

## Application Bulletin 416/3

# Determination of arsenic in water with the scTRACE Gold

### Summary

Arsenic is ubiquitous in the crust of the earth in small concentrations. But mineral and ore deposits with elevated arsenic content can occur under special geological conditions (volcanic rock, phosphate, or sulfide-containing mineral deposits). From these deposits, arsenic is eluted as arsenite ( $\text{AsO}_3^{3-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ) and contaminates the groundwater. In addition to this natural origin, also industry and agriculture can contribute to the contamination of water with arsenic as anthropogenic sources. The WHO (World Health Organization) [1] recommends a maximum content of  $\beta(\text{As}) = 10 \mu\text{g/L}$  for water used as drinking water.

This Application Bulletin describes the determination of arsenic in water samples by anodic stripping voltammetry (ASV) using the scTRACE Gold sensor. Furthermore, it is possible to distinguish between As(total) and As(III). With a deposition time of 60 s, the limit of detection for As(total) is  $0.9 \mu\text{g/L}$ , for As(III) it is  $0.3 \mu\text{g/L}$ .

### Samples

Surface water, groundwater

### 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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<i>Accessories</i>	
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
<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.

### Optional accessories to remove copper interference

IC-H sample preparation cartridge	6.1012.x10
or	
IC-Na sample preparation cartridge	6.1012.040
Syringe 10 mL with Luer connection	6.2816.020

### 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.

### Method 1: Determination of total arsenic

With method 1 the sum of As(III) and As(V) in the sample is determined. The As(V) species is electrochemically inactive. During the determination it is reduced in-situ by nascent hydrogen to As(III). Together with the As(III) present in the sample it is further reduced electrochemically to As(0) and deposited on the gold working electrode in the same step. During the subsequent stripping step the deposited As(0) is reoxidized to As(III) giving the analytical signal.

With 60 s for deposition the limit of detection is approx. 1 µg/L and the calibration is linear up to a concentration of 20 µg/L.

### Method 2: Determination of arsenic(III)

With method 2, only the concentration of As(III) in the sample is determined. In this method the potential used for deposition is less negative than in method 1. At this potential only As(III)

is reduced to As(0) and deposited on the gold working electrode. As(V) is not reduced and deposited under these conditions. During the subsequent stripping step the deposited As(0) is reoxidized to As(III) giving the analytical signal.

With 60 s for deposition the limit of detection is approx. 0.3 µg/L and the calibration is linear up to a concentration of 20 µg/L.

### 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

- As(V) standard stock solution,  $\beta(\text{As(V)}) = 1 \text{ g/L}$ , commercially available (e.g. Sigma-Aldrich 76686)
- As(III) standard stock solution,  $\beta(\text{As(III)}) = 1 \text{ g/L}$ , commercially available (e.g. Sigma-Aldrich 72718)
- Sulfuric acid,  $w(\text{H}_2\text{SO}_4) = 96\%$ , for trace analysis\*, CAS 7664-93-9
- Nitric acid,  $w(\text{HNO}_3) = 65\%$ , for trace analysis\*, CAS 7697-37-2
- Sulfamic acid,  $\text{NH}_2\text{SO}_3\text{H}$ ,  $\geq 99.5\%$ , for analysis, CAS 5329-14-6
- Citric acid monohydrate,  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , for trace analysis\*, CAS 5949-29-1
- Potassium chloride, KCl, for trace analysis\*, CAS 7447-40-7
- Potassium permanganate,  $\text{KMnO}_4$ , for analysis, CAS 7722-64-7
- Hydrochloric acid,  $w(\text{HCl}) = 30\%$ , for analysis, CAS 7647-01-0
- Ultrapure water, resistivity  $>18 \text{ M}\Omega \cdot \text{cm}$  (25 °C), type I grade (ASTM D1193)

\* 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	$c(\text{sulfamic acid}) = 1 \text{ mol/L}$ $c(\text{citric acid}) = 0.5 \text{ mol/L}$ $c(\text{KCl}) = 0.45 \text{ mol/L}$ 9.71 g sulfamic acid, 10.51 g citric acid and 3.35 g KCl are dissolved in ultrapure water using an ultrasonic bath. When everything is dissolved the solution is made up to 100 mL with ultrapure water.
KMnO <sub>4</sub> solution	$c(\text{KMnO}_4) = 0.2 \text{ mmol/L}$ 1.6 mg KMnO <sub>4</sub> are dissolved and made up to 50 mL with ultrapure water.
10% HCl	$w(\text{HCl}) = 10\%$ 33 mL $w(\text{HCl}) = 30\%$ are diluted to 100 mL with ultrapure water. This solution is only required for the regeneration of IC-H sample preparation cartridges.

the mark with oxygen-free ultrapure water.

When the standard is stored dark and cool, it is stable for approx. 1 week.

## Sample preparation

### As(total) and As(V)

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.

### As(III)

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

If a digestion of the sample is necessary a quantification of As(III) is not possible. In this case only total arsenic can be determined, using method 1.

## Standard solutions

As(V) standard	$\beta(\text{As(V)}) = 0.5 \text{ mg/L}$ Approx. 40 mL ultrapure water are filled into a 50 mL volumetric flask. 0.05 mL $w(\text{HNO}_3) = 65\%$ and 0.025 mL As(V) standard stock solution are added. The solution is made up to the mark with ultrapure water.
As(III) standard	$\beta(\text{As(III)}) = 0.5 \text{ mg/L}$ Approx. 40 mL oxygen-free ultrapure water are filled into a 50 mL volumetric flask. 0.05 mL $w(\text{HNO}_3) = 65\%$ and 0.025 mL As(III) standard stock solution are added. The solution is made up to

## 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 for the 946 Portable VA Analyzer

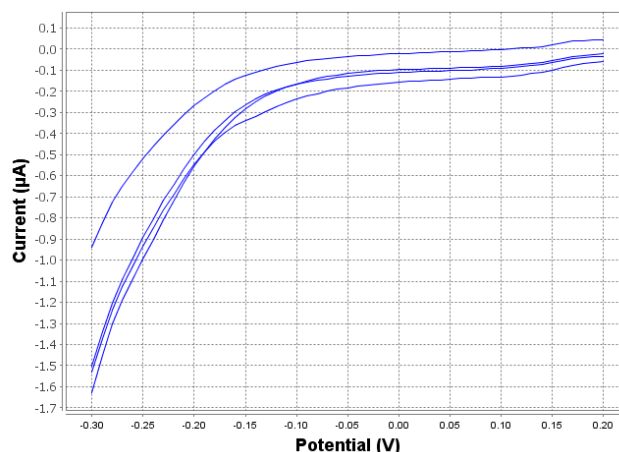
18 mL cleaning solution

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

Voltammetric	
Measuring mode	LSV – Linear sweep
Stirring rate	2000 min <sup>-1</sup>
<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 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.

