

Application Bulletin 433/1

Determination of lead in water with the scTRACE Gold modified with a silver film

Summary

Lead is known to be highly toxic and lead salts are easily absorbed by creatures. By interfering with enzyme reactions, lead can affect all parts of the human body. It can cause severe damage to brain and kidneys and can cross the blood-brain barrier. Cases of chronic lead poisoning caused by lead metal used in the water piping system are well known. Therefore, the control of drinking water for lead content is of utmost importance. In many countries (e.g., EU, USA), the limit for lead in drinking water is between 10 and 15 µg/L. These concentrations can reliably be determined with the method described in this Application Bulletin. The determination is carried out by anodic stripping voltammetry at a silver film applied to the scTRACE Gold electrode.

Both, the limit of detection and the linear range depend on the instrument used for the application. With a deposition time of 30 s, the limit of detection is in the range of 0.4 to 0.6 µg/L. The linear range stretches from approx. 25 µg/L with the 946 Portable VA Analyzer, through approx. 35 µg/L with the 884 Professional VA to approx. 50 µg/L with the 797 VA Computrace. With 60 s deposition time, the limit of detection can be lowered to approx. 0.2 µg/L.

For drinking water samples, a sample preparation is not required.

Samples

Surface water, ground water

Instrument 946 Portable VA Analyzer

946 Portable VA Analyzer	2.946.0010
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or

Instrument 884 Professional VA

884 Professional VA	2.884.0110
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Accessories

viva 2.0	6.6065.20x
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Electrode equipment with scTRACE Gold for 884 Professional VA	6.5339.050
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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
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Accessories

Electrode equipment with scTRACE Gold for 797 VA Computrace	6.5340.000
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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
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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 the 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.

Cleaning of the scTRACE Gold

To maintain the scTRACE Gold the sensor has to be electrochemically cleaned. The same procedure is also used to remove the silver film.

The cleaning procedure is carried out at the beginning of the working day, before the silver film is applied, in between determinations when it is necessary to apply a fresh silver film and at the end of the working day before the electrode is stored.

Plating of the silver film

The silver film is plated ex-situ in a plating solution containing the alkaline plating electrolyte with sulfosalicylic acid and 2 mg/L silver. The plating solution is discarded after the plating.

Determination of lead

Lead is determined by anodic stripping voltammetry. In an acidic electrolyte, free Pb^{2+} ions are reduced and deposited as metallic lead on the silver film. In the subsequent stripping step the lead is re-oxidized giving the analytical signal.

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»

Standard operating procedure

- Activation of the scTRACE Gold (only for a new electrode)
- Cleaning of the scTRACE Gold
- Plating of the silver film
- Determination of lead in check standard and samples
- Cleaning of the scTRACE Gold (to remove the silver film)

For more information on the standard operating procedure please refer to the «Comments» at the end of this document.

Reagents

- Pb standard stock solution, $\beta(Pb^{2+}) = 1$ g/L, commercially available
- Ag standard stock solution, $\beta(Ag^+) = 1$ g/L, commercially available
- Sulfuric acid, $w(H_2SO_4) = 96\%$, for trace analysis*, CAS 7664-93-9
- Nitric acid, $w(HNO_3) = 65\%$, for trace analysis*, CAS 7697-37-2
- Citric acid monohydrate, $C_6H_8O_7 \cdot H_2O$, for trace analysis*, CAS 5949-29-1
- Potassium chloride, KCl, for trace analysis*, CAS 7447-40-7
- 5-Sulfosalicylic acid dihydrate, $C_7H_6O_6S \cdot 2H_2O$, for analysis, CAS 5965-83-3
- Sodium hydroxide solution, $w(NaOH) = 30\%$, for trace analysis*, CAS 1310-73-2
- Ultrapure water, resistivity >18 M Ω -cm (25 °C), type I grade (ASTM D1193)

In addition, if UV digestion is required:

- Hydrogen peroxide solution, $w(H_2O_2) = 30\%$, for trace analysis*, CAS 7722-84-1

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

Solutions

Activation solution	$c(\text{H}_2\text{SO}_4) = 0.5 \text{ mol/L}$ $c(\text{KCl}) = 0.05 \text{ mol/L}$ In a 100 mL volumetric flask 0.373 g KCl are dissolved in approx. 80 mL ultrapure water. 2.78 mL $w(\text{H}_2\text{SO}_4) = 96\%$ 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.
Plating electrolyte	$c(\text{sulfosalicylic acid}) = 0.4 \text{ mol/L}$ $c(\text{NaOH}) = 1 \text{ mol/L}$ 5.084 g 5-sulfosalicylic acid dehydrate are dissolved in approx. 40 mL ultrapure water. 5 mL sodium hydroxide solution $w(\text{NaOH}) = 30\%$ are added. The solution is made up to 50 mL with ultrapure water.
Ag solution	$\beta(\text{Ag}^+) = 20 \text{ mg/L}$ $c(\text{HNO}_3) = 0.14 \text{ mol/L}$ 1 mL Ag standard stock solution and 0.5 mL nitric acid are made up to 50 mL with ultrapure water.
Supporting electrolyte	$c(\text{citric acid}) = 0.5 \text{ mol/L}$ $c(\text{KCl}) = 0.1 \text{ mol/L}$ $c(\text{NaOH}) = 0.1 \text{ mol/L}$ 10.51 g citric acid monohydrate and 0.746 g KCl are dissolved in approx. 80 mL ultrapure water. 1 mL NaOH solution is added. The solution is made up to 100 mL with ultrapure water. The electrolyte has pH 2.2 – 2.3.

Standard solutions

Pb standard solution 1 mg/L	$\beta(\text{Pb}^{2+}) = 1 \text{ mg/L}$ Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL $w(\text{HNO}_3) = 65\%$ and 0.05 mL Pb standard stock solution are added. The solution is made up to the mark with ultrapure water.
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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 $w(\text{HNO}_3) = 65\%$ and 50 μL $w(\text{H}_2\text{O}_2) = 30\%$ 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

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

Activation solution for 946 Portable VA Analyzer

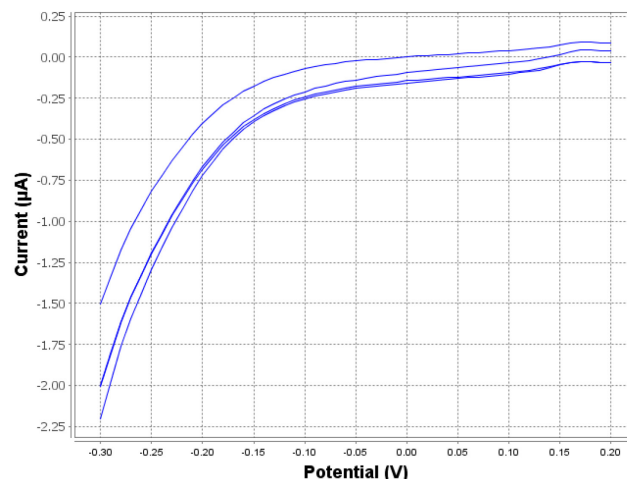
16 mL activation solution

Parameters for activation with 946 Portable VA Analyzer

Voltammetric	
Measuring mode	LSV – Linear sweep
Stirring rate	2000 min ⁻¹
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-1.5 V
Vertex potential	1.0 V
No. of cycles	10
<i>Potentiostatic pretreatment</i>	
Potential 1	-1.0 V
Waiting time 1	10 s
Potential 2	-0.3 V
Waiting time 2	10 s
Equilibration time	5 s
<i>Sweep</i>	
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 curves for 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.

