

## Application Bulletin 422/2

# Determination of mercury in water with the scTRACE Gold

### Summary

Mercury and its compounds are toxic. Acute poisoning is rather seldom. More likely is a chronic poisoning with mercury compounds ingested with the food. A natural source of mercury in the environment are volcanos. However, a significant part of the mercury present in the environment is human-generated. Considerable anthropogenic sources are coal-fired power plants, steel and nonferrous metal production, waste incineration plants or the chemical industry, e.g., with the chlor-alkali plants namely the still used mercury-cell process, which is used for the production of important base chemicals such as sodium hydroxide and chlorine. Also not negligible is the contribution of artisanal gold mining where the use of elemental mercury for the extraction of gold from the ore is still common. Once in the biosphere, mercury is highly mobile and can accumulate in organisms. The WHO (World Health Organization) guideline value for inorganic mercury is 6 µg/L, but the limit value for drinking water in many countries is much lower, e.g., USA 2 µg/L, European Union and Switzerland 1 µg/L.

This Application Bulletin describes the determination of inorganic mercury in water samples by anodic stripping voltammetry using the scTRACE Gold sensor. With a deposition time of 90 s, the limit of detection is  $\beta(\text{Hg}^{2+}) = 0.5 \mu\text{g/L}$ ; the calibration is linear up to a concentration of  $\beta(\text{Hg}^{2+}) = 30 \mu\text{g/L}$ .

### Samples

Surface water, groundwater, wastewater

### 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
<i>Accessories</i>	
viva 2.0	6.6065.20X
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
<i>Accessories</i>	
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
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**Note!** It is recommended to have a separate measuring vessel and stirrer for this application, which have not been used in combination with a mercury or platinum electrode. It is also not recommended to use the same sensor for the determination of arsenic according to Application Bulletin 416.

## 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 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 mercury

Mercury is determined by anodic stripping voltammetry. With this method, first mercury is deposited on the gold microwire

working electrode and stripped off during the determination step.

With 90 s for deposition the limit of detection is approx. 0.5 µg/L and the calibration is linear up to a concentration of 30 µg/L.

#### Cleaning of the scTRACE Gold

To maintain the performance of the scTRACE Gold the sensor can be electrochemically cleaned. The cleaning can be carried out before, after, but also in between a series of determinations. However, it should only be done 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

- Hg standard stock solution,  $\beta(\text{Hg}^{2+}) = 1 \text{ g/L}$ , commercially available
- Fe standard stock solution  $\beta(\text{Fe}^{3+}) = 1 \text{ g/L}$ , commercially available
- Nitric acid,  $w(\text{HNO}_3) = 65\%$ , for trace analysis\*, CAS 7697-37-2
- Formic acid,  $w(\text{HCOOH}) = 98 - 100\%$ , for trace analysis\*, CAS 64-18-6
- Potassium chloride, KCl, for trace analysis\*, CAS 7447-40-7
- Sulfuric acid,  $w(\text{H}_2\text{SO}_4) = 96\%$ , for trace analysis\*, CAS 7664-93-9
- Ultrapure water, resistivity  $>18 \text{ M}\Omega \cdot \text{cm}$  (25 °C), type I grade (ASTM D1193)

In addition, if UV digestion is required:

- Hydrogen peroxide solution,  $w(\text{H}_2\text{O}_2) = 30\%$ , for trace analysis\*, CAS 7722-84-1

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

## Solutions

Cleaning 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.
Electrolyte	$c(\text{HCOOH}) = 0.8 \text{ mol/L}$ $c(\text{KCl}) = 0.06 \text{ mol/L}$ $\beta(\text{Fe}^{3+}) = 5 \text{ mg/L}$ 0.447 g potassium chloride is dissolved in approx. 80 mL ultrapure water in a 100 mL volumetric flask. 3 mL formic acid and 0.5 mL Fe standard stock solution are added. The mixture is made up to the mark with ultrapure water.
Electrolyte for preliminary tests	$c(\text{HCOOH}) = 0.8 \text{ mol/L}$ $c(\text{KCl}) = 0.06 \text{ mol/L}$ 0.224 g sodium chloride is dissolved in approx. 40 mL ultrapure water in a 50 mL volumetric flask. 1.5 mL formic acid is added. The mixture is made up to the mark with ultrapure water.

## Standard solutions

Hg standard solution 1 mg/L	$\beta(\text{Hg}^{2+}) = 1 \text{ mg/L}$ 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 Hg standard stock solution are added. The solution is made up to the mark with ultrapure water.
Hg standard solution 10 mg/L	$\beta(\text{Hg}^{2+}) = 10 \text{ mg/L}$ Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL $w(\text{HNO}_3) = 65\%$ and 0.5 mL Hg 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 ( $\text{pH} = 2$ ) are mixed with 10  $\mu\text{L}$   $w(\text{HNO}_3) = 65\%$  and 50  $\mu\text{L}$   $w(\text{H}_2\text{O}_2) = 30\%$  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

18 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 the 946 Portable VA Analyzer».