# Method 1: Determination of total arsenic with the 946 Portable VA Analyzer

## Analysis

15 mL sample are pipetted into the measuring vessel and 3 mL electrolyte are added. In addition 0.1 mL  $\text{KMnO}_4$  solution have to be added if the sample contains As(III) and As(V). If the sample only contains As(V), the addition of  $\text{KMnO}_4$  solution is not required. The determination is carried out using the parameters given under «Parameters for As(total) with the 946 Portable VA Analyzer».

The concentration of As(total) is quantified by two additions of As(V) standard solution.

## Measuring solution for the 946 Portable VA Analyzer

15 mL sample  
 3 mL electrolyte  
 (+ 0.1 mL  $\text{KMnO}_4$  solution)

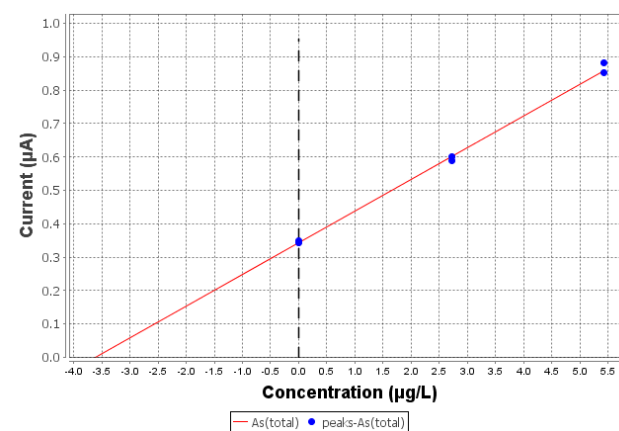
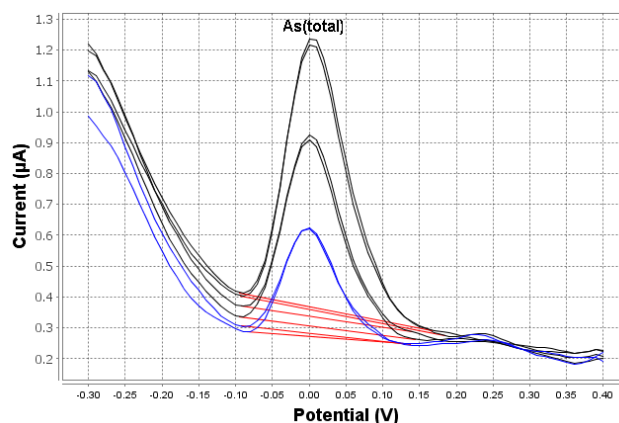
## Parameters for As(total) with the 946 Portable VA Analyzer

Voltammetric	
Measuring mode	SQW – Square wave
Stirring rate	3000 $\text{min}^{-1}$
Cyclic voltammetric pretreatment	
Start potential	-0.2 V
Vertex potential	1.0 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	-1.0 V
Waiting time 1	60 s
Potential 2	(-0.25 V) see «Comments»
Waiting time 2	5 s
Equilibration time	5 s
Sweep	
Start potential	-0.3 V
End potential	0.4 V
Potential step	0.01 V
Frequency	80 Hz
Pulse amplitude	0.02 V
Potentiostat	

Current measuring range	$\pm 10 \mu\text{A}$
Substance	
Name	As(total)
Characteristic potential	0.0 V

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

## Example for the determination of As(total) with the 946 Portable VA Analyzer



## Results

Sample	$\beta(\text{As}(\text{total}))$
Bottled mineral water	4.4 $\mu\text{g/L}$

## Comments

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

## Method 2: Determination of arsenic(III) with the 946 Portable VA Analyzer

### Analysis

15 mL sample are pipetted into the measuring vessel and 3 mL electrolyte are added. The determination is carried out using the parameters given under «Parameters for As(III) with the 884 Professional VA».

The concentration of As(III) is quantified by two additions of As(III) standard solution.

### Measuring solution for the 946 Portable VA Analyzer

15 mL sample

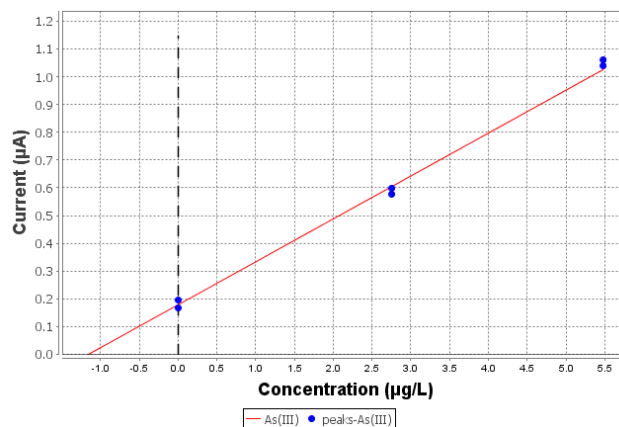
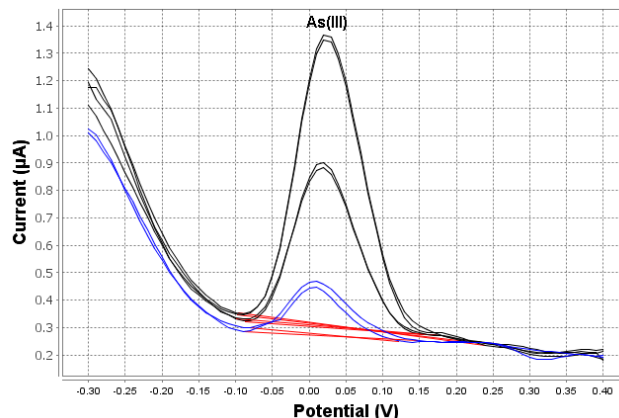
3 mL electrolyte