More comments

For more 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 1.5 mL plating electrolyte are dosed into the measuring vessel. The cleaning of the bare gold electrode as well as the removal of the silver film is carried out using the parameters given under «Parameters for cleaning of the scTRACE Gold with 946 Portable VA Analyzer».

Cleaning solution for 946 Portable VA Analyzer

15 mL H₂O

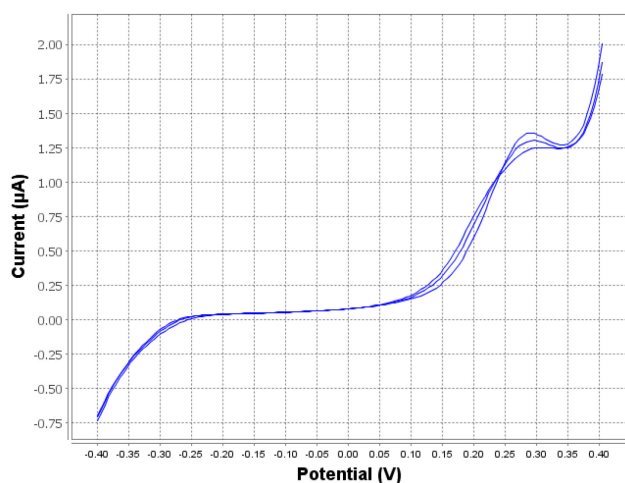
1.5 mL plating electrolyte

Parameters for cleaning of the scTRACE Gold with 946 Portable VA Analyzer

Voltammetric	
Measuring mode	LSV – Linear sweep
Stirring rate	2000 min ⁻¹
<i>Cyclovoltammetric pretreatment</i>	
No. of cycles	0
<i>Potentiostatic pretreatment</i>	
Potential 1	0.4 V
Waiting time 1	10 s
Sweep	
Start potential	-0.4 V
End potential	0.4 V
Potential step	0.006 V
Sweep rate	0.1 V/s

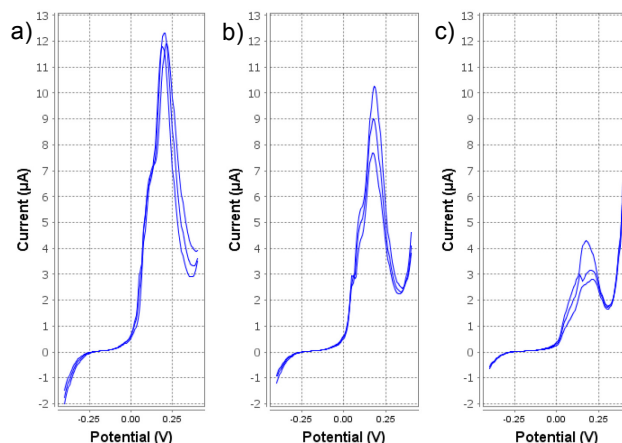
More detailed method parameters can be found in the method printout which is available as a separate document.

Example curves for cleaning with 946 Portable VA Analyzer



Comments

The same method is used to clean the scTRACE Gold electrode and to remove the silver film. Not surprisingly the resulting curves look different whether silver is removed from the electrode or not. The example curve above results from a scTRACE Gold without silver film as it is usually obtained at the beginning of the working day. When a silver film is removed, curves look more like shown in a) to c) depending on how much silver still need to be removed. In case of a) and b) the cleaning should be repeated. The cleaning solution can be reused for the repetition.



More comments

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

Plating of the silver film with the 946 Portable VA analyzer

Analysis

15 mL ultrapure water, 1.5 mL plating electrolyte and 1.5 mL Ag solution are dosed into the measuring vessel. The plating is carried out using the parameters given under «Parameters for plating of the silver film with 946 Portable VA Analyzer».

Plating solution for 946 Portable VA Analyzer

15 mL H₂O
1.5 mL plating electrolyte
1.5 mL Ag solution

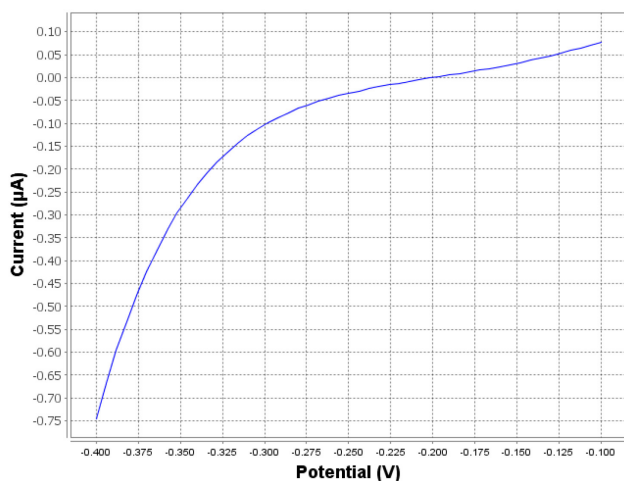
Parameters for plating of the silver film with 946 Portable VA Analyzer

Voltammetric	
Measuring mode	LSV – Linear sweep
Stirring rate	2000 min ⁻¹
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.5 V
Vertex potential	0.4 V
Sweep rate	0.1 V/s

No. of cycles	3
Potentiostatic pretreatment	
Potential 1	-1.0 V
Waiting time 1	60 s
Sweep	
Start potential	-0.4 V
End potential	-0.1 V
Potential step	0.006 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 curve for silver plating with 946 Portable VA Analyzer



Determination of lead with the 946 Portable VA analyzer

Analysis

15 mL sample and 1.5 mL supporting electrolyte are pipetted into the measuring vessel. If the concentration in the sample is too high, a diluted sample or less sample plus an adequate amount of ultrapure water have to be used.

To measure a 5 µg/L check standard 15 mL sample are replaced by 14.925 mL ultrapure water and 0.075 mL Pb standard solution.

The determination is carried out using the parameters given under «Parameters for Pb determination with 946 Portable VA Analyzer». The concentration is quantified by 2 additions of 0.1 mL Pb standard solution each.

Measuring solution sample for 946 Portable VA Analyzer

15 mL (diluted) sample
1.5 mL supporting electrolyte
→ pH 2.4 ± 0.2

Measuring solution check standard for 946 Portable VA Analyzer (5 µg/L)

14.925 mL ultrapure water
0.075 mL β(Pb) = 1 mg/L
1.5 mL supporting electrolyte
→ pH 2.5