#### Measuring solution

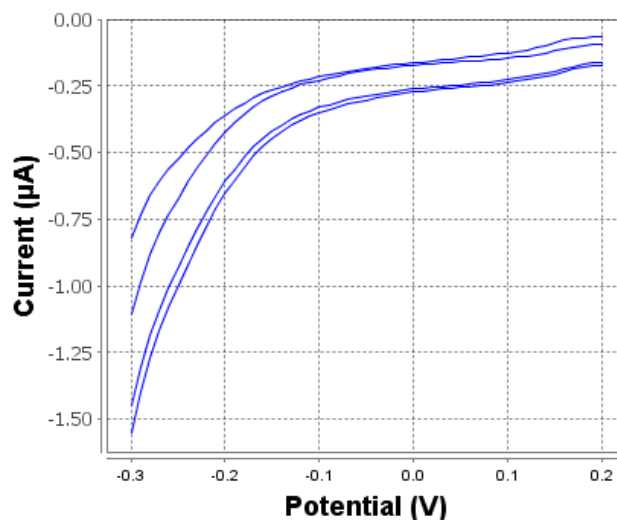
18 mL cleaning solution

#### Parameters for activation with the 946 Portable VA Analyzer

Determination	
No. of replications	4
No. of additions	0
Voltammetric	
Measuring mode	LSV – Linear sweep
Stirring rate	2000 min <sup>-1</sup>
Cyclic voltammetric pretreatment	
Start potential	-1.5 V
Vertex potential	1 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 the 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 mercury with the 946 Portable VA Analyzer

## Analysis

15 mL sample are pipetted into the measuring vessel and 1.5 mL electrolyte are added. The determination is carried out using the parameters given under «Parameters for Hg with the 946 Portable VA Analyzer».

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

## Measuring solution

15 mL sample

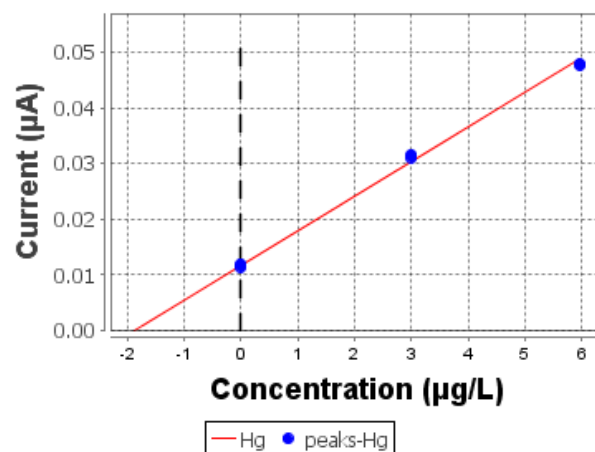
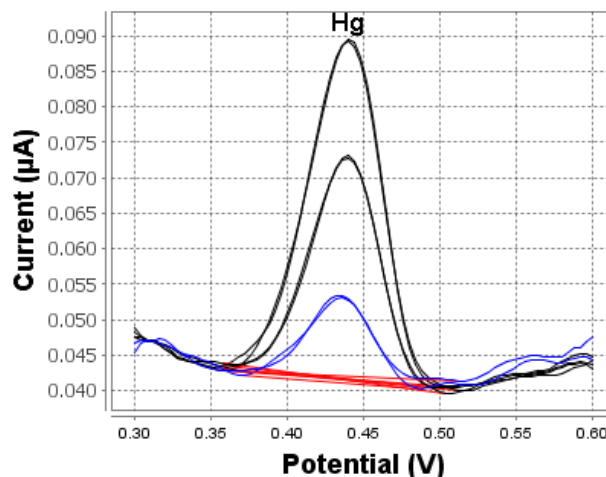
1.5 mL electrolyte

## Parameters for Hg with the 946 Portable VA Analyzer

Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min <sup>-1</sup>
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.3 V
Vertex potential	0.85 V
No. of cycles	5
<i>Potentiostatic pretreatment</i>	
Potential 1	0.75 V
Waiting time 1	10 s
Potential 2	0.3
Waiting time 2	90 s
Equilibration time	5 s
<i>Sweep</i>	
Current measuring range	± 1 µA
Start potential	0.3 V
End potential	0.6 V
Potential step	0.004 V
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
<b>Substance</b>	
Smoothing	5
Name	Hg
Characteristic potential	0.44 V

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

## Example for the determination of Hg with the 946 Portable VA Analyzer



## Results

Sample	β(Hg)
Bottled mineral water	2.1 µg/L*

\* sample spiked

## 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 electrolyte are pipetted into the measuring vessel. The cleaning is carried out using the parameters given under «Parameters for cleaning with the 946 Portable VA Analyzer».