### Parameters for As(III) with the 946 Portable VA Analyzer

Voltammetric	
Measuring mode	SQW – Square wave
Stirring rate	3000 min <sup>-1</sup>
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.2 V
Vertex potential	1.0 V
No. of cycles	5
<i>Potentiostatic pretreatment</i>	
Potential 1	-0.5 V
Waiting time 1	60 s
Potential 2	(-0.25 V) see «Comments»
Waiting time 2	5 s
Equilibration time	5 s
<i>Sweep</i>	
Start potential	-0.3 V
End potential	0.4 V
Potential step	0.01 V
Frequency	80 Hz
Pulse amplitude	0.02 V
<b>Potentiostat</b>	
Current measuring range	± 10 µA
<b>Substance</b>	
Name	As(III)
Characteristic potential	0.0 V

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

### Example for the determination of As(III) with the 946 Portable VA Analyzer



### Results

Sample	β(As(III))
Bottled mineral water	1.4 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

18 mL of the cleaning solution is 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 for the 946 Portable VA Analyzer

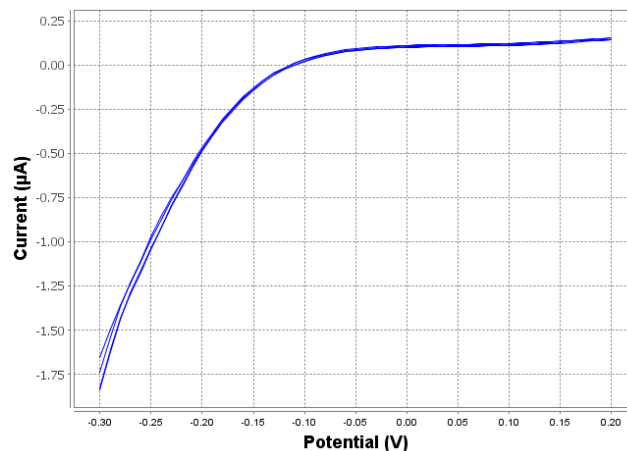
18 mL cleaning solution

## Parameters for cleaning with the 946 Portable VA Analyzer

Voltammetric	
Measuring mode	LSV – Linear sweep
Stirring rate	2000 min <sup>-1</sup>
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.3 V
Vertex potential	1.0 V
No. of cycles	10
<i>Potentiostatic pretreatment</i>	
Potential 1	-0.3 V
Waiting time 1	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 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 method 1 or 2 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

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 the 884 Professional VA».

#### Measuring solution for 884 Professional VA

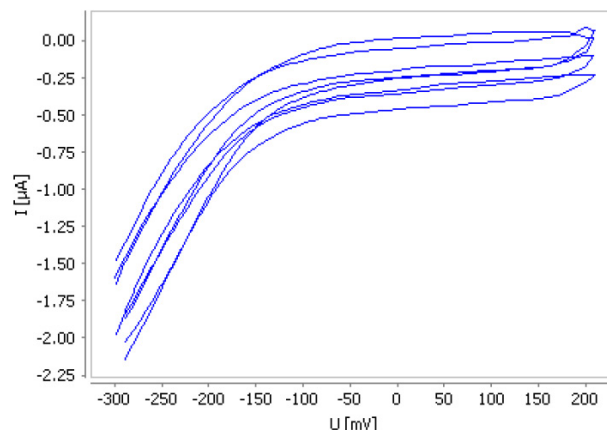
12 mL cleaning solution

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

Voltammetric	
Measuring mode	CVS – Cyclic voltammetric stripping
Stirring rate	2000 min <sup>-1</sup>
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 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.



# Method 1: Determination of total arsenic with the 884 Professional VA

## Analysis

10 mL sample are pipetted into the measuring vessel and 2 mL electrolyte are added. In addition 0.1 mL  $\text{KMnO}_4$  solution have to be added if the sample contains As(III) and As(V). If the sample only contains As(V), the addition of  $\text{KMnO}_4$  solution is not required. The determination is carried out using the parameters given under «Parameters for As(total) with the 884 Professional VA».

The concentration of As(total) is quantified by two additions of As(V) standard solution.

## Measuring solution for 884 Professional VA

10 mL sample  
 2 mL electrolyte  
 (+ 0.1 mL  $\text{KMnO}_4$  solution)

