Metrohm

Application Bulletin 416/1 e

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 (AsO_3^{3-}) and arsenate (AsO_4^{3-}) and contaminates the ground water. 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) recommends a maximum content of β(As) = 10 µg/L for water used as drinking water.

This Application Bulletin describes the determination of arsenic in water samples by anodic stripping voltammetry 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 µg/L, for As(III) it is 0.3 µg/L.

Samples

Surface water, ground water

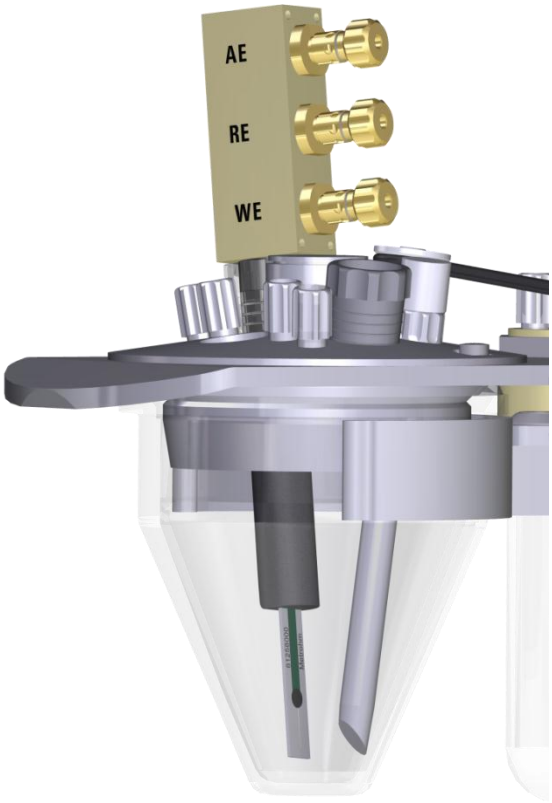
Instruments

797 VA Computrace	2.797.0020
Accessories	
Stirrer	6.1204.200
Driving belt	6.1244.020
Measuring vessel 5 mL	6.1415.150
SGJ Stopper B-14	6.1446.000
Cap	6.2753.210

Electrodes

scTRACE Gold	6.1258.000
Electrode shaft	6.1241.080

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.



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». 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», 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.

Reagents

- As(V) standard stock solution, β(As(V)) = 1 g/L, commercially available
- As(III) standard stock solution, β(As(III)) = 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
- Sulfamic acid, NH_2SO_3H, ≥ 99.5%, analytical grade, CAS 5329-14-6
- 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
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Sigma-Aldrich TraceSelect® or equivalent

Solutions

Cleaning solution	c(H_2SO_4) = 0.5 mol/L c(KCl) = 0.05 mol/L In a 100 mL volumetric flask 0.373 g KCl are dissolved in approx. 80 mL ultrapure water. 2.78 mL w(H_2SO_4) = 96% are carefully added. Attention! Solution gets very hot. After cooling down to room temperature the solution is made up to the mark with ultrapure water.
Electrolyte	c(sulfamic acid) = 1 mol/L c(citric acid) = 0.5 mol/L c(KCl) = 0.45 mol/L 9.71 g sulfamic acid, 10.51 g citric acid and 3.35 g KCl are dissolved in 100 mL ultrapure water. An ultrasonic bath is used to dissolve everything.

Standard solutions

As(V) standard	β(As(V)) = 1 mg/L Approx. 40 mL ultrapure water are filled into a 50 mL volumetric flask. 0.05 mL w(HNO_3) = 65% and 0.05 mL As(V) standard stock solution are added. The solution is made up to the mark with ultrapure water.
As(III) standard	β(As(III)) = 1 mg/L Approx. 40 mL oxygen-free ultrapure water are filled into a 50 mL volumetric flask. 0.05 mL w(HNO_3) = 65% and 0.05 mL As(III) standard stock solution are added. The solution is made up to the mark with oxygen-free ultrapure water. When the standard is stored dark and cool, it is stable for approx. 1 week.

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 chapter «Cleaning of the scTRACE Gold» should be used.