Parameters for Pb determination with 946 Portable VA Analyzer

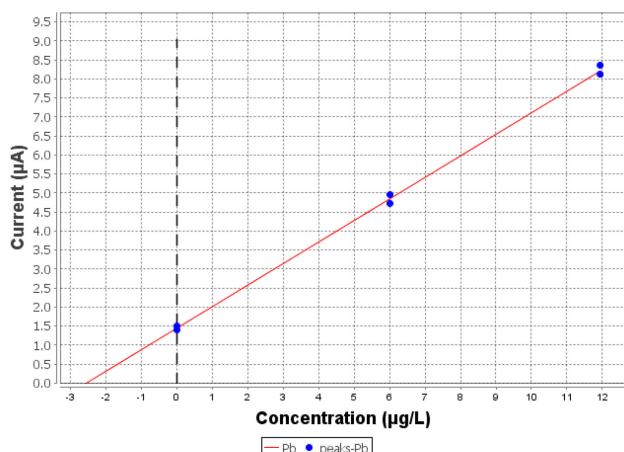
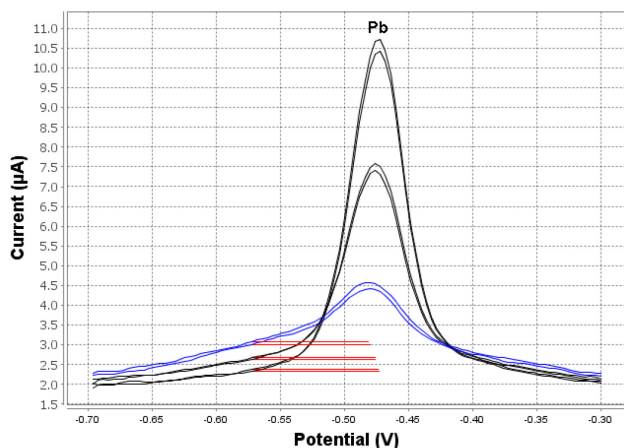
Voltammetric	
Measuring mode	SQW – Square wave
Stirring rate	3000 min ⁻¹
Cyclovoltammetric pretreatment	
Start potential	-0.3 V
Vertex potential	0 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	-0.7 V
Waiting time 1	30 s
Potential 2	(-0.57 V) [†]
Waiting time 2	5 s
Equilibration time	5 s
Sweep	
Start potential	-0.7 V
End potential	-0.3 V
Potential step	0.004 V
Frequency	300 Hz
Sweep rate	1.2 V/s
Pulse amplitude	0.02 V
Substance	
Name	Pb
Characteristic potential	-0.49 V
Baseline type	Horizontal start
Start base point	(-0.57 V) [†]

[†] «Potential 2» for selective oxidation of Cd and «Start base point» may have to be adapted depending on the peak position of Pb. It

should be 60 – 100 mV more negative than the peak maximum of the Pb peak. See also «Selective oxidation of cadmium» in the «Comments» at the end of the document.

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

Example for the determination of lead in tap water with 946 Portable VA Analyzer



Results

All results in the following tables are the average of 3 determinations.

30 s deposition time

Sample	$\beta(\text{Pb}^{2+})$ $\mu\text{g/L}$	RSD	Recovery of the spiked amount
Check standard solution 1 $\mu\text{g/L}$ Pb	1.20	5.6%	120.4%
Check standard solution 10 $\mu\text{g/L}$ Pb	9.83	3.3%	98.3%
Tap water	2.82	0.8%	--

Tap water spiked with 2 $\mu\text{g/L}$ Pb	4.61	2.6%	89.7%
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RSD - relative standard deviation of 3 determinations

60 s deposition time

Sample	$\beta(\text{Pb}^{2+})$ $\mu\text{g/L}$	RSD	Recovery of the spiked amount
Check standard solution 0.5 $\mu\text{g/L}$ Pb	0.73	0.5%	147.4%
Check standard solution 1 $\mu\text{g/L}$ Pb	1.23	2.1%	123.5%
Check standard solution 5 $\mu\text{g/L}$ Pb	5.15	1.8%	103.0%
Tap water	2.81	6.6%	--
Tap water spiked with 2 $\mu\text{g/L}$ Pb	4.65	5.5%	91.7%

RSD - relative standard deviation of 3 determinations

Comments

Peak evaluation

With the 946 Portable VA Analyzer the measuring solution cannot be purged. To overcome the interference of oxygen the measurement has to be carried out with a fast sweep rate ($> 1 \text{ V/s}$). The fast sweep rate results in an unfavorable shape of the background current why the peak evaluation has to be done with «Horizontal start» and a fixed base point. As a consequence the base point has to be adapted in case the lead peak shifts by more than 30 mV.

Limit of detection

Deposition	Limit of detection	Limit of quantification
30 s	0.4 $\mu\text{g/L}$	1.3 $\mu\text{g/L}$
60 s	0.2 $\mu\text{g/L}$	0.6 $\mu\text{g/L}$

Linear working range

Deposition	Linear range
30 s	~ 25 $\mu\text{g/L}$
60 s	~ 15 $\mu\text{g/L}$

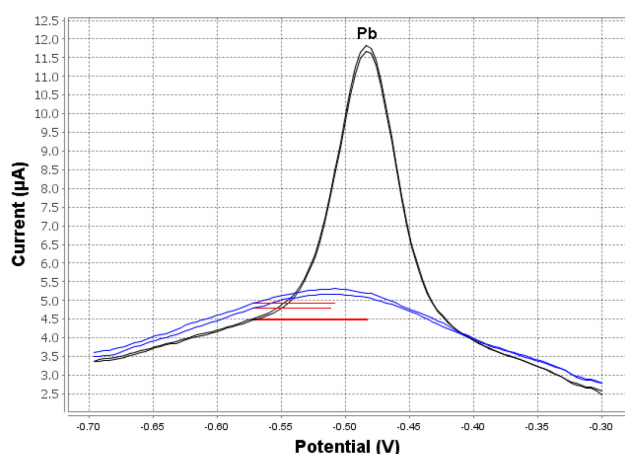
Working range

With 15 mL sample and a deposition time of 30 s the method is suitable for samples between 1.5 $\mu\text{g/L}$ and 15 $\mu\text{g/L}$.

If higher concentrations should be determined, a smaller sample volume has to be used. The volume difference to 15 mL is made up with ultrapure water.

If lower concentrations should be determined the deposition time (Waiting time 1) has to be increased, to e.g. 120 s. In this case the volume and/or the concentration of standard solution also need to be adapted. A deposition time of 60 s did not show much of an advantage over 30 s since concentrations close to the limit of quantification showed a rather high error due to the unfavorable background current (see «Blank» below).

Blank



Due to the slightly curved background current the software evaluates a blank independent from the presence of a real

reagent blank. With a deposition time of 30 s this measuring artefact is usually in the range of 0.3 µg/L to 0.6 µg/L. This leads to a comparably high error in the result when concentrations close to the limit of quantifications should be determined. Higher concentrations are not affected. If concentrations around 1 µg/L should be determined correctly it is recommended to increase the deposition time to e.g. 120 s to minimize the effect of the background current on the result.

Total cell volume

The total volume in the measuring cell should not be less than 16 mL, otherwise the scTRACE Gold is not sufficiently immersed in solution and may be damaged. The maximum volume should not exceed 23 mL.

More comments

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

Measuring solution for 884 Professional VA

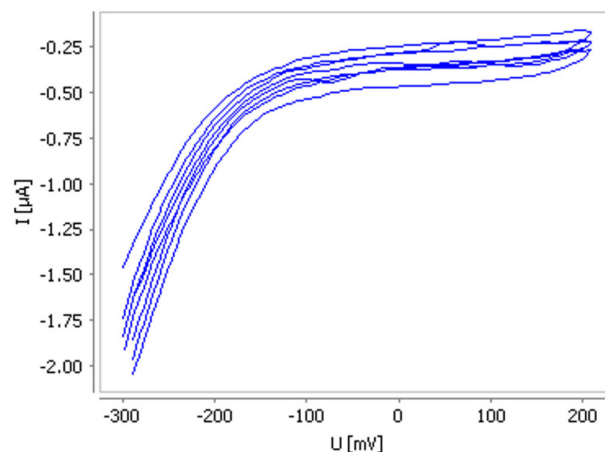
12 mL activation solution

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 curves for 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.

More comments

For more 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 1 mL plating electrolyte are dosed into the measuring vessel. The cleaning of the bare gold electrode as well as the removal of the silver film is carried out using the parameters given under «Parameters for cleaning of the scTRACE Gold with 884 Professional VA».

