [1], where the limit of detection is calculated as «$3 \cdot s_y$», with s_y as the residual standard deviation of a linear regression. With «$10 \cdot s_y$» the limit of quantification is calculated.
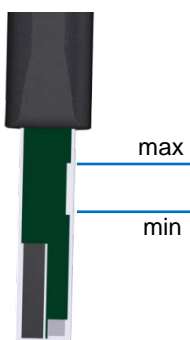
Deposition	Limit of detection	Limit of quantification
30 s	0.5 µg/L	1.6 µg/L
60 s	0.3 µg/L	0.8 µg/L

Linear working range

The linear working range was read out from a calibration curve.

Deposition	Linear range
30 s	25 µg/L
60 s	15 µg/L

Solution level

Make sure the electrode is fairly immersed into the measuring solution. A mark on the rear side of the electrode indicates the minimum (min) and maximum (max) solution level. If a measuring vessel other than 6.1415.150 is used with 884 Professional VA or 797 VA Computrace volumes of sample and reagents may need to be adapted. For 946 Portable VA Analyzer only one type of measuring vessel is available.

Interferences

The influence of different cations on the peak of $\beta(Cu)$ = 10 µg/L was tested with a deposition time of 30 s.

Ag	Will interfere due to the formation of insoluble AgCl. With concentrations of $\beta(Ag^+)$ < 200 µg/L the concentration of chloride in the measuring solution will be reduced leading to a shift of the Cu signal to more negative potentials (0.27 V … 0.16 V). With concentrations of $\beta(Ag^+)$ > 200 µg/L the determination of Cu is impossible due to an increased background current as a result of AgCl precipitations.
Bi	Peak at approx. 0.15 V. Does not interfere up to 20 time excess. With concentrations > 200 µg/L the Bi peak starts to overlap with the Cu peak. This can partially be compensated by a selective oxidation of the deposited Bi and a more positive start potential of the sweep.
Fe(III)	Peak at approx. 0.45 V. Does not interfere up to 100 time excess. With concentrations > 2 mg/L the Fe peak start to overlap with the Cu peak and may affect the determination of lower concentrations.
Hg	Peak at approx. 0.48 V. Does not interfere up to 100 µg/L, only causes a slight shift of the Cu peak (0.27 V … 0.26 V). With higher concentrations the Hg peak starts to overlap with the Cu peak. Furthermore the oxygen interference shifts to more positive potentials also interfering with the Cu peak.
Sb(III)	Peak at approx. 0 V. Decrease the sensitivity when present in excess. This can partially be compensated by a selective oxidation of the deposited Sb and a more positive start potential of the sweep.
Sb(V)	Peak at approx. 0 V. Does not interfere. The peak only gets visible at concentrations > 0.5 mg/L.

Storing the scTRACE Gold

When not in use, the electrode should be stored dry. Before the sensor is stored, it should be thoroughly rinsed with ultrapure water. To put it back into operation after it had not been used for a while it is often sufficient to run a blank determination, using the parameters for a sample determination, just replacing the sample by ultrapure water.

When the background current is unusually high or the peak shows an unusual shape, it is recommended to clean the electrode using the procedure described in the paragraph « Cleaning of the scTRACE Gold with …» of the respective instrument. This procedure can be carried out before, after, but also in between a series of determinations. Afterwards the electrode is rinsed thoroughly with ultrapure water.

Care has to be taken that the gold microwire is not damaged when the sensor is removed or stored outside the measuring stand.

References

[1] J. Mocak, A. Bond, S. Mitchell and G. Scollary, "A statistical overview of standard (IUPAC and ACS) and new procedures for determining the limits of detection and quantification: Application to voltammetric and stripping techniques," *Pure and Applied Chemistry,* vol. 69, no. 2, pp. 297-328, 1997.