Analysis

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

Measuring solution

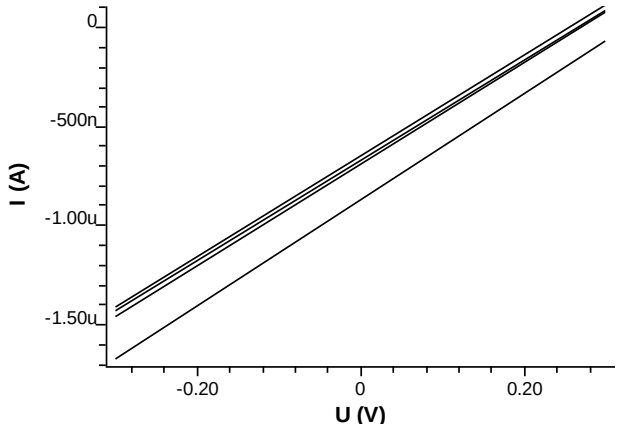
10 mL cleaning solution

Parameters for activation

Determination	
No. of additions	0
No. of replications	4
Voltammetric	
Electrode	RDE/SSE

Measuring mode	DC – Sampled direct current
Stirring speed	2400 min^{-1}
Hydrodynamic measurement	No
Conditioning cycles	
Start potential	-1.5 V
End potential	1 V
No. of cycles	10
Pretreatment	
Cleaning potential	0.1 V
Cleaning time	5 s
Deposition potential	-0.3 V
Deposition time	10 s
Sweep	
Equilibration time	5 s
Start potential	-0.3 V
End potential	0.2 V
Potential step	0.6 V
Potential step time	0.025 s
Sweep rate	24 V/s

Example for the curves obtained during activation



Comments

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

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 0.9 µg/L and the calibration is linear up to a concentration of 20 µg/L.

Sample preparation

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

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

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(total)».

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

Measuring solution

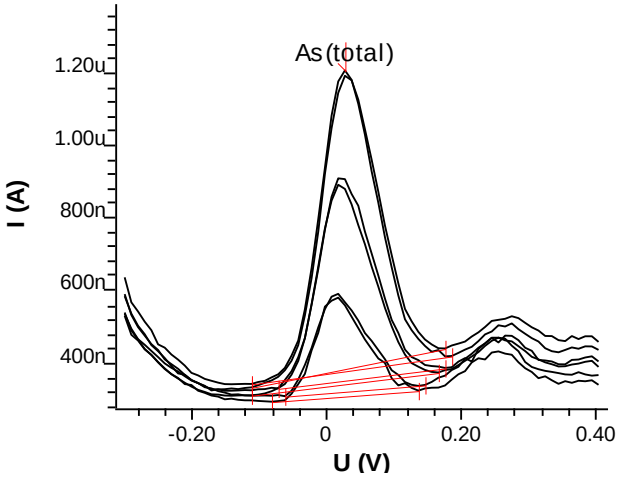
10 mL sample
2 mL electrolyte

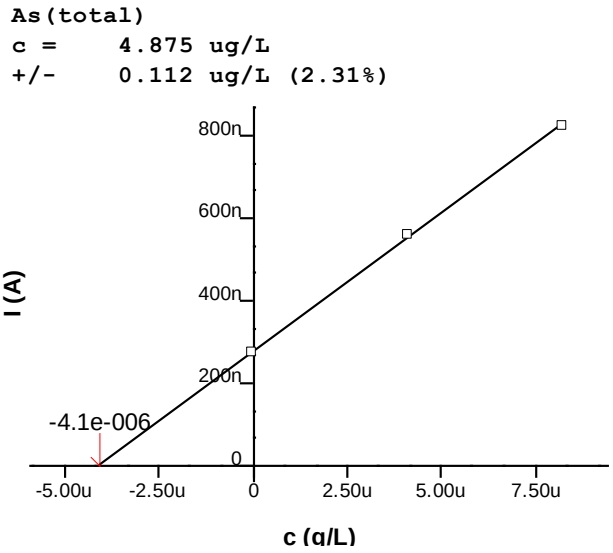
Parameters for As(total)

Determination	
No. of additions	2
No. of replications	2
Voltammetric	
Electrode	RDE/SSE
Measuring mode	SqW – Square wave
Stirring speed	2400 min^{-1}
Hydrodynamic measurement	No
Conditioning cycles	
Start potential	-0.2 V