## Measuring solution

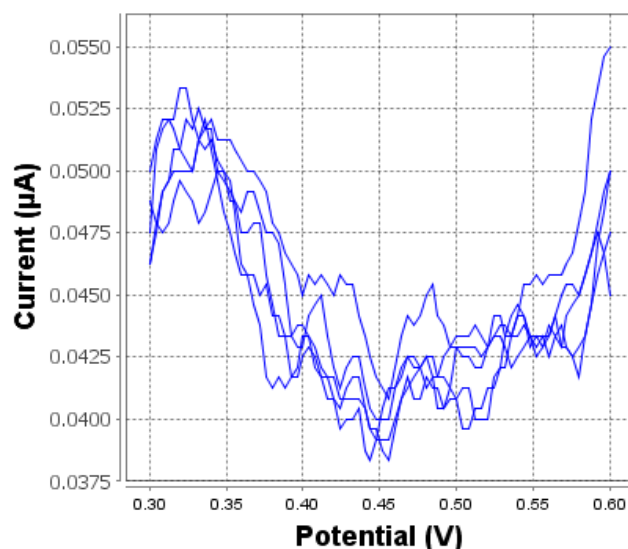
15 mL ultrapure water  
1.5 mL electrolyte

## Parameters for cleaning with the 946 Portable VA Analyzer

Determination	
No. of replications	5
No. of additions	0
Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min <sup>-1</sup>
Cyclovoltammetric pretreatment	
Start potential	-0.7 V
Vertex potential	1 V
No. of cycles	20
Potentiostatic pretreatment	
Potential 1	0.9 V
Waiting time 1	10 s
Potential 2	0.3
Waiting time 2	5 s
Equilibration time	5 s
Sweep	
Current measuring range	10 µA
Start potential	0.3 V
End potential	0.6 V
Potential step	0.004 V
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 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 the 946 Portable VA Analyzer



## Comments

Before the sensor is stored, it should be thoroughly rinsed with ultrapure water. To put it back into operation after the sensor had not been used for a while it is often sufficient to run a blank determination as described in the method «Determination of mercury with the 946 Portable VA Analyzer», just replacing the sample by 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

11 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 the 884 Professional VA».

#### Measuring solution

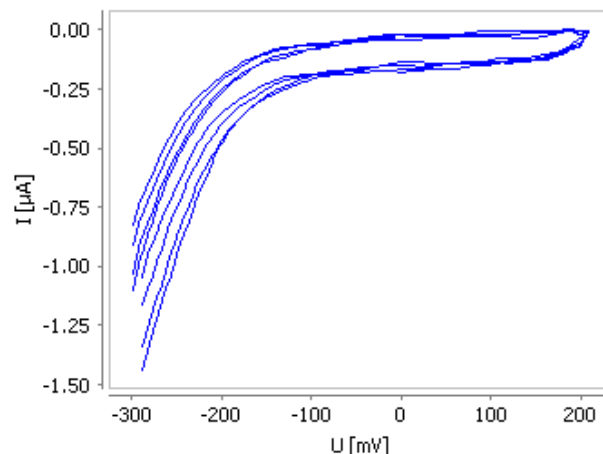
11 mL cleaning solution

#### Parameters for activation with the 884 Professional VA

Determination	
No. of replications	4
No. of additions	0
Voltammetric	
Measuring mode	CVS – Cyclic voltammetric stripping
Stirring rate	2000 min <sup>-1</sup>
Cyclic voltammetric pretreatment	
Start potential	-1.5 V
Vertex potential	1 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	-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
First vertex potential	0.2 V
Second vertex potential	-0.3
Potential step	0.01 V
Sweep rate	0.4 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 for the curves obtained during activation with the 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 mercury with the 884 Professional VA

## Analysis

10 mL sample are pipetted into the measuring vessel and 1 mL electrolyte is added. The determination is carried out using the parameters given under «Parameters for Hg with the 884 Professional VA».

