Application Bulletin 226/2 e

Metrohm

Determination of arsenic by anodic stripping voltammetry at the rotating gold electrode

Of interest to:
General analytical laboratories; Water analysis; Pharmaceutical industry; Food analysis
B 1, 2, 4, 7, 9

Summary

This Bulletin describes the determination of arsenic by anodic stripping voltammetry (ASV) at the rotating gold electrode. A determination limit of 0.5 µg/L can be achieved with 10 mL sample solution. A differentiation between the As(III) concentration and the total arsenic concentration can be made by appropriate selection of the deposition potential.

The analyses are performed with a special gold electrode whose active surface is located on the side; c(HCl) = 5 mol/L is used as supporting electrolyte. For the determination of the total arsenic content As(III) and As(V) are reduced at –1200 mV by nascent hydrogen to As^0, which is preconcentrated on the electrode surface. If the deposition is carried out at –200 mV then only As(III) is reduced; this allows the differentiation between total arsenic and As(III).

During the subsequent voltammetric determination the preconcentrated As^0 is again oxidized to As(III).

Instruments and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
- 757 VA Computrace
- Electrodes and measuring vessel; to be used for the determination of arsenic only:

WE:	Driving axle	6.1246.000
	Au electrode tip (lateral Au surface)	6.1204.150
AE:	Electrode holder	6.1241.020
	Glassy carbon pin	6.1247.000
RE:	Ag/AgCl reference system	6.0728.000
	Electrolyte vessel	6.1245.000
Stopper		6.2709.040
Polishing set		6.2802.000
Measuring vessel		6.1415.210

Sample preparation

Voltammetric determinations are sensitive to interference by organic substances. This means that samples containing organic constituents must first undergo digestion.

- Ground, drinking, sea and mineral water can usually be analyzed directly.
- Water with a low to medium degree of contamination by organic substances is digested in the 705 UV Digester:

  10 mL acidified water sample (pH = 2) is treated with 10 µL w(HCl) = 30% and 50 µL $w(H_2O_2)$ = 30% and irradiated for 60 min at 90 °C.
- Samples with an organic matrix (foodstuffs, pharmaceuticals, etc.) must be subjected to a wet digestion:
  - high-pressure ashing
  - microwave digestion

  In both methods the sample is oxidized in a closed vessel using a mixture of concentrated mineral acids.
  - An open wet digestion cannot be recommended owing to the volatility of certain arsenic compounds.

Determination of the blank of the reagents

It is very difficult to obtain reagents that are completely arsenic-free. The arsenic content can also vary from batch to batch. Owing to the high sensitivity of the described method it is therefore absolutely necessary to determine the blank of the reagents used. This determination is carried out in

10 mL ultrapure water
+ 10 mL w(HCl) = 30%

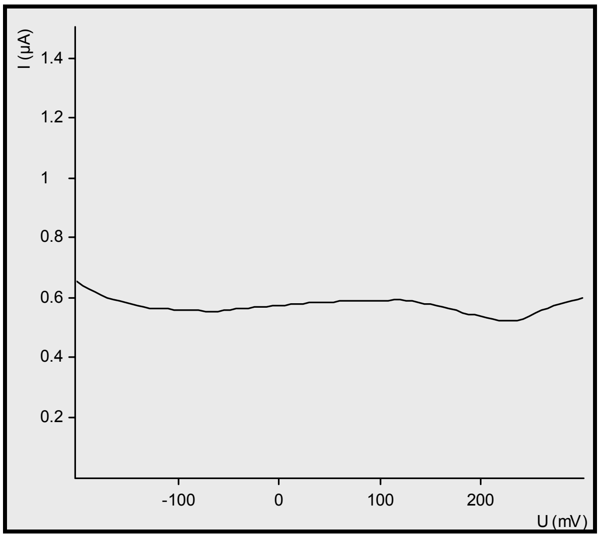
in the same way as the arsenic content of the sample is determined.