End potential	1 V
No. of cycles	10
Pretreatment	
Cleaning potential	-1.0 V
Cleaning time	60 s
Deposition potential	(-0.25 V) see «Comments»
Deposition time	5 s
Sweep	
Equilibration time	5 s
Start potential	-0.3 V
End potential	0.4 V
Potential step	0.01 V
Amplitude	0.02 V
Frequency	100 Hz
Sweep rate	1 V/s
Substance + calibration	
Calibration	Standard addition
Name	As(total)
Peak potential	0.0 V
Tolerance	0.05 V
Baseline	Linear Automatic

Example for the determination of As(total)





Results

Sample	β(As(total))
Bottled mineral water	4.9 µg/L

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·s_y», with s_y as the residual standard deviation of a linear regression. With «10·s_y» the limit of quantification is calculated.

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

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

Deposition	***Limit of detection***	***Linear working range***
30 s	2.1 µg/L	40 µg/L
60 s	0.9 µg/L	20 µg/L
90 s	0.7 µg/L	7 µg/L

Comments

Deposition

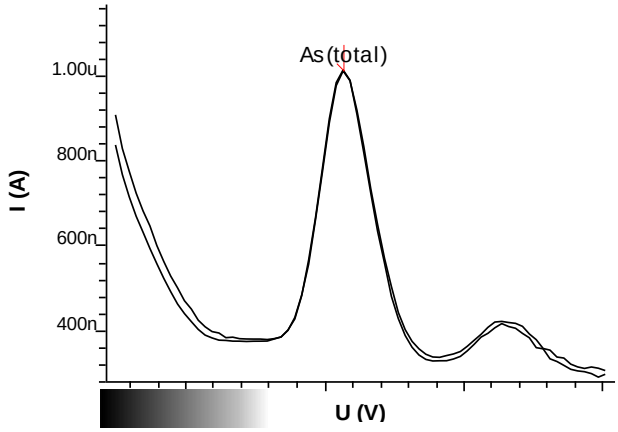
The deposition takes place when the method parameter «cleaning potential» is applied. When this potential is applied gas bubbles can be observed on the working electrode. The nascent hydrogen formed is necessary to reduce As(V) to As(III). The potential of -1 V is a compromise. On the one hand it has 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.

Adjustment of deposition potential

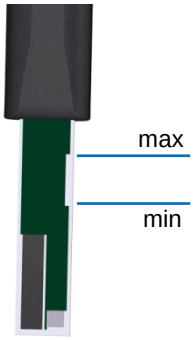
Different from the terminology in the software the deposition potential in this method is used for cleaning purposes. When this potential is applied other metals also deposited during the cleaning potential are stripped off the working electrode.

The deposition potential 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.



Potential range for deposition potential

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 β(As) = 10 µg/L was tested.

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.

Interference of anions

The influence of the anion on the peak of β(As) = 10 µg/L was tested.

I^-	The whole curve shifts to higher currents. In the presence of c(iodide) = 0.1 mmol/L the peak height of the As signal is reduced by approx. 30%.
Cl^-	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 ($c(Cl^-)$ ~ 0.5 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.
NO_2^-	In the presence of 0.4 mol/L the peak height of the As signal is reduced by approx. 40%.

Interference of cations

The influence of the cation on the peak of β(As) = 10 µg/L was tested. If nothing else is mentioned the interference was examined up to a concentration of 100 mg/L (equals 10000 time excess).

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 up to 15 times excess. With 1000 times excess the peak height of the As signal decreases by 50%.
Cr(VI)	Does not interfere 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 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 times excess cause 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 times excess cause 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 cause a deformation of the As signal and a peak at -0.2 V.
Zn	Does not interfere 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 copper interference

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_5^{3-}), and is therefore not affected by the ion exchange.

Procedure for the ion exchange:

For preparation the IC-H 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 cartridge can be regenerated by passing approx. 10 mL w(HCl) = 10% through.

Storing the scTRACE Gold

When not in use, the electrode should be stored dry. After a series of determinations it is recommended to clean the electrode using the procedure described in the paragraph «Cleaning of the scTRACE Gold». 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.

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 0.3 µg/L and the calibration is linear up to a concentration of 21 µg/L.

Sample preparation

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.

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)».