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

## Measuring solution

10 mL sample

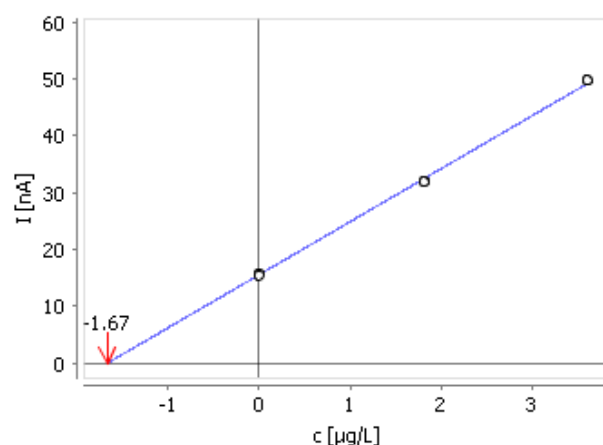
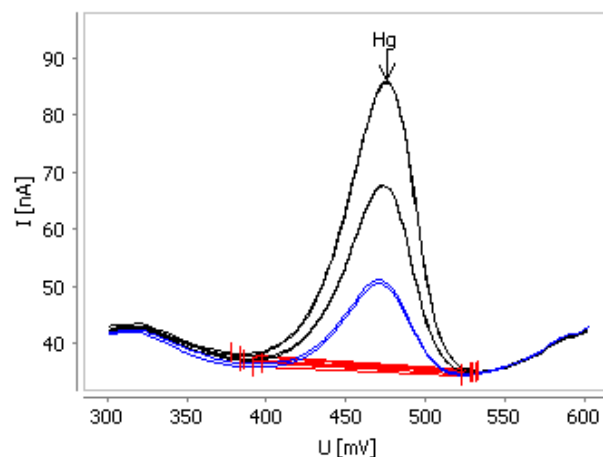
1 mL electrolyte

## Parameters for Hg with the 884 Professional VA

Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min <sup>-1</sup>
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.3 V
Vertex potential	0.85 V
No. of cycles	5
<i>Potentiostatic pretreatment</i>	
Potential 1	0.75 V
Waiting time 1	10 s
Potential 2	0.3 V
Waiting time 2	90 s
Equilibration time	5 s
<i>Sweep</i>	
Start potential	0.3 V
End potential	0.6 V
Potential step	0.004 V
Potential step time	0.4 s
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
<b>Substance</b>	
Name	Hg
Characteristic potential	0.48 V

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

## Example for the determination of Hg with the 884 Professional VA



## Results

Sample	$\beta(\text{Hg})$
Bottled mineral water	1.8 µg/L*

\* sample spiked

## 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 electrolyte are pipetted into the measuring vessel. The cleaning is carried out using the parameters given under «Parameters for cleaning with the 884 Professional VA».

## Measuring solution

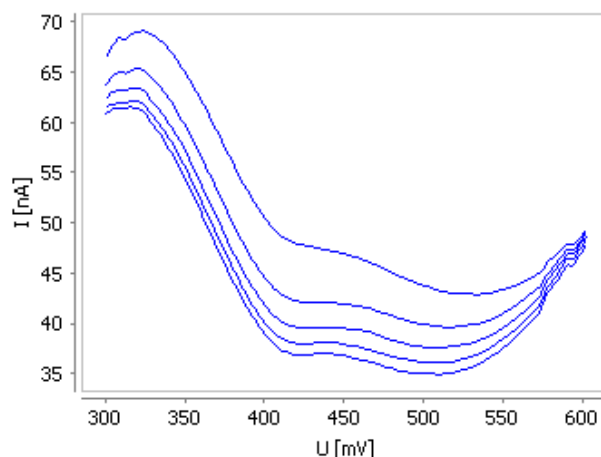
10 mL ultrapure water  
1 mL electrolyte

## Parameters for cleaning with the 884 Professional VA

Determination	
No. of replications	5
No. of additions	0
Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min <sup>-1</sup>
Cyclovoltammetric pretreatment	
Start potential	-0.7 V
Vertex potential	1.0 V
No. of cycles	20
Potentiostatic pretreatment	
Potential 1	0.9 V
Waiting time 1	10 s
Potential 2	0.3 V
Waiting time 2	5 s
Equilibration time	5 s
Sweep	
Start potential	0.3 V
End potential	0.6 V
Potential step	0.004 V
Potential step time	0.4 s
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 V

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 the 884 Professional VA



## Comments

Before the sensor is stored, it should be thoroughly rinsed with ultrapure water. To put it back into operation after the sensor had not been used for a while it is often sufficient to run a blank determination as described in the method «Determination of mercury with the 884 Professional VA», just replacing the sample by ultrapure water.

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

## Determination with the 797 VA Computrace

### Activation of scTRACE Gold with the 797 VA Computrace

#### Analysis

11 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 the 797 VA Computrace».