## Parameters for As(total) with the 884 Professional VA

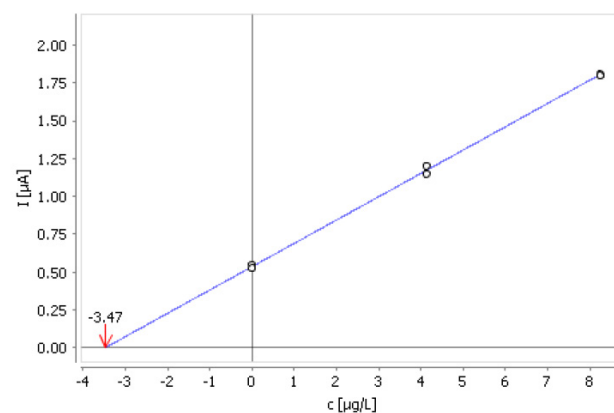
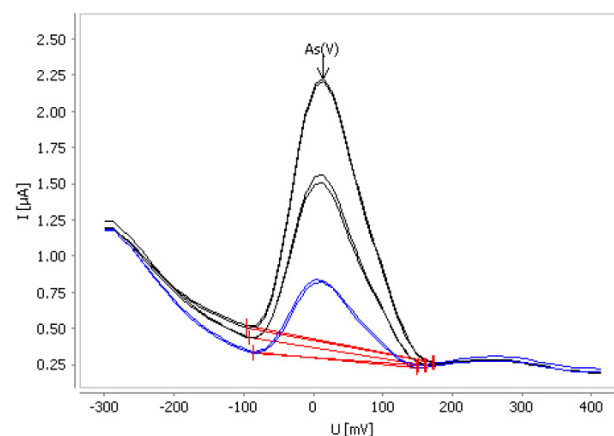
Voltammetric	
Measuring mode	SQW – Square wave
Stirring rate	2000 $\text{min}^{-1}$
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.2 V
Vertex potential	1.0 V
No. of cycles	5
<i>Potentiostatic pretreatment</i>	
Potential 1	-1.0 V
Waiting time 1	60 s
Potential 2	(-0.25 V) see «Comments»
Waiting time 2	5 s
Equilibration time	5 s
<i>Sweep</i>	
Start potential	-0.3 V
End potential	0.4 V
Potential step	0.012 V
Frequency	100 Hz
Pulse amplitude	0.02 V
<b>Potentiostat</b>	
Highest current range	2 mA
Lowest current range	20 $\mu\text{A}$

## Substance

Name	As(total)
Characteristic potential	0.0 V

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

## Example for the determination of As(total) with the 884 Professional VA



## Results

Sample	$\beta(\text{As}(\text{total}))$
Bottled mineral water	4.2 $\mu\text{g/L}$

## Comments

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

## Method 2: Determination of arsenic(III) with the 884 Professional VA

### Analysis

10 mL sample are pipetted into the measuring vessel and 2 mL electrolyte are added. The determination is carried out using the parameters given under «Parameters for As(III) with the 884 Professional VA».

The concentration of As(III) is quantified by two additions of As(III) standard solution.

### Measuring solution for 884 Professional VA

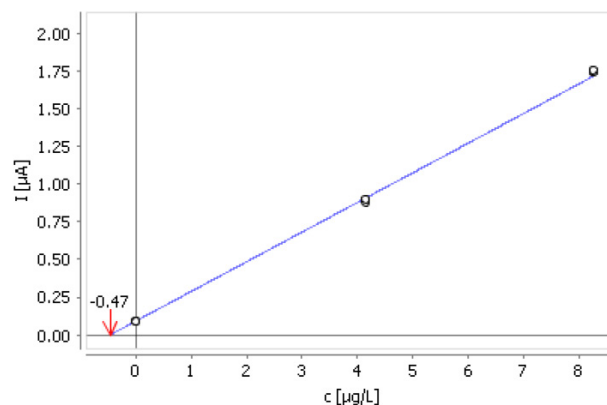
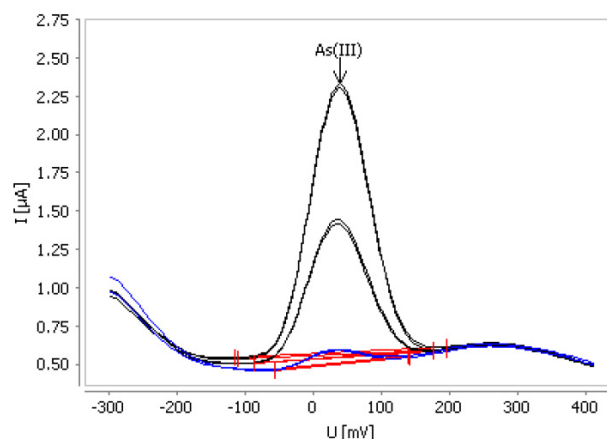
10 mL sample  
2 mL electrolyte

### Parameters for As(III) with the 884 Professional VA

Voltammetric	
Measuring mode	SQW – Square wave
Stirring rate	2000 min <sup>-1</sup>
Cyclovoltammetric pretreatment	
Start potential	-0.2 V
Vertex potential	1.0 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	-0.5 V
Waiting time 1	60 s
Potential 2	(-0.25 V) see «Comments»
Waiting time 2	5 s
Equilibration time	5 s
Sweep	
Start potential	-0.3 V
End potential	0.4 V
Potential step	0.012 V
Frequency	100 Hz
Pulse amplitude	0.02 V
Potentiostat	
Highest current range	2 mA
Lowest current range	20 µA
Substance	
Name	As(III)
Characteristic potential	0.0 V

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

### Example for the determination of As(III) with the 884 Professional VA



### Results

Sample	β(As(III))
Bottled mineral water	0.56 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

12 mL of the cleaning solution is 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 for 884 Professional VA

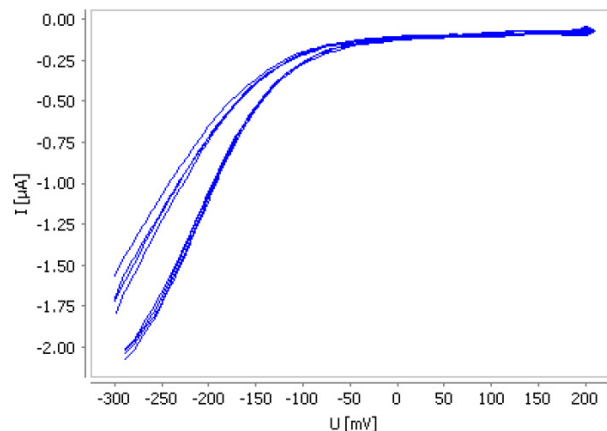
12 mL cleaning solution

## Parameters for cleaning with the 884 Professional VA

Voltammetric	
Measuring mode	CVS – Cyclic voltammetric stripping
Stirring rate	2000 min <sup>-1</sup>
Hydrodynamic measurement	No
Cyclovoltammetric pretreatment	
Start potential	-1.0 V
Vertex potential	1.0 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	-0.3 V
Waiting time 1	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 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 method 1 or 2 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

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 the 797 VA Computrace».