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

Measuring solution

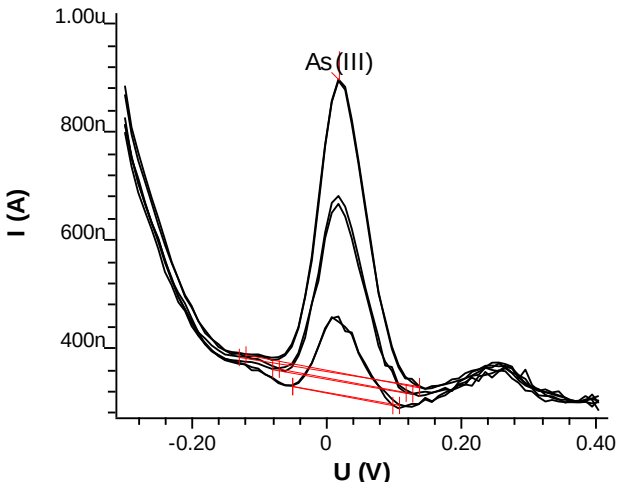
10 mL.sample

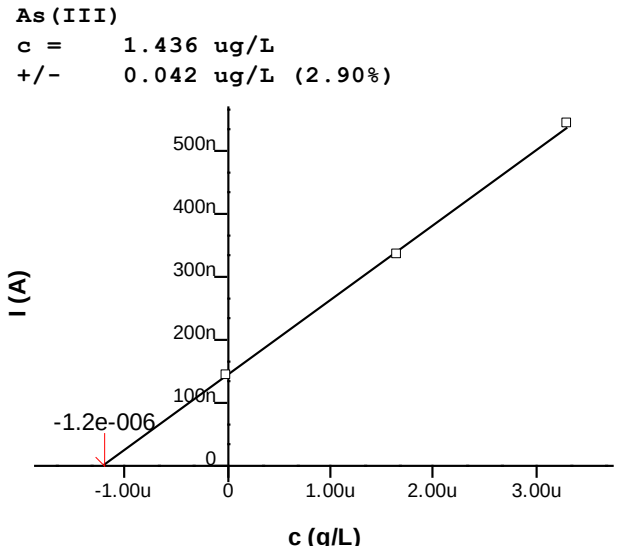
2 mL electrolyte

Parameters for As(III)

Determination	
No. of additions	2
No. of replications	2
Voltammetric	
Electrode	RDE/SSE
Measuring mode	SqW – Square wave
Stirring speed	2400 min^{-1}
Hydrodynamic measurement	No
Conditioning cycles	
Start potential	-0.2 V
End potential	1 V
No. of cycles	10
Pretreatment	
Cleaning potential	-0.5 V
Cleaning time	60 s
Deposition potential	(-0.25 V) see «Comments»
Deposition time	5 s
Sweep	
Equilibration time	5 s
Start potential	-0.3 V
End potential	0.4 V
Potential step	0.01 V
Amplitude	0.02 V
Frequency	100 Hz
Sweep rate	1 V/s
Substance + calibration	
Calibration	Standard addition
Name	As(III)
Peak potential	0.0 V
Tolerance	0.05 V
Baseline	Linear Automatic

Example for the determination of As(III)





Results

Sample	β(As(III))
Bottled mineral water	1.4 µg/L*

* sample spiked

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·s_y», with s_y as the residual standard deviation of a linear regression. With «10·s_y» the limit of quantification is calculated.

The linear working range was readout from a calibration curve.

The following table gives an overview over limit of detection and linear working range 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

Comments

Deposition

The deposition takes place when the method parameter «cleaning potential» is applied. This potential should not be more negative than -0.7 V otherwise also As(V) is partly reduced and deposited.

Adjustment of deposition potential (potential 2)

See comments in method 1.

Solution level

See comments in method 1.

Interference of organic substances

See «Interference of organic substances» in method 1.

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

I^-	Even traces of iodide make the determination impossible.

Other anions, see «Interference of anions» in method 1.

Interference of cations

Interferences are only listed if they differ from method 1. Conditions as described in method 1.

Co	Does not interfere.
Cr(VI)	Oxidizes As(III) to As(V), therefore no As(III) can be expected when Cr(VI) is present.
Zn	Does not interfere.

Reduction of copper interference

See comments in method 1.

Storing the scTRACE Gold

See comments in method 1.

Cleaning of the scTRACE Gold

To maintain the scTRACE Gold the sensor can be electrochemically cleaned. The cleaning should be carried out before the sensor is stored and when it is put back into operation. But the cleaning can also be performed in between determinations to remove contaminations.