Cleaning solution for 884 Professional VA

10 mL H₂O

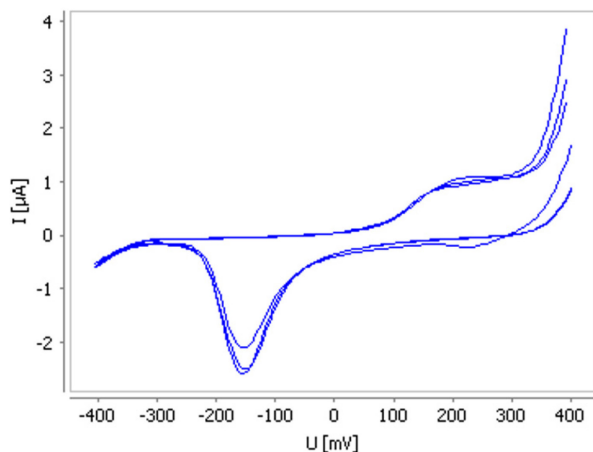
1 mL plating electrolyte

Parameters for cleaning of the scTRACE Gold with 884 Professional VA

Voltammetric	
Measuring mode	CVS – Cyclic Voltammetric Stripping
Stirring rate	2000 min ⁻¹
Cyclovoltammetric pretreatment	
No. of cycles	off
Potentiostatic pretreatment	
Potential 1	0.4 V
Waiting time 1	10 s
Sweep	
Start potential	0.4 V
1st vertex potential	-0.4 V
2nd vertex potential	0.4 V
Potential step	0.01 V
Sweep rate	0.1 V/s
Preparation cycles	0
Measuring cycles	1

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

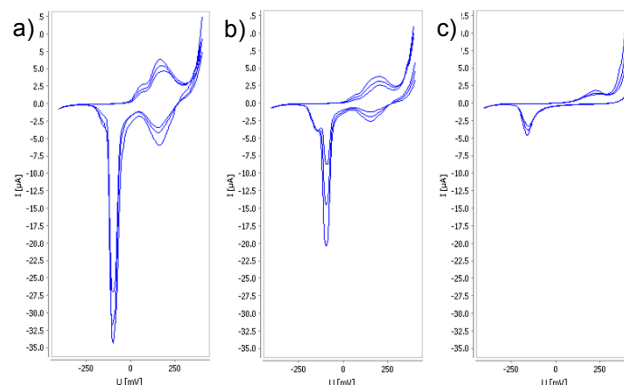
Example curves for cleaning with 884 Professional VA



Comments

The same method is used to clean the scTRACE Gold electrode and to remove the silver film. Not surprisingly the resulting curves look different whether silver is removed from the electrode or not. The example curve above results from a scTRACE Gold without silver film as it is usually obtained at the beginning of the working day. When a silver film is removed, curves look more like shown in a) to c) depending

on how much silver still need to be removed. In case of a) and b) the cleaning should be repeated. The cleaning solution can be reused for the repetition.



More comments

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

Plating of the silver film with the 884 Professional VA

Analysis

10 mL ultrapure water, 1 mL plating electrolyte and 1 mL Ag solution are dosed into the measuring vessel. After purging the plating solution for 90 s, the plating is carried out using the parameters given under «Parameters for plating of the silver film with 884 Professional VA».

Plating solution for 884 Professional VA

10 mL H₂O
1 mL plating electrolyte
1 mL Ag solution

Parameters for plating of the silver film with 884 Professional VA

CVS for electrode pretreatment

Voltammetric	
Measuring mode	CVS – Cyclic Voltammetric Stripping
Initial purging	90 s

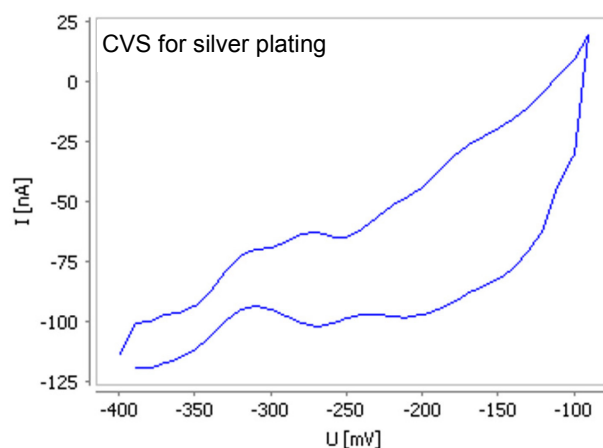
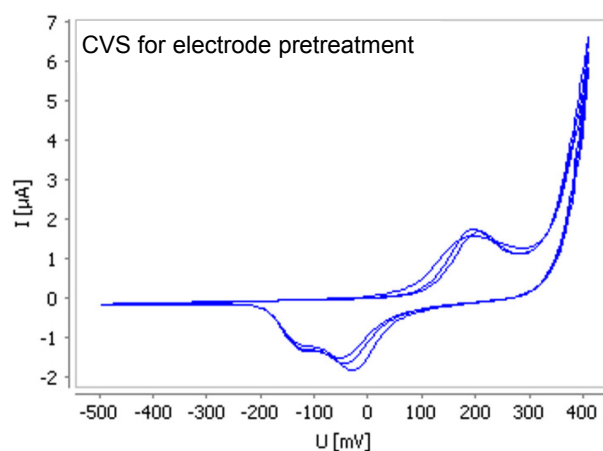
Stirring rate	2000 min ⁻¹
Cyclic voltammetric pretreatment	
No. of cycles	off
Potentiostatic pretreatment	
Potential	off
Sweep	
Start potential	-0.5 V
1st vertex potential	0.4 V
2nd vertex potential	-0.5 V
Potential step	0.01 V
Sweep rate	0.1 V/s
Preparation cycles	0
Measuring cycles	3

CVS for silver plating

Voltammetric	
Measuring mode	CVS – Cyclic Voltammetric Stripping
Stirring rate	2000 min ⁻¹
Cyclic voltammetric pretreatment	
No. of cycles	off
Potentiostatic pretreatment	
Potential 1	-1.0 V
Waiting time 1	60 s
Sweep	
Start potential	-0.4 V
1st vertex potential	-0.1 V
2nd vertex potential	-0.4 V
Potential step	0.01 V
Sweep rate	0.1 V/s
Preparation cycles	0
Measuring cycles	1

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

Example curve for silver plating with 884 Professional VA



Determination of lead with the 884 Professional VA

Analysis

10 mL sample and 1 mL supporting electrolyte are pipetted into the measuring vessel.

If the concentration in the sample is too high, a diluted sample or less sample plus an adequate amount of ultrapure water have to be used.

To measure a 5 µg/L check standard 10 mL sample are replaced by 9.95 mL ultrapure water and 0.05 mL Pb standard solution.

After 5 minutes purging, to remove oxygen from the measuring solution, the determination is carried out using the parameters given under «Parameters for Pb determination with 884 Professional VA».

The concentration of Pb is quantified by two additions of 0.05 mL Pb standard solution each in case of 60 s deposition time and 0.075 mL in case of 30 s.