#### Measuring solution for 797 VA Computrace

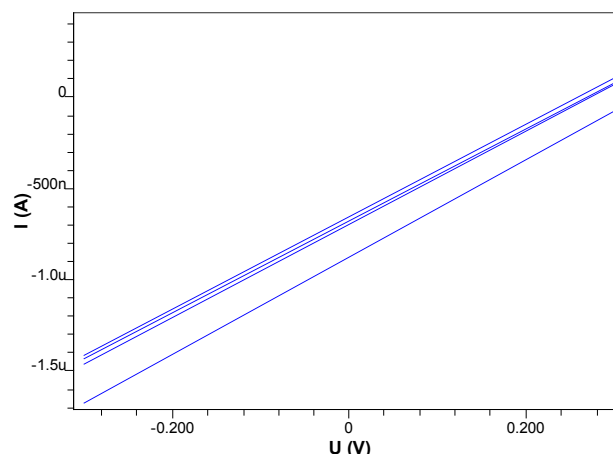
12 mL cleaning solution

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

Voltammetric	
Measuring mode	DC – Sampled direct current
Stirring rate	2000 min <sup>-1</sup>
<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 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.

# Method 1: Determination of total arsenic with the 797 VA Computrace

## Analysis

10 mL sample are pipetted into the measuring vessel and 2 mL electrolyte are added. In addition 0.1 mL  $\text{KMnO}_4$  solution have to be added if the sample contains As(III) and As(V). If the sample only contains As(V), the addition of  $\text{KMnO}_4$  solution is not required. The determination is carried out using the parameters given under «Parameters for As(total) with the 797 VA Computrace».

The concentration of As(total) is quantified by two additions of As(V) standard solution.

## Measuring solution for 797 VA Computrace

10 mL sample  
2 mL electrolyte  
(+ 0.1 mL  $\text{KMnO}_4$  solution)

## Parameters for As(total) with the 797 VA Computrace

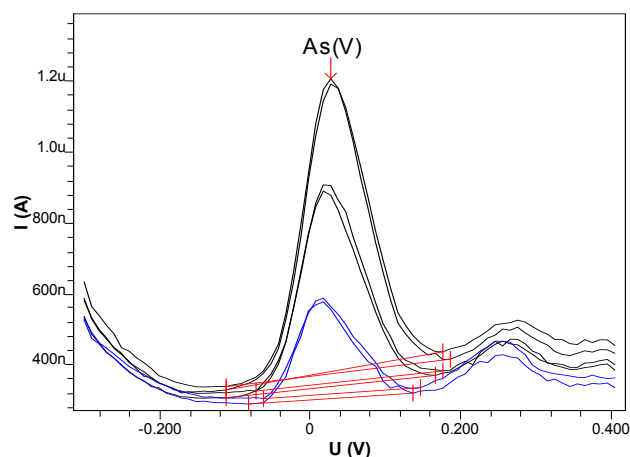
Voltammetric	
Measuring mode	SQW – Square wave
Stirring rate	2000 $\text{min}^{-1}$
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.2 V
Vertex potential	1.0 V
No. of cycles	5
<i>Potentiostatic pretreatment</i>	
Potential 1	-1.0 V
Waiting time 1	60 s
Potential 2	(-0.25 V) see «Comments»
Waiting time 2	5 s
Equilibration time	5 s
<i>Sweep</i>	
Start potential	-0.3 V
End potential	0.4 V
Potential step	0.01 V
Frequency	100 Hz
Pulse amplitude	0.02 V
<b>Substance</b>	
Name	As(total)

Characteristic potential

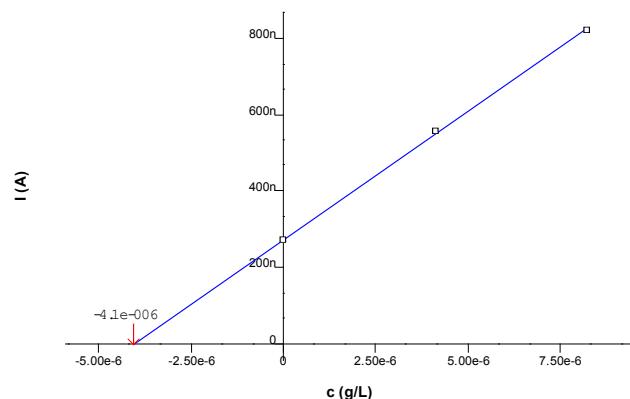
0.0 V

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

## Example for the determination of As(total) with the 797 VA Computrace



As (V)  
c = 4.875  $\mu\text{g/L}$   
+/- 0.112  $\mu\text{g/L}$  (2.31%)



## Results

Sample	$\beta(\text{As}(\text{total}))$
Bottled mineral water	4.9 $\mu\text{g/L}$

## Comments

See chapter «Comments» at the end of the document

## Method 2: Determination of arsenic(III) with the 797 VA Computrace

### Analysis

10 mL sample are pipetted into the measuring vessel and 2 mL electrolyte are added. The determination is carried out using the parameters given under «Parameters for As(III) with the 797 VA Computrace».

The concentration of As(III) is quantified by two additions of As(III) standard solution.