Analysis

10 mL of the cleaning solution is pipetted into the measuring vessel. The cleaning is carried out using the parameters given under «Parameters for cleaning».

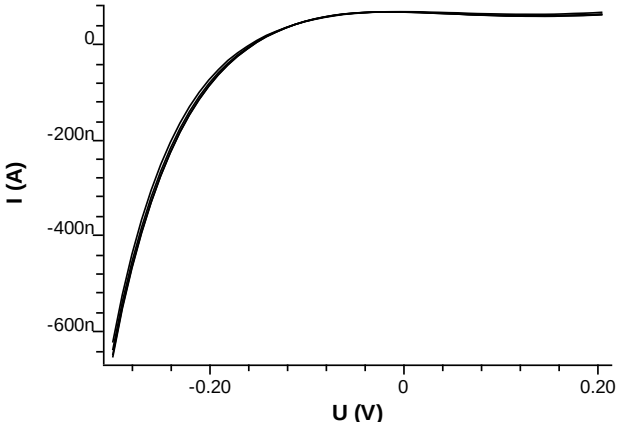
Measuring solution

10 mL cleaning solution

Parameters for cleaning

Determination	
No. of additions	0
No. of replications	4
Voltammetric	
Electrode	RDE/SSE
Measuring mode	DC – Sampled direct current
Stirring speed	2400 min^{-1}
Hydrodynamic measurement	No
Conditioning cycles	
Start potential	-0.3 V
End potential	1 V
No. of cycles	10
Pretreatment	
Cleaning potential	0.1 V
Cleaning time	5 s
Deposition potential	-0.3 V
Deposition time	10 s
Sweep	
Equilibration time	5 s
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

Example for the curves obtained during cleaning



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] 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.

Appendix

Method print for «Activation of the scTRACE Gold»

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB416_Activation scTRACE Gold.mth
Title           : Activation of the scTRACE Gold
Remark1         : 10 mL cleaning solution
Remark2         : Cleaning solution: 0.5 M H2SO4, 0.05 M KCl

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Activation scTRACE Gold
Sample amount (mL): 10.000
Cell volume (mL): 10.000

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                                : DC - Sampled Direct Current

Highest current range               : 10  mA
Lowest current range                : 100 nA

Electrode                           : SSE/RDE
Stirrer speed (rpm)                 : 2400

Initial electr. conditioning        : No

No. of additions                    : 0
No. of replications                 : 4

Measure blank                       : No
Addition purge time (s)             : 0

Initial purge time (s)              :        0

Conditioning cycles
Start potential (V)                 :   -1.500
End potential (V)                   :    1.000
No. of cycles                       :       10

Hydrodynamic (measurement)          :      No
Cleaning potential (V)              :    0.100
Cleaning time (s)                   :    5.000
Deposition potential (V)            :   -0.300
Deposition time (s)                 :   10.000

Sweep
Equilibration time (s)              :    5.000
Start potential (V)                 :   -0.300
End potential (V)                   :    0.200
Voltage step (V)                    :    0.600
Voltage step time (s)               :    0.025
Sweep rate (V/s)                    :   24.000

Cell off after measurement          :      Yes

Peak evaluation
--------------------------------------------------------------------------------
Regression technique                : Linear Regression
Peak evaluation                     : Height
Minimum peak width (V.steps)        : 5
Minimum peak height (A)             : 1.000e-010
Reverse peaks                       : No
Smooth factor                       : 4
Eliminate spikes                    : Yes