#### Measuring solution

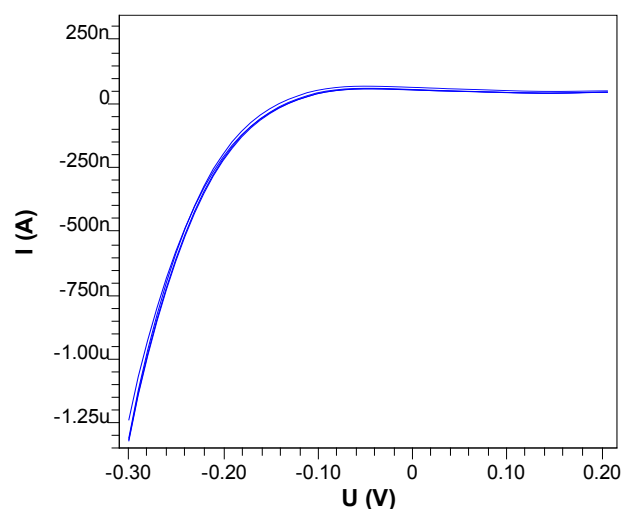
11 mL cleaning solution

#### Parameters for activation with the 797 VA Computrace

Determination	
No. of replications	4
No. of additions	0
Voltammetric	
Measuring mode	DC – Sampled direct current
Stirring rate	2000 min <sup>-1</sup>
Cyclovoltammetric pretreatment	
Start potential	-1.5 V
Vertex potential	1 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
Potential step time	0.025 s
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 the 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 mercury with the 797 VA Computrace

## Analysis

10 mL sample are pipetted into the measuring vessel and 1 mL electrolyte is added. The determination is carried out using the parameters given under «Parameters for Hg with the 797 VA Computrace».

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

## Measuring solution

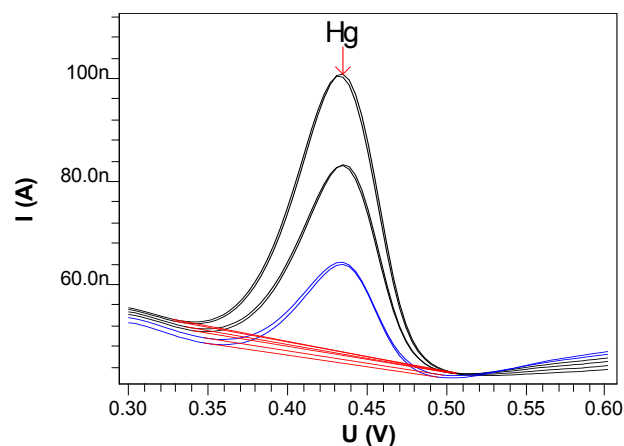
10 mL sample  
1 mL electrolyte

## Parameters for Hg with the 797 VA Computrace

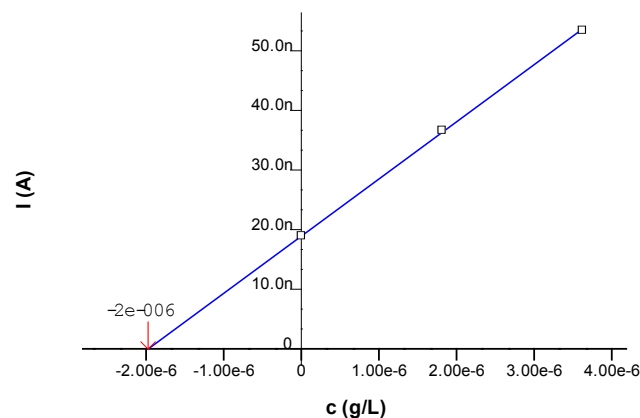
Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min <sup>-1</sup>
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.3 V
Vertex potential	0.85 V
No. of cycles	5
<i>Potentiostatic pretreatment</i>	
Potential 1	0.75 V
Waiting time 1	10 s
Potential 2	0.3 V
Waiting time 2	90 s
Equilibration time	5 s
<i>Sweep</i>	
Start potential	0.3 V
End potential	0.6 V
Potential step	0.004 V
Potential step time	0.4 s
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
<b>Substance</b>	
Smoothing	5
Name	Hg
Characteristic potential	0.48 V

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

## Example for the determination of Hg with the 797 VA Computrace



Hg  
c = 2.174 µg/L  
+/- 0.038 µg/L (1.75%)



## Results

Sample	β(Hg)
Bottled mineral water	2.2 µg/L*

\* sample spiked

## 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 electrolyte are pipetted into the measuring vessel. The cleaning is carried out using the parameters given under «Parameters for cleaning with the 797 VA Computrace».

## Measuring solution

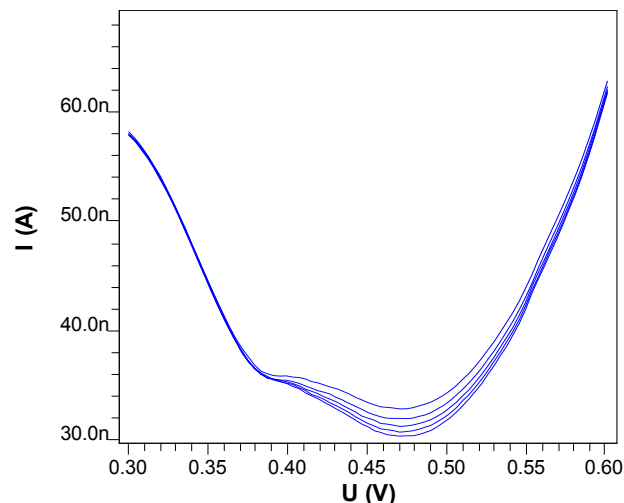
10 mL ultrapure water  
1 mL electrolyte