Conditioning of the gold electrode

In order to obtain reproducible curves the gold electrode must be electrochemically conditioned. This should be done every day before starting the measurements and also when the background current varies strongly from measurement to measurement.

In principle the background current should be as small as possible. For a well-functioning gold electrode it should be between 0.5 and 1.5 µA at –200 mV.

Example for the background current in c(HCl) = 5 mol/L



Conditioning solution:

10 mL ultrapure water
+ 10 mL w(HCl) = 30%

Parameters for conditioning with the 757 VA Computrace in the *Cleaning procedure* window:

Stirrer / RDE	2000 rpm
Purge time	300 s
Conditioning cycle	
Start potential	–1000 mV
End potential	–1400 mV
No. of cycles	50
Cleaning potential	+400 mV
Cleaning time	60 s
Sweep	
Equilibration time	5 s
Start potential	–200 mV
End potential	+300 mV
Voltage step	6 mV
Voltage step time	0.3 s
Sweep rate	20 mV/s
No. of repetition cycles	20

Parameters for conditioning with the 746 VA Trace Analyzer:

Working electrode	RDE
Stirrer speed	2000 rpm
Purge time	300 s
Conditioning cycle	
Cleaning potential 1	–1500 mV
Cleaning time 1	30 s
Cleaning potential 2	+400 mV
Cleaning time 2	60 s
No. of repetition cycles	16
Sweep	
Equilibration time	5 s
Start potential	–200 mV
End potential	+300 mV
Voltage step	6 mV
Voltage step time	0.3 s
Sweep rate	20 mV/s

Remarks

- Before their first use new gold electrodes should be immersed for 30 min in c(NaOH) = 0.1 mol/L and then thoroughly rinsed with ethanol and ultrapure water.
- With new electrodes, or electrodes which have not been used for a long time, it may be necessary to repeat the conditioning process several times.
- We recommend that additional conditioning is carried out in c(NaOH) = 0.1 mol/L from time to time.
- Gold electrodes should only be polished with aluminum oxide if rinsing with sodium hydroxide and ethanol as well as electrochemical conditioning no longer provide satisfactory results.

Method 1: Determination of total arsenic

Reagents

All reagents used should have the highest possible degree of purity and be as arsenic-free as possible (p.a. or «suprapur»). Only ultrapure water is to be used.

- Hydrochloric acid, w(HCl) = 30%, suprapur
- As(V) stock solution, β[As(V)] = 1 g/L (commercially available)

Ready-to-use solution

As(V) standard solution	**β[As(V)] = 1 mg/L** This solution is prepared from the As(V) stock solution by dilution with c(HCl) = 0.1 mol/L.

Analysis

Sample solution:

10 mL (diluted) sample
+ 10 mL w(HCl) = 30%

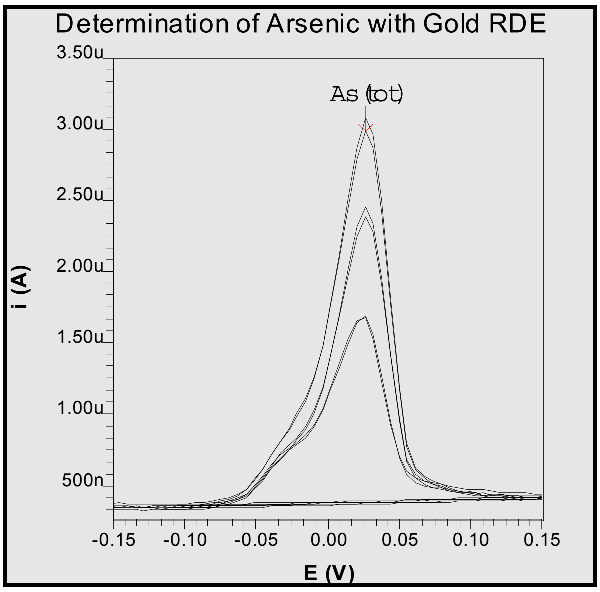
The voltammogram is recorded with the following parameters:

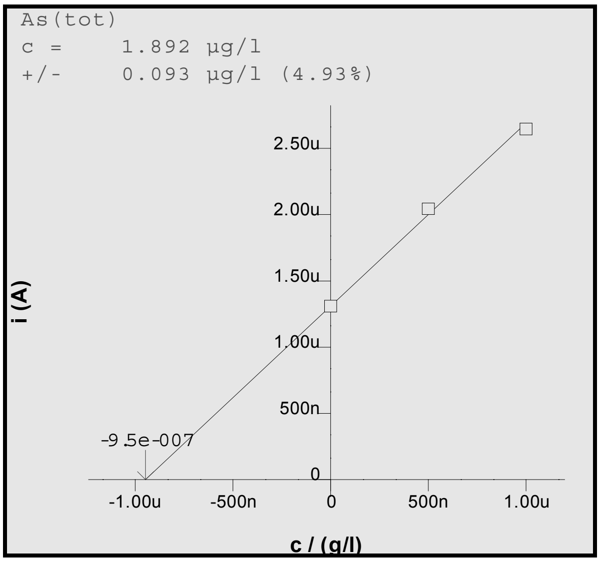
Working electrode	RDE
Stirrer speed	2000 rpm
Mode	DP
Purge time	300 s
Deposition	
Cleaning potential (deposition potential 1)	–1200 mV
Cleaning time (deposition time 1)	120 s
Deposition potential (deposition potential 2)	0 mV
Deposition time (deposition time 2)	10 s
Equilibration time	2 s
Sweep	
Pulse amplitude	50 mV
Start potential	–200 mV
End potential	+300 mV
Voltage step	6 mV
Voltage step time	0.3 s
Sweep rate	20 mV/s
Peak potential As	+50 mV

The concentration is determined by standard addition.

Example

Determination of total arsenic in mineral water with the 757 VA Computrace





```
As(tot)
c =     1.892 µg/l
+/-     0.093 µg/l (4.93%)
```

Sample volume:	10 mL
Result:	1.9 µg/L As

Remarks

- We recommend that a complete set of electrodes together with measuring vessel is reserved for the determination of arsenic. These should not be used for any other application and never in combination with a mercury electrode.
- The PTFE tubing (6.1819.000) for gassing the sample solution should be positioned so that nitrogen flows round the auxiliary electrode during the gassing process.
- If too many gas bubbles adhere to the auxiliary electrode during the determination then the electrode can be polished by using the 6.2802.000 Polishing set.
- During deposition chlorine gas is generated at the auxiliary electrode. In order to prevent corrosion the sample solution should be removed as quickly as possible after each determination
- When using the 746 VA Trace Analyzer the current display shows *_overload_* during electrolytic conditioning and voltammetric determination (MEAS – 1200 mV). Depending on the condition of the gold electrode the current strength may exceed 1.2 mA. The error message *VA STAND - ERROR 6: IR current overload* then appears; this terminates the determination. In such a case the use of a lower electrolysis potential (e.g. –1.15 V or –1.10 V) will help.
- If when using the 746 VA Trace Analyzer only a little nascent hydrogen develops during deposition then deposition can be carried out at a potential of –1.5 V.
- In order not to exceed the linear working range there should be no more than 500 ng As in the measuring vessel including the two standard additions. Samples with a higher arsenic content must be diluted accordingly with ultrapure water.
- If 10 mL sample solution is used then the method is linear up to 50 µg/L; the determination limit is 0.5 µg/L As.
- Recovery with «synthetic» water samples:

As added	As found	Absolute error	Relative error
5.00 ppb	5.30 ppb	+0.30 ppb	+6.0%
7.50 ppb	7.59 ppb	+0.09 ppb	+1.2%
9.00 ppb	8.94 ppb	-0.06 ppb	–0.7%
15.00 ppb	14.07 ppb	–0.93 ppb	–6.2%
20.00 ppb	19.08 ppb	–0.92 ppb	–4.6%