Substances
--------------------------------------------------------------------------------
Baseline
--------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
--------------------------------------------------------------------------------
```

Method print «Method 1: Determination of total arsenic»

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB416_Determination As(total) with scTRACE Gold.mth
Title           : Determination of As(total) with the scTRACE Gold
Remark1         : 10 mL sample + 2 mL electrolyte
Remark2         : Electrolyte: 1 M sulfamic acid, 0.5 M citric acid, 0.45 M KCl

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : sample
Sample amount (mL): 10.000
Cell volume (mL): 12.000

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                              : SqW - Square Wave

Highest current range             : 10  mA
Lowest current range              : 100 nA

Electrode                         : SSE/RDE
Stirrer speed (rpm)               : 2400

Initial electr. conditioning      : No

No. of additions                  : 2
No. of replications               : 2

Measure blank                     : No
Addition purge time (s)           : 10

Initial purge time (s)            :       10

Conditioning cycles
Start potential (V)               :   -0.200
End potential (V)                 :    1.000
No. of cycles                     :       10

Hydrodynamic (measurement)        :      No
Cleaning potential (V)            :   -1.000
Cleaning time (s)                 :   60.000
Deposition potential (V)          :   -0.250
Deposition time (s)               :    5.000

Sweep
Equilibration time (s)            :    5.000
Start potential (V)               :   -0.300
End potential (V)                 :    0.400
Voltage step (V)                  :    0.010
Amplitude (V)                     :    0.020
Frequency (Hz)                    :  100.000
Sweep rate (V/s)                  :    0.992

Cell off after measurement        :      Yes

Peak evaluation
--------------------------------------------------------------------------------
Regression technique              : Linear Regression
Peak evaluation                   : Height
Minimum peak width (V.steps)      : 5
Minimum peak height (A)           : 1.000e-010
Reverse peaks                     : No
Smooth factor                     : 4
Eliminate spikes                  : Yes

Substances
--------------------------------------------------------------------------------
As(total)               : 0.000 V   +/- 0.050 V

Standard solution       : 2   1.000 mg/L
Addition volume (mL)    : 0.050

Total arsenic           : Final result (As(total)) =
                          Conc * (12 / 10) * (1e+006 / 1) + 0 - 0
```

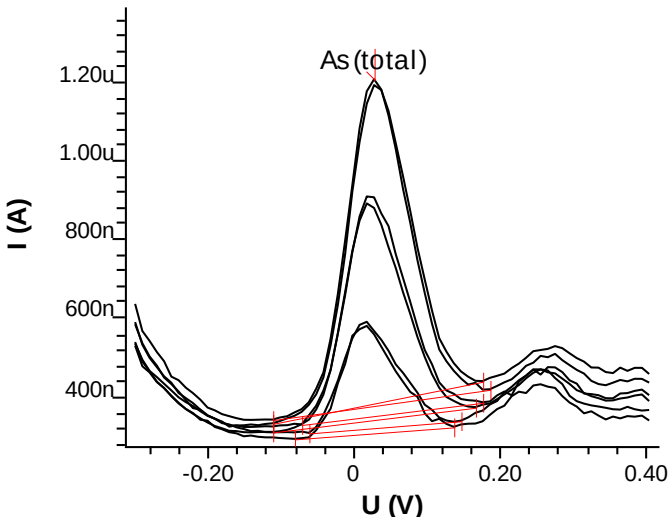
Method print «Method 2: Determination of arsenic(III)»

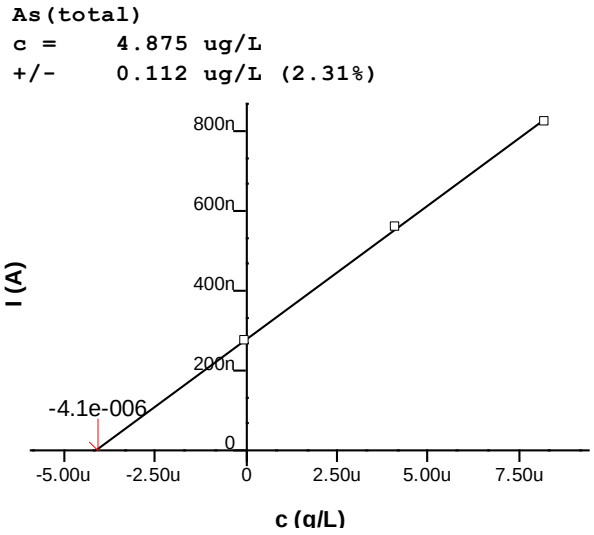
```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB416_Determination As(III) with scTRACE Gold.mth
Title           : Determination of As(III) with the scTRACE Gold
Remark1         : 10 mL sample + 2 mL electrolyte
Remark2         : Electrolyte: 1 M sulfamic acid, 0.5 M citric acid, 0.45 M KCl

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : As(III) Mineral Water
Sample amount (mL): 10.000
Cell volume (mL): 12.000

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                              : SqW - Square Wave

Highest current range             : 10  mA
Lowest current range              : 100 nA

Electrode                         : SSE/RDE
Stirrer speed (rpm)               : 2000

Initial electr. conditioning      : No

No. of additions                  : 2
No. of replications               : 2

Measure blank                     : No
Addition purge time (s)           : 10

Initial purge time (s)            :       10

Conditioning cycles
Start potential (V)               :   -0.200
End potential (V)                 :    1.000
No. of cycles                     :       10

Hydrodynamic (measurement)        :      No
Cleaning potential (V)            :   -0.500
Cleaning time (s)                 :   60.000
Deposition potential (V)          :   -0.250
Deposition time (s)               :    5.000

Sweep
Equilibration time (s)            :    5.000
Start potential (V)               :   -0.300
End potential (V)                 :    0.400
Voltage step (V)                  :    0.010
Amplitude (V)                     :    0.020
Frequency (Hz)                    :  100.000
Sweep rate (V/s)                  :    0.992

Cell off after measurement        :      Yes

Peak evaluation
--------------------------------------------------------------------------------
Regression technique              : Linear Regression
Peak evaluation                   : Height
Minimum peak width (V.steps)      : 5
Minimum peak height (A)           : 1.000e-010
Reverse peaks                     : No
Smooth factor                     : 4
Eliminate spikes                  : Yes

Substances
--------------------------------------------------------------------------------
As(III)                 : 0.000 V   +/- 0.050 V

Standard solution       : 2   1.000 mg/L
Addition volume (mL)    : 0.020

Arsenic(III)            : Final result (As(III)) =
                          Conc * (12 / 10) * (1e+006 / 1) + 0 - 0
```