Measuring solution for 884 Professional VA

10 mL (diluted) sample
 1 mL supporting electrolyte
 → pH 2.4 ± 0.2

Measuring solution check standard for 884 Professional VA (e.g. 5 µg/L)

9.95 mL ultrapure water
 0.05 mL β(Pb) = 1 mg/L
 1 mL supporting electrolyte
 → pH 2.5

Parameters for Pb determination with 884 Professional VA

Voltammetric	
Measuring mode	SQW – Square Wave
Initial purging	300 s
Stirring rate	2000 min ⁻¹
Cyclovoltammetric pretreatment	
No. of cycles	off
Potentiostatic pretreatment	
Potential 1	-0.05 V
Waiting time 1	5 s
Potential 2	-0.7 V
Waiting time 2	60 s
Potential 3	(-0.55 V) [†]
Waiting time 3	5 s
Equilibration time	5 s
Sweep	
Start potential	-0.7 V
End potential	-0.3 V
Potential step	0.004 V
Frequency	150 Hz
Sweep rate	0.6 V/s
Pulse amplitude	0.01 V
Potentiostat – current measuring range	
Highest range	2 mA
Lowest range	200 µA

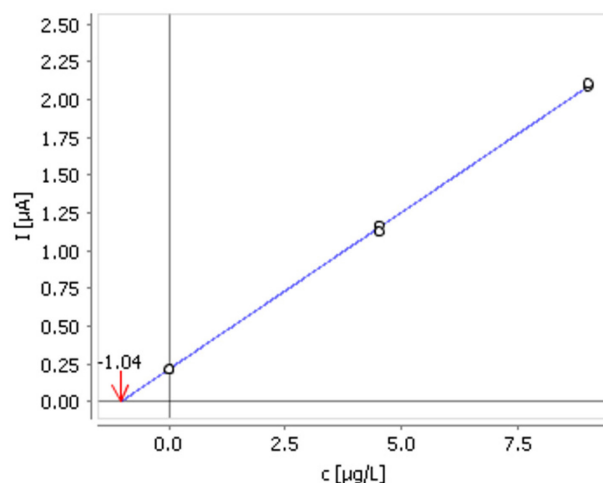
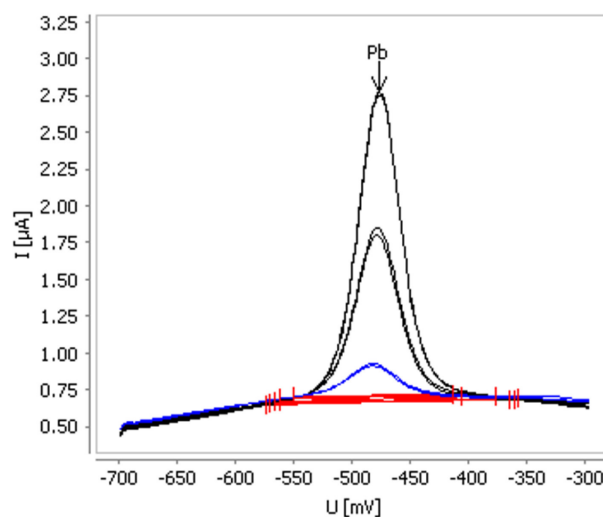
Substance

Name	Pb
Characteristic potential	-0.49 V

[†] «Potential 3» for selective oxidation of Cd may have to be adapted depending on the peak position of Pb. It should be 60 – 100 mV more negative than the peak maximum of the Pb peak. See also «Selective oxidation of cadmium» in the «Comments» at the end of the document.

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

Example for the determination of lead in tap water with 884 Professional VA



Results

All results in the following tables are the average of 3 determinations.

30 s deposition time

Sample	$\beta(\text{Pb}^{2+})$ $\mu\text{g/L}$	RSD	Recovery of the spiked amount
Check standard solution 1.5 $\mu\text{g/L}$	1.58	2.8%	105.1%
Check standard solution 10 $\mu\text{g/L}$	10.11	7.9%	101.1%
Check standard solution 20 $\mu\text{g/L}$	20.81	4.9%	104.1%

RSD - relative standard deviation of 3 determinations

60 s deposition time

Sample	$\beta(\text{Pb}^{2+})$ $\mu\text{g/L}$	RSD	Recovery of the spiked amount
Check standard solution 0.7 $\mu\text{g/L}$	0.85	13.5%	126.6%
Check standard solution 5 $\mu\text{g/L}$	5.07	4.1%	101.4%
Check standard solution 10 $\mu\text{g/L}$	10.98	3.1%	109.8%
Tap water	1.19	10.0%	--
Tap water spiked 1 $\mu\text{g/L}$	2.31	8.3%	111.9%

RSD - relative standard deviation of 3 determinations

Comments

Limit of detection

Deposition	Limit of detection	Limit of quantification
30 s	0.5 $\mu\text{g/L}$	1.5 $\mu\text{g/L}$
60 s	0.2 $\mu\text{g/L}$	0.6 $\mu\text{g/L}$

Linear working range

Deposition	Linear range
30 s	~35 $\mu\text{g/L}$
60 s	~20 $\mu\text{g/L}$

Working range

With 10 mL sample and a deposition time of 60 s the method is suitable for samples between 1 $\mu\text{g/L}$ and 10 $\mu\text{g/L}$ and with 30 s deposition time for samples between 1.5 $\mu\text{g/L}$ and 20 $\mu\text{g/L}$.

If higher concentrations should be determined, a smaller sample volume has to be used. The volume difference to 10 mL is made up with ultrapure water.

If lower concentrations should be determined the deposition time (Waiting time 2) has to be increased, to e.g. 120 s. In this case the volume and/or the concentration of standard solution also need to be adapted.

Grounding Dosinos (only 884 Professional VA)

In semiautomatic and fully automatic systems using the 884 Professional VA it is required to ground the solutions in the dosing units in order to minimize electromagnetic interferences during the measurement. For this purpose the optional grounding equipment for Professional VA systems is available. The 946 Portable VA Analyzer and 797 VA Computrace do not require this additional equipment.

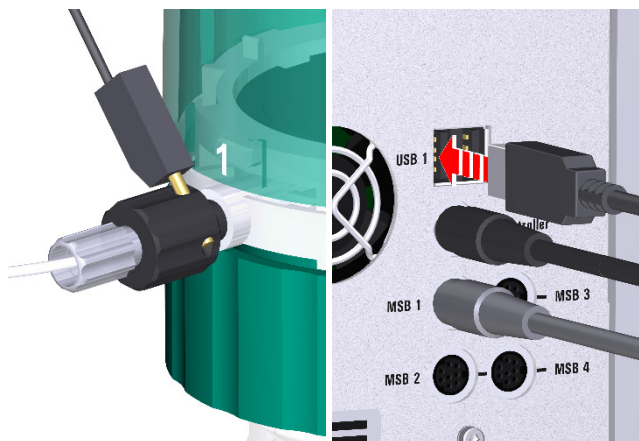
Grounding equipment	6.5334.020
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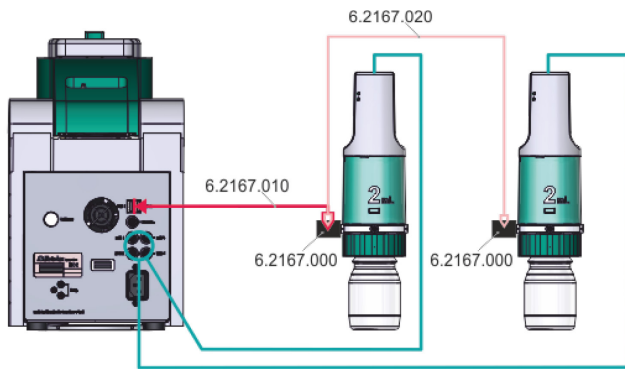
Consisting of:

2 x Grounding adapter for Dosino	6.2167.000
1 x Grounding cable USB A / plug 2 mm	6.2167.010
1 x Connecting cable 2 x 2 mm	6.2167.020

The grounding adapter (6.2167.000) has to be screwed in between the dosing port, usually port 1, of the dosing unit and the tubing of the 4-way micro dosing tip (6.1824.000). The 2 mm banana plug of the grounding cable (6.2167.010) is connected to the adapter plug, whereas the USB plug is plugged into USB 1 or 2 on the rear of the 884 Professional VA. If a second Dosino is used it can be interconnected to the first one using the connection cable (6.2167.020).