## Parameters for cleaning with the 797 VA Computrace

Determination	
No. of replications	5
No. of additions	0
Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min <sup>-1</sup>
Cyclovoltammetric pretreatment	
Start potential	-0.7 V
Vertex potential	1.0 V
No. of cycles	20
Potentiostatic pretreatment	
Potential 1	0.9 V
Waiting time 1	10 s
Potential 2	0.3 V
Waiting time 2	5 s
Equilibration time	5 s
Sweep	
Start potential	0.3 V
End potential	0.6 V
Potential step	0.004 V
Potential step time	0.4 s
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 V

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 the 797 VA Computrace



## Comments

Before the sensor is stored, it should be thoroughly rinsed with ultrapure water. To put it back into operation after the sensor had not been used for a while it is often sufficient to run a blank determination as described in the method «Determination of mercury with the 797 VA Computrace», just replacing the sample by ultrapure water.

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

## Comments

### Electrolyte

The iron in the electrolyte is used as a baseline modifier. Usually the Hg peak is placed on a hump, which makes it difficult to detect the start of the Hg peak. The presence of  $\beta(\text{Fe}) = 500 \mu\text{g/L}$  causes a peak right in front of the Hg peak which facilitates the evaluation of the Hg peak but does not interfere with the determination. In general, the application also works without iron in the electrolyte.

### Reagent blank

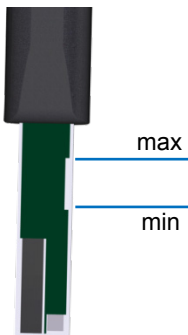
Since formic acid as well as potassium chloride can contain traces of mercury, it is recommended to determine a reagent blank on a regular basis.

Measuring solution for the reagent blank:

10 mL ultrapure water + 1 mL electrolyte

Measuring parameters are the same as those used for the mercury determination.

### 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 volumes of sample and reagents may need to be adapted.

### 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 respective cleaning method. 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.

### Measurement artefact

After a few determinations, a measurement artefact can appear, which looks like a blank, but with a 10 to 20 mV more negative peak potential. The occurrence of the measurement artefact is usually an indication, that the end potential of the cleaning cycles is too positive.

### Automation

If Dosinos are used for automatic addition of electrolyte and standard, those parts of the Dosing Unit that get in contact with the solution have to be completely free of grease. If the Dosing Unit had been greased it can be cleaned with n-hexane. For cleaning, the Dosing Unit has to be disassembled and completely dried. Then, piston, glass dosing cylinder, cylinder plate, valve, and distributor disk and the four ports of the distributor can be cleaned with n-hexane. Before reassembling, the parts have to be dried again. For disassembling and assembling of the Dosing Unit, please refer to the manual of the 807 Dosing Unit.

### Limit of detection and linear working range

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 linear working range was read out from a calibration curve.

For a deposition time of 90 s the limit of detection was  $0.5 \mu\text{g/L}$  and the working range was linear up to  $30 \mu\text{g/L}$ .

Deposition	Limit of detection	Linear working range
90 s	$0.5 \mu\text{g/L}$	$30 \mu\text{g/L}$

### Deposition time

With shorter deposition times than 90 s the linear working range can be extended, but simultaneously also the limit of detection will increase. Longer deposition times than 90 s are not recommended due to less reproducible Hg peaks.

### Miscellaneous interferences

The influence on the determination of  $\beta(\text{Hg}) = 1 \mu\text{g/L}$  was tested. If nothing else is mentioned the interference was examined up to a concentration of 1 mg/L (equals 1000 time excess). The sensitivity mentioned in the table below corresponds to the slope of the standard addition curve.

O <sub>2</sub>	Peak at approx. -0.25 V. Not quantified. Does not interfere.
EDTA	Peak at approx. 0.55 V. A ratio of EDTA:Hg of 1000:1 does not interfere. Higher excess can completely cover the Hg peak.
Humic acids	Do not interfere. A ratio of humic acid:Hg of 1000:1 shows a slightly reduced sensitivity (approx. 10%).
Triton X-100	Does not interfere. A ratio of Triton X-100:Hg of 1000:1 shows a slightly reduced sensitivity (approx. 10%).

### Interference of anions

The influence of the anion on the peak of  $\beta(\text{Hg}) = 10 \mu\text{g/L}$  was tested.