Method print «Cleaning of the scTRACE Gold»

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB416_Cleaning scTRACE Gold.mth
Title           : Cleaning of the scTRACE Gold
Remark1         : 10 mL cleaning solution
Remark2         : Cleaning solution: 0.5 M H2SO4, 0.05 M KCl

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Cleaning scTRACE Gold
Sample amount (mL): 10.000
Cell volume (mL): 10.000

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                              : DC - Sampled Direct Current

Highest current range             : 10  mA
Lowest current range              : 100 nA

Electrode                         : SSE/RDE
Stirrer speed (rpm)               : 2400

Initial electr. conditioning      : No

No. of additions                  : 0
No. of replications               : 4

Measure blank                     : No
Addition purge time (s)           : 0

Initial purge time (s)            :        0

Conditioning cycles
Start potential (V)               :   -0.300
End potential (V)                 :    1.000
No. of cycles                     :       10

Hydrodynamic (measurement)        :      No
Cleaning potential (V)            :    0.100
Cleaning time (s)                 :    5.000
Deposition potential (V)          :   -0.300
Deposition time (s)               :   10.000

Sweep
Equilibration time (s)            :    5.000
Start potential (V)               :   -0.300
End potential (V)                 :    0.200
Voltage step (V)                  :    0.010
Voltage step time (s)             :    0.025
Sweep rate (V/s)                  :    0.397

Cell off after measurement        :      Yes

Peak evaluation
--------------------------------------------------------------------------------
Regression technique              : Linear Regression
Peak evaluation                   : Height
Minimum peak width (V.steps)      : 5
Minimum peak height (A)           : 1.000e-010
Reverse peaks                     : No
Smooth factor                     : 4
Eliminate spikes                  : Yes