The following pictures illustrate the setup.





More comments

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 activation 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

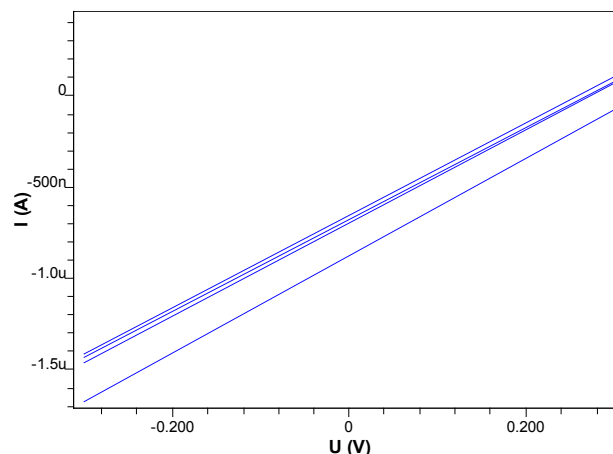
12 mL activation solution

Parameters for activation with 797 VA Computrace

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

More comments

For more 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 1 mL plating electrolyte are dosed into the measuring vessel. The cleaning of the bare gold electrode as well as the removal of the silver film is carried out using the parameters given under «Parameters for cleaning with 797 VA Computrace».

Cleaning solution for 797 VA Computrace

10 mL ultrapure water

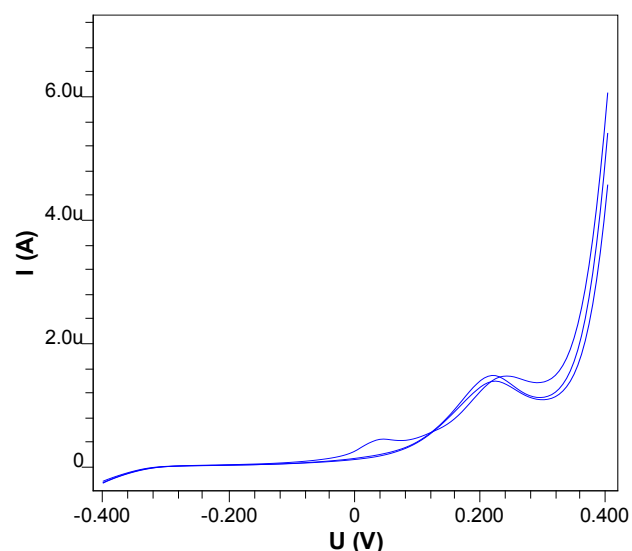
1 mL plating electrolyte

Parameters for cleaning with 797 VA Computrace

Voltammetric	
Measuring mode	DC – Sampled direct current
Stirring rate	2000 min ⁻¹
<i>Cyclovoltammetric pretreatment</i>	
No. of cycles	0
<i>Potentiostatic pretreatment</i>	
Potential 1	0.4 V
Waiting time 1	10 s
Equilibration time	5 s
<i>Sweep</i>	
Start potential	-0.4 V
End potential	0.4 V
Potential step	0.006 V
Potential step time	0.06 s
Sweep rate	0.1 V/s

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

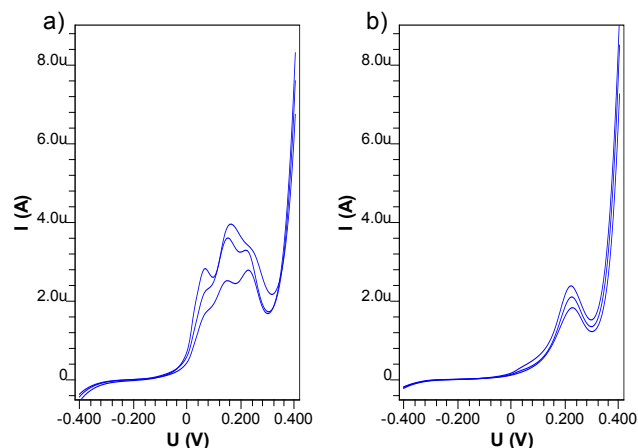
Example for cleaning with 797 VA Computrace



Comments

The same method is used to clean the scTRACE Gold electrode and remove the silver film. Not surprisingly the resulting curves look different whether silver is removed from the electrode or not. The example curve above results from a scTRACE Gold without silver film as it is usually obtained at the beginning of the working day. When a silver film is

removed, curves look more like shown in a) and b) depending on how much silver still need to be removed. In case of a) the cleaning should be repeated. The cleaning solution can be reused for the repetition.



More comments

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

Plating of the silver film with the 797 VA Computrace

Analysis

10 mL ultrapure water, 1 mL plating electrolyte and 1 mL Ag solution are dosed into the measuring vessel. After purging the plating solution for 90 s, the plating is carried out using the parameters given under «Plating of the silver film with the 797 VA Computrace».

Plating solution for 797 VA Computrace

10 mL H₂O
 1 mL plating electrolyte
 1 mL Ag solution

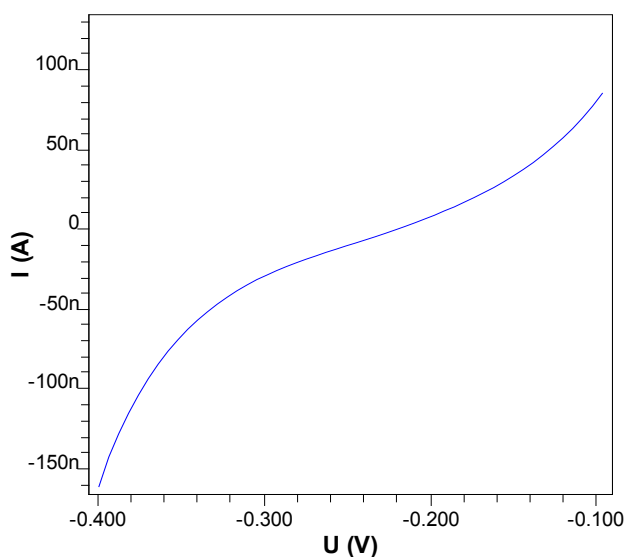
Parameters for plating of the silver film with 797 VA Computrace

Voltammetric	
Measuring mode	DC – Sampled direct current
Initial purging	90 s

Stirring rate	3000 min ⁻¹
Cyclic voltammetric pretreatment	
Start potential	-0.5 V
Vertex potential	0.4 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	-1.0 V
Waiting time 1	60 s
Sweep	
Start potential	-0.4 V
End potential	-0.1 V
Potential step	0.006 V
Potential step time	0.06 s
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 curve for silver plating with 797 VA Computrace



Determination of lead with the 797 VA Computrace

Analysis

10 mL sample and 1 mL supporting electrolyte are pipetted into the measuring vessel.

If the concentration in the sample is too high, a diluted sample or less sample plus an adequate amount of ultrapure water have to be used. To measure a 5 µg/L check standard 10 mL sample are replaced by 9.95 mL ultrapure water and 0.05 mL Pb standard solution.

After 5 minutes purging, to remove oxygen from the measuring solution, the determination is carried out using the parameters given under «Parameters for Pb determination with 884 Professional VA».

The concentration of Pb is quantified by two additions of 0.05 mL Pb standard solution each in case of 60 s deposition time and 0.1 mL in case of 30 s.