- The following table shows the interference or influence of various elements on the determination (where n x As gives the maximum amount of the element referred to the As concentration which does not cause interference):

Element	Remarks
Bi	Peak at 0 mV, max. 2 x As
Cu	Peak at +350 mV, As peak positive, max. 0.25 x As
Hg	Peak at +250 mV, As peak at 2 x is approx. 25% smaller, max. 1 x As
Sb	Peak at +40 mV, max. 2 x As
Se	Peak outside As determination, As peak at 2 x is approx. 50% smaller, max. 1 x As
Sn	Peak at approx. –300 mV, As peak is smaller, max. 1 x As
Te	Peak outside As determination, As peak at 2 x is approx. 60% smaller, max. 0.25 x As

Much of this interference can be traced back to inter-elementary compounds.

Literature

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  Anal. Chim. Acta 119 (1980) 225–233.
- D. Jagner, M. Josefson, S. Westerlund
  Anal. Chem. 53 (1981) 2144–2146.
- P. C. Leung, K. S. Subramanian, J. C. Méranger
  Talanta 29 (1982) 515–518.
- H. Huiliang, C. Hua, D. Jagner, L. Renman
  Anal. Chim. Acta 193 (1987) 61–69.
- H. Huiliang, D. Jagner, L. Renman
  Anal. Chim. Acta 202 (1987) 117–122.
- C. Hua, D. Jagner, L. Renman
  Anal. Chim. Acta 201 (1987) 263–268.
- H. Huiliang, D. Jagner, L. Renman
  Anal. Chim. Acta 207 (1988) 37–46.

Method 2: Determination of As(III)

Reagents

All reagents used should have the highest possible degree of purity and be as arsenic-free as possible (p.a. or «suprapur»). Only ultrapure water is to be used.

- Hydrochloric acid, w(HCl) = 30%, suprapur
- Ascorbic acid, puriss. p.a., CAS 50-81-7
- As(III) stcok solution, β[As(III)] = 1 g/L (commercially available)

Ready-to-use solutions

As(III) standard solution	**β[As(III)] = 1 mg/L** This solution is prepared from the As(III) stock solution by dilution with c(HCl) = 0.1 mol/L (oxygen-free).
Ascorbic acid solution	**w(ascorbic acid) = 1%** 100 mg ascorbic acid is dissolved in 10 mL oxygen-free ultrapure water.

Analysis

Sample solution:

10 mL w(HCl) = 30%

is first degassed for 5 min. Then

100 µL w(ascorbic acid) = 1% and
10 mL (diluted) sample

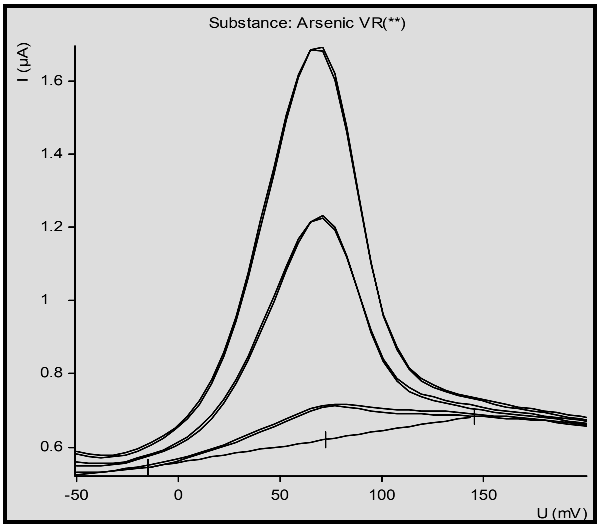
are added and the voltammogram is recorded with the following parameters:

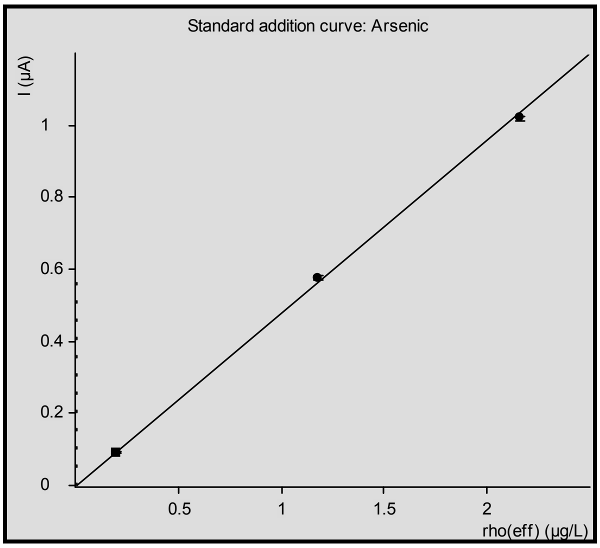
Working electrode	RDE
Stirrer speed	2000 rpm
Mode	DP
Purge time	10 s
Deposition	
Cleaning potential (deposition potential 1)	–200 mV
Cleaning time (deposition time 1)	120 s
Deposition potential (deposition potential 2)	0 mV
Deposition time (deposition time 2)	10 s
Equilibration time	2 s
Sweep	
Pulse amplitude	50 mV
Start potential	–200 mV
End potential	+300 mV
Voltage step	6 mV
Voltage step time	0.3 s
Sweep rate	20 mV/s
Peak potential As	50 mV

The concentration is determined by standard addition.

Example

Determination of As(III) in mineral water (without carbon dioxide) with the 746 VA Trace Analyzer





Sample volume:	3 mL
Result:	0.6 µg/L As(III)

Remarks

- As(III) is sensitive to oxidation; this is why the sample is only added after the hydrochloric acid has been degassed and the analysis is carried out immediately. With the 757 VA Computrace degassing must be carried out before the method is started.
- The addition of ascorbic acid stabilizes the As(III).
- The As(III) stock solution can also be prepared from arsenic(III) oxide. This is done by dissolving 0.132 g As_2O_3 (CAS 1327-53-3) in approx. 60 mL oxygen-free ultrapure water with 0.5 mL w(NaOH) = 30%, acidifying with 1 mL w(HCl) = 30% and making up to 100 mL with ultrapure water.

Appendix

Method for the conditioning of the gold electrode with the 746 VA Trace Analyzer

```
================= METROHM 746 VA TRACE ANALYZER (5.746.0101) =================
 Method: AB226_C .mth        OPERATION SEQUENCE
 Title : Conditioning of the RDE-Au for the det. of arsenic
-------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    PURGE
 2    STIR          300.0  Rot.speed      2000 /min
 3    RDE                  Rot.speed      2000 /min
 4    (REP
 5      DPMODE             U.ampl           50 mV     t.meas          20.0 ms
                           t.step         0.30 s      t.pulse         30.0 ms
 6      MEAS        30.0   U.meas        -1500 mV
 7      MEAS        60.0   U.meas          400 mV
 8      MEAS        30.0   U.meas        -1500 mV
 9      MEAS        60.0   U.meas          400 mV
10    REP)8
11    SEGMENT              Segm.name   SWEEP
12    0MEAS                U.standby           mV
13    END

 Method: AB226_2               SEGMENT
                                  SWEEP
-------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    RDE                  Rot.speed      2000 /min
 2    DPMODE               U.ampl           50 mV     t.meas          20.0 ms
                           t.step         0.30 s      t.pulse         40.0 ms
 3    0PURGE
 4    0STIR
 5    SWEEP         26.1   U.start        -200 mV     U.step             6 mV
                           U.end           300 mV     Sweep rate        20 mV/s
 6    END
```