### Measuring solution for 797 VA Computrace

10 mL sample

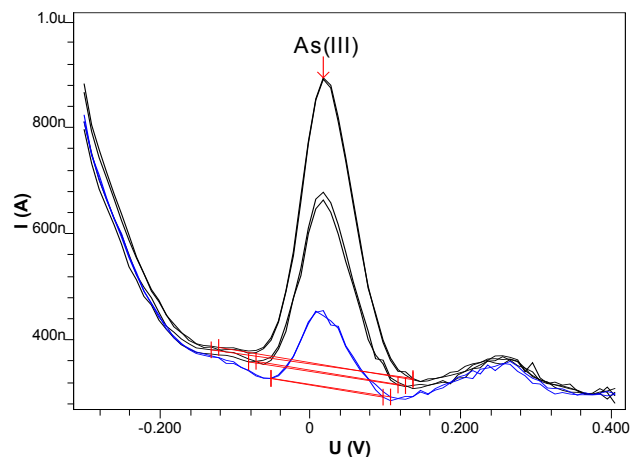
2 mL electrolyte

### Parameters for As(III) with the 797 VA Computrace

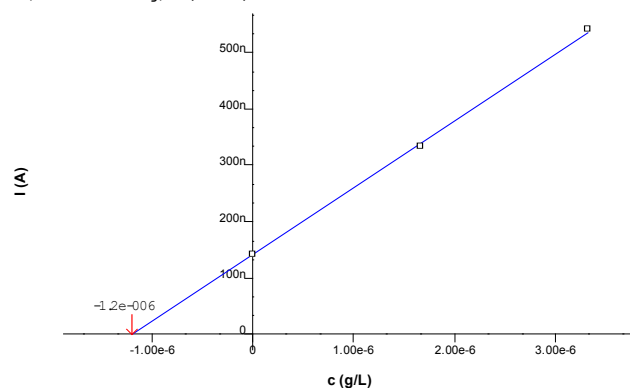
Voltammetric	
Measuring mode	SQW – Square wave
Stirring rate	2000 min <sup>-1</sup>
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.2 V
Vertex potential	1.0 V
No. of cycles	5
<i>Potentiostatic pretreatment</i>	
Potential 1	-0.5 V
Waiting time 1	60 s
Potential 2	(-0.25 V) see «Comments»
Waiting time 2	5 s
Equilibration time	5 s
<i>Sweep</i>	
Start potential	-0.3 V
End potential	0.4 V
Potential step	0.01 V
Frequency	100 Hz
Pulse amplitude	0.02 V
<b>Substance</b>	
Name	As(III)
Characteristic potential	0.0 V

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

### Example for the determination of As(III) with the 797 VA Computrace



As (III)  
c = 1.436 µg/L  
+/- 0.042 µg/L (2.90%)



### Results

Sample	β(As(III))
Bottled mineral water	1.4 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

12 mL of the cleaning solution is 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 for 797 VA Computrace

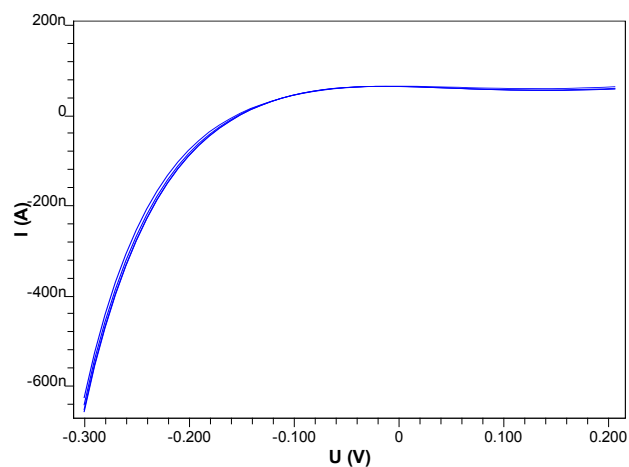
12 mL cleaning solution

## Parameters for cleaning with the 797 VA Computrace

Voltammetric	
Measuring mode	DC – Sampled direct current
Stirring rate	2000 min <sup>-1</sup>
<i>Cyclovoltammetric pretreatment</i>	
Start potential	-0.3 V
Vertex potential	1.0 V
No. of cycles	10
<i>Potentiostatic pretreatment</i>	
Potential 1	0.1 V
Waiting time 1	5
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
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 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 method 1 or 2 just replacing the sample by ultrapure water.

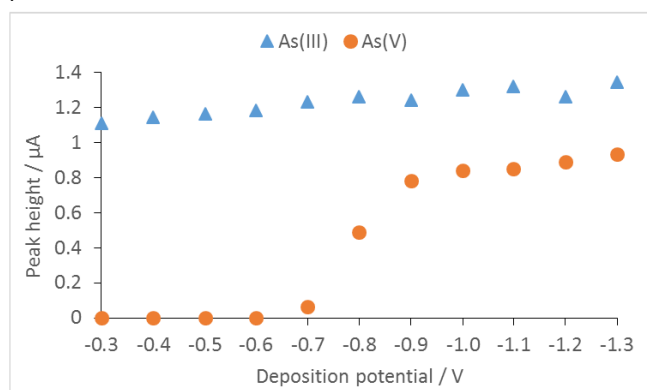
For more comments see chapter «Comments» at the end of the document.

## Comments

### Deposition

The deposition takes place when «Potential 1» (or «Cleaning potential» in case of the 797 VA Computrace) is applied.

The following graph shows the pseudopolarogram for As(III) and As(V). It represents the peak height of  $\beta(\text{As(III)}) = 10 \mu\text{g/L}$  and  $\beta(\text{As(III)}) = 10 \mu\text{g/L}$  depending on the deposition potential.



For the determination of As(III) the deposition potential should not be more negative than -0.6 V otherwise also As(V) is partly reduced and deposited.

For the determination of As(V) a more negative potential is necessary. When this potential is applied to the working electrode gas bubbles can be observed. The nascent hydrogen formed at this potential is necessary to reduce As(V) to As(III). The potential of -1 V used in method 1 is a compromise. On the one hand it has to be as negative as possible to generate enough nascent hydrogen for the reduction of As(V). On the other hand a too negative potential results in worse reproducibility of the signals and reduced lifetime of the sensor.