Substances
--------------------------------------------------------------------------------
Baseline
--------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
--------------------------------------------------------------------------------
```

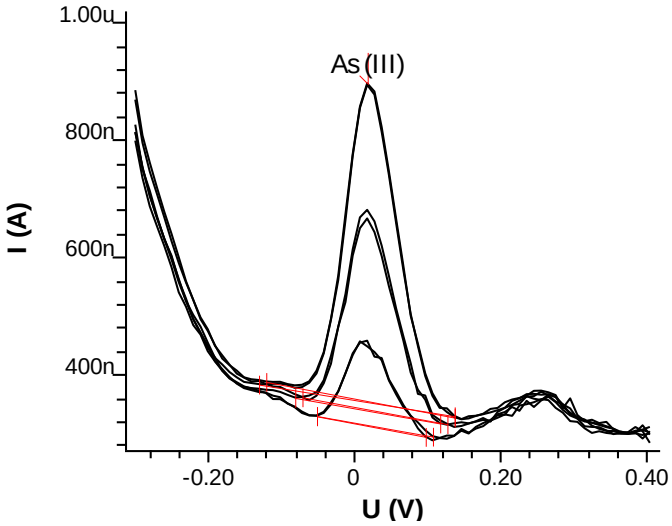
Report «Example for the determination of As(total)»

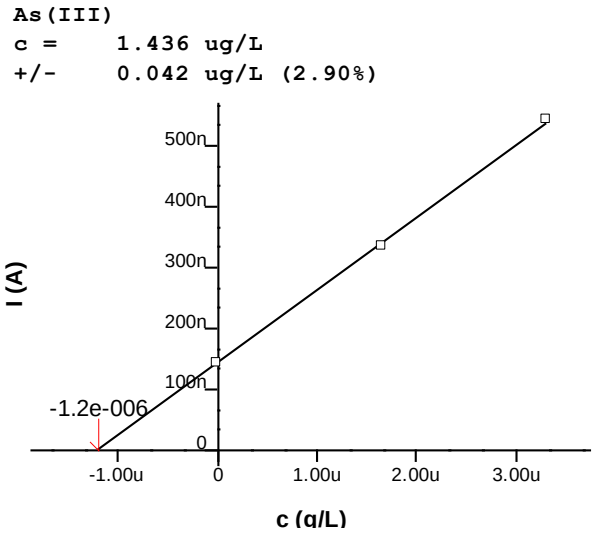





```
======== METROHM 797 VA COMPUTRACE (Version 1.3.2.85) (Serial No. 9161) ========
 Determination  : 1309021500_As(total) Mineral Water.dth
 Sample ID      : As(total) Mineral Water
 Creator method : p-fni             Date : 2013-04-30          Time:  17:00:41
 Creator determ.: p-fni             Date : 2013-09-16          Time:  16:13:15
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : Automation AsV 5 ppb cell volume12.mth
 Title          : As(V) Bestimmung mit sTrace
 Remark1        : 10mL Probe+2mL Elektrolyt
 Remark2        : Zitronensäure, Amidoschwefelsäure, KCl
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.000 mL
--------------------------------------------------------------------------------
 Substance      : As(V)
 Conc.          :   4.062 ug/L
 Conc.dev.      :   0.094 ug/L     ( 2.31%)
 Amount         :  48.749 ng
 Add.amount     :  50.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1   0.017   270.7   272.0     1.877       0.0
 1 - 2   0.017   273.3
 2 - 1   0.017   551.9   555.7     5.415     283.7
 2 - 2   0.017   559.5
 3 - 1   0.027   829.5   818.9    14.926     263.3
 3 - 2   0.027   808.4

 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 As(V)        std.add.       2.727e-007   6.712e-002   8.156e-009      0.99940

 Final results                          +/- Res. dev.   %     Comments
--------------------------------------    ------------------    --------------------

 As(V):
 default           =    4.875  ug/L    0.112        2.307
```

Report «Example for the determination of As(III)»






```
======== METROHM 797 VA COMPUTRACE (Version 1.3.2.85) (Serial No. 9161) ========
 Determination  : 1309021543_As(III) Mineral Water.dth
 Sample ID      : As(III) Mineral Water
 Creator method : p-fni             Date : 2013-05-01          Time:  14:32:51
 Creator determ.: p-fni             Date : 2013-09-16          Time:  17:02:14
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : As(III) 5ppb.mth
 Title          : As(III) Bestimmung
 Remark1        :
 Remark2        : Zitronensäure, Amidoschwefelsäure, KCl
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.000 mL
--------------------------------------------------------------------------------
 Substance      : As(III)
 Conc.          :   1.196 ug/L
 Conc.dev.      :   0.035 ug/L     ( 2.90%)
 Amount         :  14.356 ng
 Add.amount     :  20.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1   0.017   143.0   142.0     1.356       0.0
 1 - 2   0.007   141.1
 2 - 1   0.017   327.1   333.3     8.769     191.3
 2 - 2   0.017   339.5
 3 - 1   0.017   540.3   540.8     0.672     207.5
 3 - 2   0.017   541.3

 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 As(III)      std.add.       1.416e-007   1.183e-001   6.102e-009      0.99946

 Final results                          +/- Res. dev.   %     Comments
--------------------------------------    ------------------    --------------------

 As(III):
 Arsenic(III)      =    1.436  ug/L    0.042        2.896
```