Method for the determination of total arsenic with the 746 VA Trace Analyzer (method 1)

```
================= METROHM 746 VA TRACE ANALYZER (5.746.0101) =================
 Method: AB226_1 .mth        OPERATION SEQUENCE
 Title : Determination of As(total)
-------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    SMPL>M               V.fraction          mL     V.total               L
 2    DOS>M                Soln.name   HCl_30%        V.add         10.000 mL
 3    PURGE
 4    STIR          300.0  Rot.speed      2000 /min
 5    SEGMENT              Segm.name   Cleaning
 6    (ADD
 7      PURGE
 8      STIR        10.0   Rot.speed      2000 /min
 9      (REP
10        SEGMENT          Segm.name   As_ASV
11      REP)1
12      PURGE
13      ADD>M              Soln.name   As_Std         V.add          0.020 mL
14    ADD)2
15    END
```

```
 Method: AB226                 SEGMENT
                                 As_ASV
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    0PURGE
 2    RDE            3.0   Rot.speed      2000 /min
 3    DPMODE               U.ampl           50 mV     t.meas         20.0 ms
                           t.step         0.30 s      t.pulse        40.0 ms
 4    MEAS          60.0   U.meas        -1200 mV
 5    MEAS          10.0   U.meas            0 mV
 6    MEAS          60.0   U.meas        -1200 mV
 7    MEAS          10.0   U.meas            0 mV
 8    0STIR          2.0
 9    SWEEP         18.6   U.start        -200 mV     U.step            6 mV
                           U.end           300 mV     Sweep rate       20 mV/s
10    PURGE
11    RDE                  Rot.speed      2000 /min
12    MEAS          60.0   U.meas          400 mV
13    0MEAS                U.standby           mV
14    END

 Method: AB226                 SEGMENT
                               Cleaning
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    RDE                  Rot.speed      2000 /min
 2    DCTMODE              t.step         0.30 s      t.meas         40.0 ms
 3    MEAS          60.0   U.meas        -1500 mV
 4    MEAS          30.0   U.meas          400 mV
 5    DSWEEP        13.8   U.start        -200 mV     U.step           12 mV
                           U.end           300 mV     Sweep rate       40 mV/s
 6    0MEAS                U.standby           mV
 7    END
```

Full report for the determination of total arsenic in mineral water with the 757 VA Computrace (method 1)

```
==================== METROHM 757 VA COMPUTRACE (5.757.0010) ====================
 Determ.     :  05021631_As(total).dth
 Date        :  2001-05-02           Time:  16:31:03
 Modified    :  2001-05-03 09:59:55   User:               Cell volume: 20.000 ml
--------------------------------------------------------------------------------
  Ident                                                            Sample volume
                                                                       10.000 ml
--------------------------------------------------------------------------------
 Method  :  AB226_1_Determination of As(total).mth
 Title   :  Determination of Arsenic with Gold RDE
 Remark1 :  10 mL sample + 10 mL HCl (30%)
 Remark2 :  1.Add 10 ng As3; 2.Add 10 ng As5
--------------------------------------------------------------------------------
  Substance : As(tot)                                        Comments
  Mass conc.:  946.129  ng/l                                 ------------------
  MC.dev.   :   46.676  ng/l      (    4.93%)
  Mass      :   18.923  ng
  Add.mass  :   10.000  ng

              VR     V    uA      i.mean  Std.Dev. i.delta   Comments
             ----  -----  ------  ------  -------  -------   ------------------
             1-1   0.026   1.294  1.306   0.017              Ovl. in CDE
             1-2   0.026   1.318                             Ovl. in CDE
             2-1   0.026   2.072  2.044   0.039    0.739     Ovl. in CDE
             2-2   0.026   2.017                             Ovl. in CDE
             3-1   0.026   2.691  2.651   0.056    0.607     Ovl. in CDE
             3-2   0.026   2.611                             Ovl. in CDE

 Substance    Calibr.    Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
  As(tot)     std.add.     1.310e-006   1.387e+000                  1.657e-008

 Final results                         +/- Res. dev.   %     Comments
 ---------------------------------     ------------------    ------------------
    As(tot) =       1.892 µg/l         0.093        4.933
```