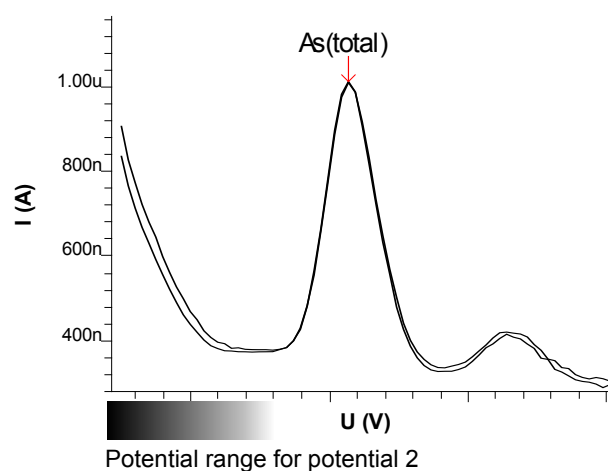
### Sensitivity of As(III) and As(V)

Using the method for the determination of As(total) the oxidation state As(III) is more sensitive than As(V) (see also the pseudopolarogram shown above under «Deposition»). When both species are present in a sample As(III) is chemically oxidized to As(V) by the addition of  $\text{KMnO}_4$  solution in order to guarantee correct results. The oxidation happens spontaneously after the addition of  $\text{KMnO}_4$ , no reaction time is necessary. The addition of  $\text{KMnO}_4$  is not required if it is certain that only As(V) is present in the sample.

### Adjustment of potential 2

«Potential 2» (or «Deposition potential» in case of the 797 VA Computrace) is used for cleaning purposes. When this potential is applied other metals, also deposited during potential 1, are stripped off the working electrode.

Potential 2 should be chosen as close as possible to the arsenic signal. Depending on the matrix the exact position of the arsenic signal can change. Therefore care has to be taken that the arsenic is not stripped off during this step.



### Limit of detection and linear working range

The limit of detection was determined using the «regression approach» [2], where the limit of detection is calculated as  $\llbracket 3 \cdot s_y \rrbracket$ , with  $s_y$  as the residual standard deviation of a linear regression. With  $\llbracket 10 \cdot s_y \rrbracket$  the limit of quantification is calculated.

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

### As(total) and As(V)

The following table gives an overview over limit of detection and linear working range for As(V) as well as As(total) depending on the time for deposition.

Deposition	Limit of detection	Linear working range
30 s	2.1 $\mu\text{g/L}$	40 $\mu\text{g/L}$
60 s	0.9 $\mu\text{g/L}$	20 $\mu\text{g/L}$
90 s	0.7 $\mu\text{g/L}$	7 $\mu\text{g/L}$

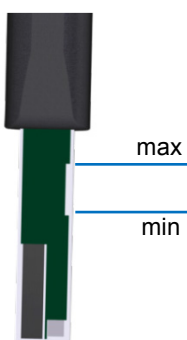


### As(III)

The following table gives an overview over limit of detection and linear working range for As(III) depending on the time for deposition.

Deposition	Limit of detection	Linear working range
30 s	0.5 µg/L	30 µg/L
60 s	0.3 µg/L	21 µg/L
90 s	0.2 µg/L	11 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 volumes of sample and reagents may need to be adapted.

### Interference of organic substances

The influence of the organic substance on the peak of  $\beta(\text{As(V)}) = 10 \mu\text{g/L}$  was tested. If nothing else is mentioned the interference equally affects As(III) and As(V).

EDTA	Does not interfere. Tested up to a concentration where EDTA starts to precipitate (approx. 0.03 mol/L).
Triton X-100	25 mg/L reduce the peak height of the As signal by approx. 35%.

Organic interferences can be eliminated as described under «Sample preparation» for low and moderately contaminated samples.

When As(III) should be determined it is not possible to eliminate organic interferences by digestion. A digestion would affect the oxidation state.

### Interference of anions

The influence of the anion on the peak of  $\beta(\text{As(V)}) = 10 \mu\text{g/L}$  was tested. If nothing else is mentioned the interference equally affects As(III) and As(V).

I <sup>-</sup>	Due to the oxidation capabilities of iodide, even traces make the determination of As(III) impossible.
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For the determination of As(V) the whole curve shifts to higher currents. In the presence of  $c(\text{iodide}) = 0.1 \text{ mmol/L}$  the peak height of the As(V) signal is reduced by approx. 30%.

Cl <sup>-</sup>	The chloride concentration has an influence on the reference potential. Therefore cleaning and deposition potential have to be adapted for samples with higher chloride concentration in order not to lose sensitivity. For sea water ( $c(\text{Cl}^-) \sim 0.5 \text{ mol/L}$ ), the potential shift is approx. +100 mV. Furthermore chloride facilitates the oxidation of gold. Therefore the positive potential in the conditioning cycles has to be adapted for higher chloride concentrations. For sea water, +0.85 V are used instead of +1.0 V.
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NO <sub>2</sub> <sup>-</sup>	In the presence of 0.4 mol/L the peak height of the As signal is reduced by approx. 40%.
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### Interference of cations on the determination of As(V)

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

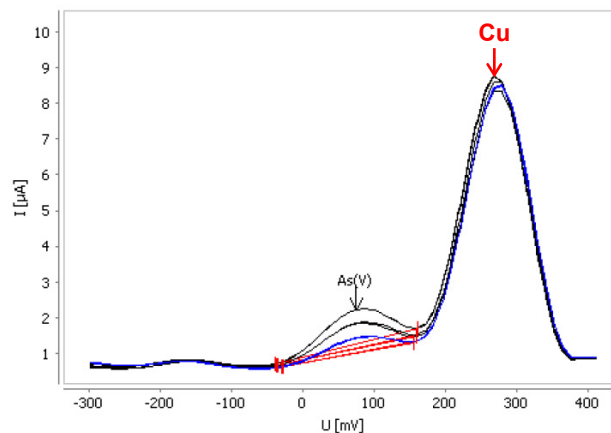
Al	Does not interfere.
Bi	Peak at +0.15 V, overlaps with the rear of the As signal. With 25 times excess the As signal vanishes in the Bi signal.
Ca	Does not interfere.
Cd	Peak at -0.15 V, appears as shoulder on the front of the As signal. Up to 15 times excess do not show an influence on the peak height of the As signal.
Co	Does not interfere with the determination of As(III). Does not interfere with the determination of As(V) up to 15 times excess. With 1000 times