Measuring solution for 797 VA Computrace

10 mL (diluted) sample

1 mL supporting electrolyte

→ pH 2.4 ± 0.2

Measuring solution check standard for 797 VA Computrace (e.g. 5 µg/L)

9.95 mL ultrapure water

0.05 mL β(Pb) = 1 mg/L

1 mL supporting electrolyte

→ pH 2.5

Parameters for Pb determination with 797 VA Computrace

Voltammetric

Measuring mode SQW – Square wave

Initial purging 300 s

Stirring rate 2000 min⁻¹

Cyclic voltammetric pretreatment

Start potential -0.4 V

Vertex potential 0 V

No. of cycles 10

Potentiostatic pretreatment

Potential 1	-0.7 V
Waiting time 1	60 s
Potential 2	(-0.55 V) [†]
Waiting time 2	5 s
Equilibration time	5 s
Sweep	
Start potential	-0.6 V
End potential	-0.35 V
Potential step	0.004 V
Frequency	150 Hz
Sweep rate	0.6 V/s
Pulse amplitude	0.005 V

Potentiostat – current measuring range

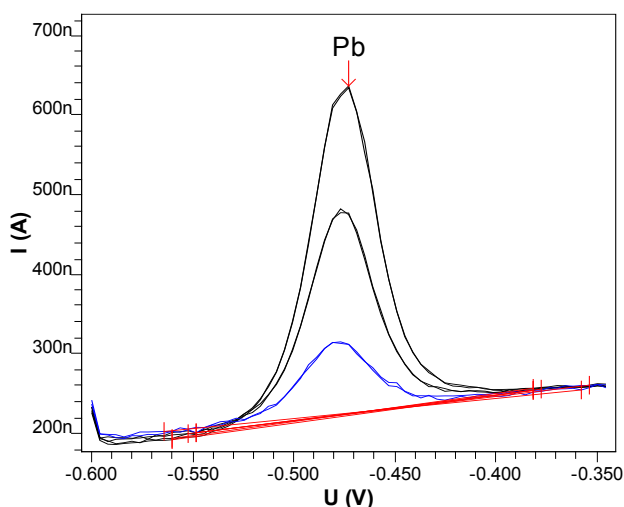
Highest range	1 μ A
Lowest range	1 μ A

Substance

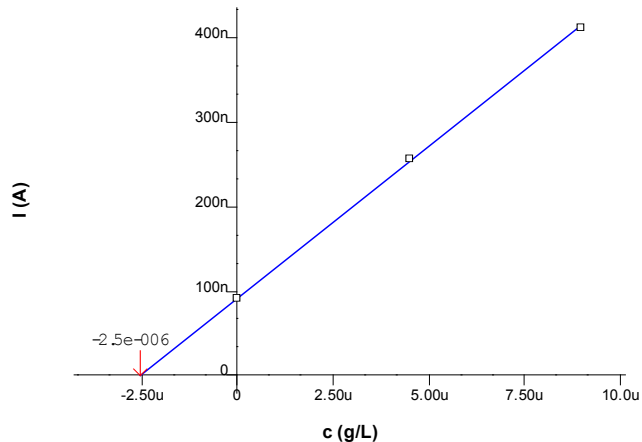
Name	Pb
Characteristic potential	-0.48 V

[†] «Potential 2» for selective oxidation of Cd may have to be adapted depending on the peak position of Pb. It should be 60 – 100 mV more negative than the peak maximum of the Pb peak. See also «Selective oxidation of cadmium» in the «Comments» at the end of the document.

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

Example for the determination of lead in tap water with 797 VA Computrace


Pb
 c = 2.790 μ g/L
 +/- 0.051 μ g/L (1.83%)


Results

All results in the following tables are the average of 3 determinations.

30 s deposition time

Sample	β (Pb ²⁺) μ g/L	RSD	Recovery of the spiked amount
Check standard solution 5 μ g/L	4.98	3.1%	99.6%
Check standard solution 10 μ g/L	10.23	2.8%	102.3%
Check standard solution 30 μ g/L	30.58	4.0%	101.9%

RSD - relative standard deviation of 3 determinations

60 s deposition time

Sample	β (Pb ²⁺) μ g/L	RSD	Recovery of the spiked amount
Check standard solution 1 μ g/L	1.40	6.2%	139.6%
blank:	0.99		- blank: 99.3%
Check standard solution 10 μ g/L	10.61	2.6%	106.1%
Tap water	2.81	3.2%	--
Tap water spiked with 2 μ g/L Pb	5.11	2.8%	114.9%

RSD - relative standard deviation of 3 determinations

Comments

Limit of detection

Deposition	Limit of detection	Limit of quantification
30 s	0.6 µg/L	1.8 µg/L
60 s	0.2 µg/L	0.7 µg/L

Linear working range

Deposition	Linear range
30 s	~ 50 µg/L
60 s	~ 25 µg/L

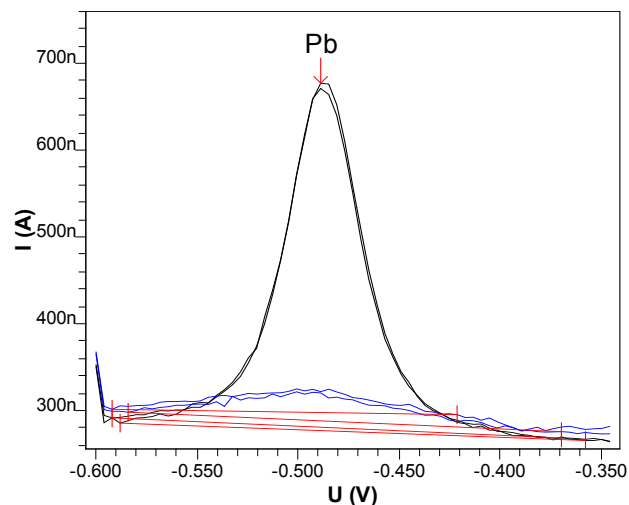
Working range

With 10 mL sample and a deposition time of 60 s the method is suitable for samples between 1.5 µg/L and 15 µg/L and with 30 s deposition time for samples between 2 µg/L and 30 µg/L.

Concentrations close to the limit of quantification showed a rather high error due to the unfavorable background current (see «Blank» below). If lower concentrations should be determined the deposition time (Waiting time 1) has to be increased, to e.g. 120 s. In this case the volume and/or the concentration of standard solution also need to be adapted.

If higher concentrations should be determined, a smaller sample volume has to be used. The volume difference to 10 mL is made up with ultrapure water.

Blank



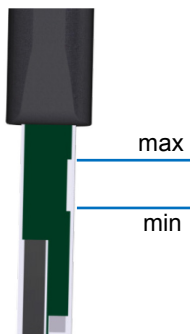
Due to the slightly curved background current the software evaluates a blank independent from the presence of real reagent blank. With a deposition time of 60 s this measuring artefact is usually in the range of 0.3 µg/L to 0.6 µg/L. This leads to a comparably high error in the result when concentrations close to the limit of quantifications should be determined. Higher concentrations are not affected. If concentrations around 1 µg/L should be determined correctly it is recommended to increase the deposition time to e.g. 120 s to minimize the effect of the background current on the result.

More comments

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

Comments

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.

Standard operating procedure

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 in the given order, before the first determination of sample:

- 1) Activation of the scTRACE Gold
- 2) Cleaning of the scTRACE Gold
- 3) Plating of the silver film
- 4) Determination of lead in a blank or check standard

Since the electrode surface cannot be renewed, solid state electrodes undergo a constant change in performance. To guarantee the quality of the results, it is recommended to check the performance in regular intervals with a blank or check standard determination. The check should be carried out:

- after plating a fresh silver film
- after 5-10 determinations

Assessment criteria

Assessment criteria are the slope and the correlation coefficient R^2 of the calibration curve, the curve shape and the recovery in check standard solution.