Method for the determination of As(III) with the 746 VA Trace Analyzer (method 2)

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB226_2 .mth         OPERATION SEQUENCE
 Title : Determination of As(III)
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    DOS>M                Soln.name   HCl_30%        V.add        10.000 mL
 2    PURGE
 3    STIR          300.0  Rot.speed      2000 /min
 4    SEGMENT              Segm.name   Cleaning
 5    DOS>M                Soln.name   VitC           V.add         0.100 mL
 6    SMPL>M               V.fraction          mL     V.total             L
 7    (ADD
 8      PURGE
 9      STIR        10.0   Rot.speed      2000 /min
10      (REP
11        SEGMENT          Segm.name   As3_ASV
12      REP)1
13      PURGE
14      ADD>M              Soln.name   As3_Std        V.add         0.010 mL
15    ADD)2
16    END

 Method: AB226_1               SEGMENT
                                As3_ASV
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    0PURGE
 2    RDE             3.0  Rot.speed      2000 /min
 3    DPMODE               U.ampl           50 mV     t.meas         20.0 ms
                           t.step         0.30 s      t.pulse        40.0 ms
 4    MEAS           60.0  U.meas         -200 mV
 5    MEAS           10.0  U.meas            0 mV
 6    MEAS           60.0  U.meas         -200 mV
 7    MEAS           10.0  U.meas            0 mV
 8    0STIR           2.0
 9    SWEEP          18.6  U.start        -200 mV     U.step            6 mV
                           U.end           300 mV     Sweep rate       20 mV/s
10    PURGE
11    RDE                  Rot.speed      2000 /min
12    MEAS           30.0  U.meas          400 mV
13    0MEAS                U.standby           mV
14    END

 Method: AB226_1               SEGMENT
                               Cleaning
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    RDE                  Rot.speed      2000 /min
 2    DCTMODE              t.step         0.30 s      t.meas         40.0 ms
 3    MEAS           30.0  U.meas        -1500 mV
 4    MEAS           60.0  U.meas          400 mV
 5    DSWEEP         13.8  U.start        -200 mV     U.step           12 mV
                           U.end           300 mV     Sweep rate       40 mV/s
 6    MEAS           30.0  U.meas          400 mV
 7    0MEAS                U.standby           mV
 8    END
```

Full report for the determination of As(III) in mineral water (without carbon dioxide) with the 746 VA Trace Analyzer (method 2)

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 04251553           User:                       Date: 2001-04-25
 Modified    : no                 Run :  20                   Time: 15:53:29
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        mineralwater                                                      3 mL
--------------------------------------------------------------------------------
 Method  :  AB226_2
 Title   :  Determination of As(III)
 Remark1 :  2 mL H2O + 5 mL HCl (30 %)
 Remark2 :  + 100 uL VitC + 3 mL mineral water
--------------------------------------------------------------------------------

  Substance : Arsenic                                       Comments
  Mass conc.:    637.4 ng/L           Mass     : 1.912 ng   ------------------
  MC.dev.   :     17.3 ng/L (2.71%)   Add.mass :    10 ng
  Cal.dev.  :    -                    V0.sample:     3 mL

              VR   U/mV    I/uA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00    72    0.0889  0.0904   0.0022            rear overlapping
              01    72    0.0919
              10    70    0.5802  0.5757   0.0064   0.4853
              11    70    0.5712
              20    69     1.021   1.017   0.0069   0.4409
              21    68     1.012

 Substance    Techn.     Y.reg/offset   Slope       Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------  ----------   ------------
 Arsenic      std.add.     9.054e-08        0.4783                 3.723e-09

 Final results                         +/- Res.dev.   %      Comments
 --------------------------------      -----------------     ------------------
    Arsenic =   637.36 ng/L                17.3    2.71
```