Cl <sup>-</sup>	Chloride facilitates the oxidation of the gold electrode. Besides, it has an influence on the potential of the reference electrode. For concentrations $c(\text{Cl}^-) > 100 \text{ mmol/L}$ , adapted method parameters should be used. Refer to the chapter «Adaption of method parameters to an unknown sample matrix».
CN <sup>-</sup>	Cyanide forms together with mercury hardly soluble $\text{Hg}_2(\text{CN})_2$ . Solubility product $K_{\text{sp}}(\text{Hg}_2(\text{CN})_2) = 5 \cdot 10^{-40}$ .
Br <sup>-</sup>	Shifts the Hg peak up to 50 mV into cathodic direction. A ratio of Br <sup>-</sup> :Hg of 1000:1 reduces the sensitivity by approx. 20%.
I <sup>-</sup>	Peak at approx. 0.55 V. Shifts the Hg peak up to 200 mV into cathodic direction. Higher concentrations shift the peak back into anodic direction due to the

influence on the reference electrode potential.

Determination in the presence of  $\beta(\text{I}^-) = 10 \mu\text{g/L}$  possible but strong influence on the shape of the background current.

NO <sub>2</sub> <sup>-</sup>	Broad peak at approx. 0.45 V. A ratio of NO <sub>2</sub> <sup>-</sup> :Hg of 4000:1 does not interfere. With higher excess the NO <sub>2</sub> <sup>-</sup> peak overlaps with the Hg peak.
NO <sub>3</sub> <sup>-</sup>	A ratio of NO <sub>3</sub> <sup>-</sup> :Hg of 10 <sup>6</sup> :1 does not interfere.
SO <sub>4</sub> <sup>2-</sup>	A ratio of SO <sub>4</sub> <sup>2-</sup> :Hg of 10 <sup>5</sup> :1 does not interfere.
PO <sub>4</sub> <sup>3-</sup>	A ratio of PO <sub>4</sub> <sup>3-</sup> :Hg of 10 <sup>5</sup> :1 does not interfere.

### Interference of cations

The influence of the cation on the peak of  $\beta(\text{Hg}) = 10 \mu\text{g/L}$  was tested. If nothing else is mentioned, the interference was examined up to a concentration of 100 mg/L (equals 10000 time excess).

Ag <sup>+</sup>	Does not interfere up to a concentration of $\beta(\text{Ag}) = 10 \mu\text{g/L}$ in the measuring cell. Higher concentrations alter the working electrode due to the formation of a gold-silver alloy which inhibits the determination of mercury.
As <sup>3+</sup>	Does not interfere.
As <sup>5+</sup>	Does not interfere.
Bi <sup>3+</sup>	Sharp peak at approx. 0 V. A ratio of Bi <sup>3+</sup> :Hg of 1000:1 reduces the sensitivity by approx. 40%.
Ca <sup>2+</sup>	Does not interfere. A ratio of Ca <sup>2+</sup> :Hg of 5·10 <sup>5</sup> :1 reduces the sensitivity by approx. 20%.
Cd <sup>2+</sup>	Does not interfere.
Co <sup>2+</sup>	Does not interfere.
Cu <sup>2+</sup>	Peak at approx. 0.15 V. Does not interfere.
Cr <sup>3+</sup>	Does not interfere.
Cr <sup>6+</sup>	Broad peak at approx. 0.14 V. Does not interfere.
Fe <sup>2+</sup>	Peak at approx. 0.3 V.

	A ratio of Fe <sup>2+</sup> :Hg of 500:1 reduces the recovery by approx. 15% due to an overlapping with the Hg peak. If the sample contains Fe <sup>2+</sup> , it is possible to reduce the concentration of Fe <sup>3+</sup> in the electrolyte.
Fe <sup>3+</sup>	Peak at approx. 0.3 V. A ratio of Fe <sup>3+</sup> :Hg of 500:1 reduces the recovery by approx. 15% due to an overlapping with the Hg peak. If the sample contains Fe <sup>3+</sup> , it is possible to reduce the concentration of Fe <sup>3+</sup> in the electrolyte.
Mg <sup>2+</sup>	Does not interfere. A ratio of Mg <sup>2+</sup> :Hg of 5 · 10 <sup>5</sup> :1 reduces the sensitivity by approx. 25%.
Mn <sup>2+</sup>	Does not interfere.
Ni <sup>2+</sup>	Does not interfere.
Pb <sup>2+</sup>	Does not interfere. A ratio of Pb <sup>2+</sup> :Hg of 1000:1 reduces the sensitivity by approx. 20%.
Sb <sup>3+</sup>	Broad peak at approx. 0.25 V. A ratio of Sb <sup>3+</sup> :Hg of 10:1 reduces the sensitivity by approx. 30%. Higher excess inhibits the determination of mercury.
Sb <sup>5+</sup>	Does not interfere.
Se <sup>4+</sup>	Peak at approx. 0.55 V. Does not interfere. Solubility product $K_{sp}(\text{HgSeO}_3) = 1.5 \cdot 10^{-14}$ .
Se <sup>6+</sup>	Does not interfere.
Sn <sup>2+</sup>	Does not interfere.
Sn <sup>4+</sup>	Does not interfere up to a ratio of Sn <sup>4+</sup> :Hg of 100:1. Higher concentrations deteriorate the shape of the background current.
Zn <sup>2+</sup>	Does not interfere.