- The slope depends on measuring parameters, instrument, deposition time and age of the electrode. Compare with existing good determinations. The table below shows some typical values for the slope depending on the deposition time, (measurement in in standard solutions with the voltammetric parameters

specified under «Determination of lead» for the respective instrument).

	Slope A/(g*L ⁻¹) 30 s dep.	Slope A/(g*L ⁻¹) 60 s dep.
946 Portable VA Analyzer	0.7 – 1.0	1.0 – 1.3
884 Professional VA	0.1 – 0.3	0.3 – 0.5
797 VA Computrace	0.03 – 0.08	0.05 – 0.13

- The correlation coefficient R^2 gives an impression about the reproducibility of peaks and the linearity of the standard additions
 - $R^2 > 0.99$ very good
 - $R^2 > 0.98$ reproducibility of peaks and/or linearity not very good, but still good results
 - $R^2 < 0.96$ renew the silver film
- The curve shape (background current and peak) depends on measuring parameters and instrument, compare with an existing good determination.
- Recovery of check standard 80 – 120%

When the blank determination or the determinations of the check standard indicates a bad performance of the electrode remove the silver film as described under «Cleaning of the scTRACE Gold» and plate a fresh film as described under «Plating of the silver film». If it is not possible anymore to plate a proper film, replace the scTRACE Gold.

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. The respective limits of detection and quantification can be found in the comments of the instruments.

Linear working range

The linear working range was read out from a calibration curve. The respective linear working range can be found in the comments of the instruments.

Interferences

The influence of different anions and cations on the peak of $\beta(\text{Pb}) = 10 \mu\text{g/L}$ was tested with a deposition time of 30 s.

Anions

Chloride	Decreases the sensitivity and shifts the peak potential. With $c(\text{Cl}^-) = 0.1 \text{ mol/L}$ the sensitivity drops to approx. 40% compared to a standard solution. Higher concentrations do not change the sensitivity significantly anymore. Due to the influence of the chloride concentration on the potential of the reference electrode the Pb peak shifts from -0.48 V to approx. -0.45 V in the presence of $c(\text{Cl}^-) = 0.05 \text{ mol/L}$ and -0.43 V with $c(\text{Cl}^-) = 0.4 \text{ mol/L}$.
Nitrate	Decreases the sensitivity of the determination. With $c(\text{NO}_3^-) = 0.05 \text{ mol/L}$ the sensitivity drops to approx. 70% compared to a standard solution. Higher concentrations do not change the sensitivity significantly anymore.

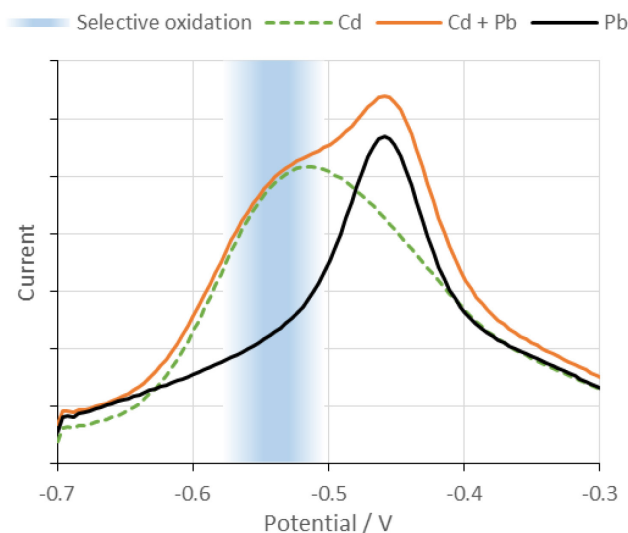
Cations

Bi	Peak potential -0.07 V. Decreases the sensitivity since it also deposits at the silver film. 10 times excess decreases the sensitivity by approx. 40%. Has to be removed by a cleaning potential of -0.05 V or by cyclic voltammetric pretreatment with a vertex potential of 0 V.
Ca	Does not interfere. 10000 times excess decrease the sensitivity by approx. 15%.
Cd	Peak potential -0.55 V At the silver film it is not possible to separate the two signals completely. Up to 10 times excess does not interfere if cadmium is removed by selective oxidation (see also comment on «Selective oxidation of cadmium» below).
Cu	Peak potential -0.05 V Decreases the sensitivity since it also deposits at the silver film. 10 times excess decreases the sensitivity by approx. 30%. Has to be removed by a cleaning potential of -0.05 V or by cyclic voltammetric pretreatment with a vertex potential of 0 V.

Fe(II)	Does not interfere. Tested up to 10000 times excess.
Fe(III)	Does not interfere up to 10 times excess. With up to 100 times excess the sensitivity decreases and the silver film need to be renewed more frequently. With 500 times excess the peaks are not reproducible anymore. By the addition of vitamin C (ascorbic acid) Fe(III) can be reduced to Fe(II) which does not interfere with the determination. Also vitamin C does not interfere.
Ga	Peak potential approx. -1.1 V (only visible in ppm level) Does not interfere. Tested up to 1000 time excess.
Hg	Peak more positive than silver oxidation. Equal concentrations do not interfere, but mercury is accumulated at the silver film and cannot be stripped off due to the too positive potential. Therefore the silver film should be renewed more frequently. With 10 times excess the sensitivity decrease to approx. 40%.
Mg	Does not interfere. 10000 times excess decrease the sensitivity by approx. 10%.
Sb(III)	Peak potential approx. -0.15 V (only visible in ppm level). With equal concentrations the sensitivity is reduced by approx. 20%. With 5 times excess peaks are not reproducible anymore.
Sb(V)	With 10 times excess the sensitivity decreases by approx. 20%.
Tl	Peak potential -0.65 V Does not interfere up to 100 times excess. Sensitivity decreases if the deposition potential is chosen more negative than -0.7 V (e.g. -0.9 V) at which also Tl is deposited.

Selective oxidation of cadmium

At a silver film it is not possible to separate the signals for cadmium and lead. If both elements are present with cadmium in excess, the measured curve looks as shown in the figure below.



$\beta(\text{Cd}) = 50 \mu\text{g/L}$ (green broken line), $\beta(\text{Pb}) = 10 \mu\text{g/L}$ (black line), and the resulting curve if both elements are present (orange line)

To overcome the problem with the overlapping signals cadmium needs to be stripped off by selective oxidation prior to the sweep. This can be achieved by applying a second potential after the deposition. This potential should be 60 – 100 mV more negative than the peak maximum of the Pb peak. If the potential is more negative, the cadmium is not stripped off. If the potential is too close to the Pb signal the lead is also stripped off. If the Pb signal shifts, e.g. because of the chloride concentration of the measuring solution, and the potential for the selective oxidation is not in the specified window anymore, the potential for selective oxidation must be adapted.

Influence of pH

The determination can be carried out at a pH between 2.2 and 3.5. The highest sensitivity is obtained between pH 2.2 and 2.6. At pH between 2.6 and 3.5 the application still works, but with reduced sensitivity. At pH <2 the formation of hydrogen interferes with the deposition of lead.

A higher pH shifts the peak to a more negative potential.

Storage of the silver film

The silver film cannot be preserved for a longer period of time. For approx. 1 h the silver film can be kept in diluted measuring electrolyte. If the electrode is not used for more than one

hour, it is recommended to remove the silver film with the procedure described under «Cleaning of the scTRACE Gold». After that the electrode is rinsed with ultrapure water and stored dry.

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.