	excess the peak height of the As signal decreases by 50%.
Cr(VI)	Oxidizes As(III) to As(V), therefore no As(III) can be expected when Cr(VI) is present. Does not interfere with the determination of As(V) up to 100 times excess. With 1000 times excess the peak height of the As signal decreases by 30% and an additional peak at +0.25 V appears.
Cu	Peak at +0.25 V, does not interfere up to about 5 times excess. With higher excess the Cu signal overlaps with the rear of the As signal and the sensitivity decreases. With 20 times excess the As signal vanishes in the Cu signal. Please see comment on «Reduction of the copper interference».
Fe(III)	Does not interfere. With 100 times excess formation of a yellow Fe(III)-tri-citrate complex with the electrolyte and peak at +0.4 V.
Hg	Does not interfere up to 10 times excess. With 100 times excess formation of an amalgam working electrode which makes the determination of arsenic impossible.
Mg	Does not interfere.
Mn	Does not interfere up to 100 times excess. A 4000 time's excess causes a deformation of the As signal and a reduced sensitivity. The As peak is approx. 30% smaller.
Ni	Does not interfere. Slightly reduced sensitivity for the As signal. With 4000 times excess peak at +0.25 V appears.
Pb	Peak at -0.15 V, does not interfere if equal in concentration. If higher in concentration it overlaps with the front of the As signal. With over 10 times excess also the sensitivity is affected. With 25 times excess the peak height of the As signal is reduced by approx. 60%.
Sb(III)	Peak at 0 V with the same sensitivity as arsenic.

Sb(V)	Does not interfere up to 1000 times excess. Higher concentrations show a peak at 0 V which appears as a shoulder on the As signal.
Se(IV)	Does not interfere if equal in concentration. But already a 5 time's excess causes a deformation of the As signal and a loss in sensitivity. The As signal is about 30% smaller.
Se(VI)	Does not interfere up to 1000 times excess. Higher concentrations cause a deformation of the As signal and a loss in sensitivity.
Sn(IV)	10 times excess does not interfere. 100 times excess causes a deformation of the As signal and a peak at -0.2 V.
Zn	Does not interfere with the determination of As(III). Does not interfere with the determination of As(V) up to 10 times excess. Higher concentrations interfere with the formation of the nascent hydrogen which results in a reduced signal height. With 40 times excess, the As signal is approx. 50% smaller.

### Reduction of the copper interference

A common problem in tap water and ground water analysis is the presence of significant amounts of copper.



The example shows the determination of 10.8 µg/L As(V) besides approx. 50 µg/L Cu in a ground water sample. An excess of Cu can cause false low readings for arsenic (in the above example the recovery was only about 70%) or can even completely hide the As peak.

The concentration of copper and other cations in a sample can significantly be reduced using the IC-H sample preparation cartridge (6.1012.x10). Passing the sample through the IC-H cartridge cations are replaced by  $H^+$  ions. In aqueous solution arsenic is present as arsenite ( $AsO_3^{3-}$ ) and arsenate ( $AsO_4^{3-}$ ), and is therefore not affected by the ion exchange.

In case also As(III) should be determined it is recommended to use the IC-Na cartridge (6.1012.040) instead. Here the cations are replaced by  $Na^+$  ions, why the pH of the sample solution does not change.

#### Procedure for the ion exchange:

For preparation the IC-H or IC-Na cartridge is rinsed with 10 mL ultrapure water. Then the sample is slowly forced through the cartridge using a disposable plastic syringe. The first few milliliters are discarded to avoid dilution of the sample. The IC-H cartridge can be regenerated by passing approx. 10 mL  $w(HCl) = 10\%$  through. The IC-Na cartridge cannot be regenerated.

#### 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 the 884 Professional VA». 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.

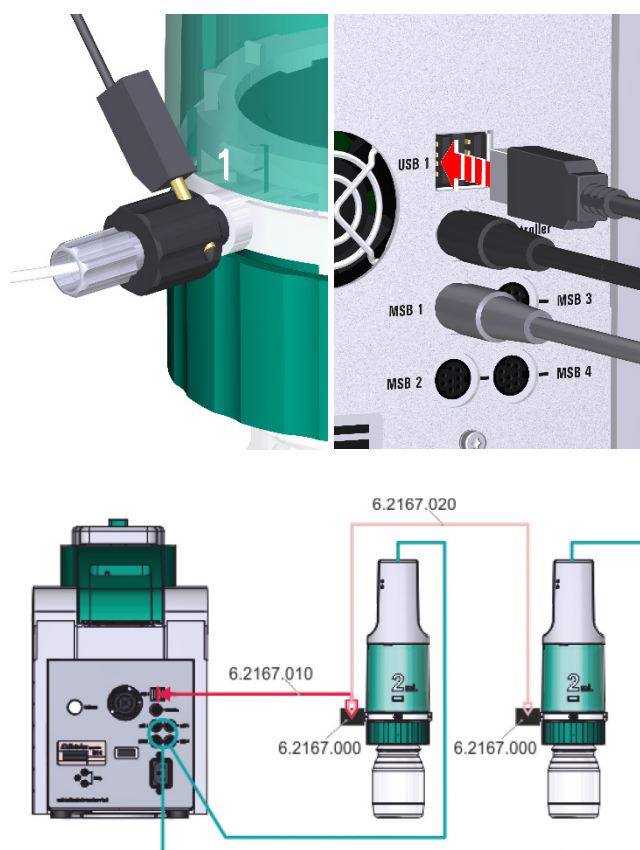
#### Grounding Dosinos (only 884 Professional VA)

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
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.



#### References

- [1] WHO, Guidelines for Drinking-water Quality, 4 ed., World Health Organization, 2017.
- [2] 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.

- [3] P. Salaün, B. Planer-Friedrich and C. M. van den Berg, "Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode," *Analytica Chimica Acta*, vol. 585, no. 2, pp. 312-322, 2007.