## Adaption of method parameters to an unknown sample matrix

Halides, pseudo-halides and other substances forming complexes with gold can facilitate the oxidation and therefore accelerate the degradation of the working electrode. Since the electrode surface cannot be renewed, this usually means the electrode has to be replaced. In addition, the potential of the reference electrode can be influenced by the sample matrix since it depends on the concentrations of those anions, which form sparingly soluble compounds with silver.

To avoid damage to the electrode and to ensure that the mercury signal is found within the potential window, it can be useful to do some preliminary tests, if the sample matrix is not known in detail.

For the preliminary tests, use the electrolyte without iron «Electrolyte for preliminary tests». If iron is already present in the sample it can be adverse to use more iron with the electrolyte, see comment for Fe in the chapter «Interference of cations».

### Analysis

10 mL (diluted) sample and 1 mL electrolyte for preliminary tests are pipetted into the measuring vessel. Run a sweep using the parameters given under «Parameters for preliminary tests». Manually stop the sweep when the current exceeds 50 nA.

Add 0.1 mL β(Hg<sup>2+</sup>) = 10 mg/L and repeat the sweep to identify the position of the Hg peak.

### Measuring solution for preliminary tests

10 mL (diluted) sample

1 mL electrolyte for preliminary tests

### Parameters for preliminary tests

Voltammetric	
Measuring mode	DC – Sampled direct current
Stirring speed	2000 min <sup>-1</sup>
Hydrodynamic measurement	No
Cyclovoltammetric pretreatment	No
Potentiostatic pretreatment	No
Equilibration time	5 s

Sweep	
Start potential	0.0 V
End potential	0.8 V
Potential step	0.004 V
Potential step time	0.4 s
Sweep rate	0.01 V/s

### Example for preliminary tests

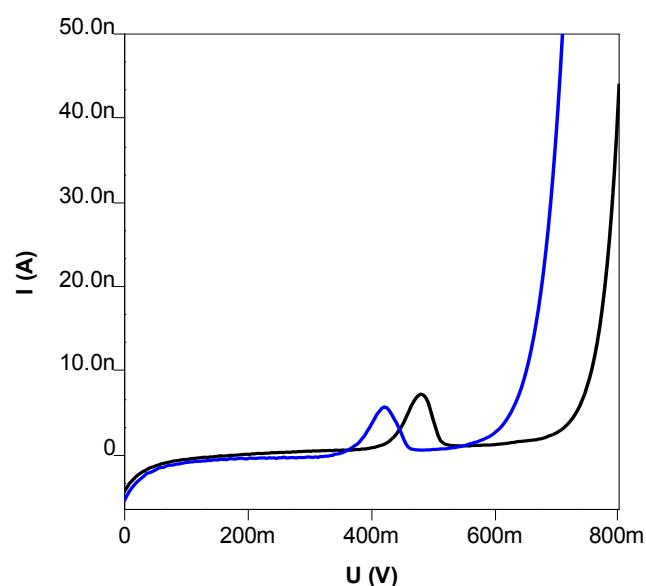


Fig. 1: Black line – curve in standard solution (Hg peak at 0.48 V, oxidation of gold starts at approx. 0.7 V); blue line – curve in artificial sea water (Hg peak at 0.42 V, oxidation of gold starts at approx. 0.6 V)

### Adjustment of method parameters

#### Pretreatment

Choose a start potential, which ensures that the potential of the Hg peak will be included in the conditioning cycles. Choose an end potential, which ensures that the background current increase has started, but the current does not exceed 50 nA. The potentiostatic pretreatment used for cleaning (potential 1) has to be adapted as well. For sea water the following parameters are recommended:

<i>Cyclic voltammetric pretreatment</i>	
Vertex potential	0.75 V
<i>Potentiostatic pretreatment</i>	
Potential 1	0.65 V

The sea water to determine these parameters was artificially mixed according to Römpp [2] with the following concentrations:

$\beta(\text{NaCl})$	28 g/L
$\beta(\text{MgSO}_4 \cdot 7 \text{H}_2\text{O})$	7 g/L
$\beta(\text{MgCl}_2 \cdot 6 \text{H}_2\text{O})$	5 g/L
$\beta(\text{CaCl}_2 \cdot 6 \text{H}_2\text{O})$	2.4 g/L
$\beta(\text{NaHCO}_3)$	0.2 g/L

#### Deposition potential

Choose a deposition potential 150 to 200 mV more negative than the peak potential of the Hg peak.

#### Sweep

Choose start and end potentials, which make sure that the Hg peak is well inside the potential interval.

#### 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.
- [2] Römpp, «Chemie Lexikon (Version 1.0),» Stuttgart/New York, 1995.