Application Bulletin 96/5 e

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

Of interest to:
General analytical laboratories; water analysis; food analysis; trace analysis
B 1, 2, 7, 9

Summary

This Application Bulletin describes the determination of mercury by anodic stripping voltammetry (ASV) at the rotating gold electrode. With a deposition time of 90 s the calibration curve is linear from 0.4 µg/L to 15 µg/L; the limit of quantification is 0.4 µg/L.

The method has primarily been drawn up for investigating water samples. After appropriate digestion the determination of mercury is possible even in samples with a high load of organic substances (wastewater, food and semi-luxuries, biological fluids, pharmaceuticals).

Instruments and accessories

- 797 VA Computrace

  or

  746 VA Trace Analyzer + 747 VA Stand
- Electrodes and measuring vessel:
  For this application the measuring cell must be completely free from platinum. This means that neither a measuring vessel nor electrodes can be used that have already been used once with a platinum working or auxiliary electrode. This is why it is rgently recommended that electrodes and measuring vessel are only used for the determination of mercury.

WE	Driving axle	6.1204.210
	Au electrode tip	6.1204.140
AE	Electrode holder	6.1241.020
	Glassy carbon rod	6.1247.000
RE	Ag/AgCl reference electrode c(KCl) = 3 mol/L	6.0728.020
	Electrolyte vessel ***c(NaCl) = 3 mol/L***	6.1245.010
Stopper		6.2709.040
Measuring vessel		6.1415.150

- 705 UV Digester

Sample preparation

Voltammetric determinations are sensitive to interference by organic substances. This means that samples that contain organic substances must first be digested.

- Groundwater, drinking water, seawater and mineral water can usually be analyzed directly.
- Water that is lightly to moderately polluted with organic substances is digested using the 705 UV Digester:

  10 mL acidified water sample (pH = 2) is treated with 10 µL w(HNO_3) = 65% and 50 µL w(H_2O_2) = 30% and irradiated for 60 min at 90 °C.
- Samples with an organic matrix (food, drugs, etc.) must undergo a wet digestion:
  - High-pressure ashing
  - Microwave digestion

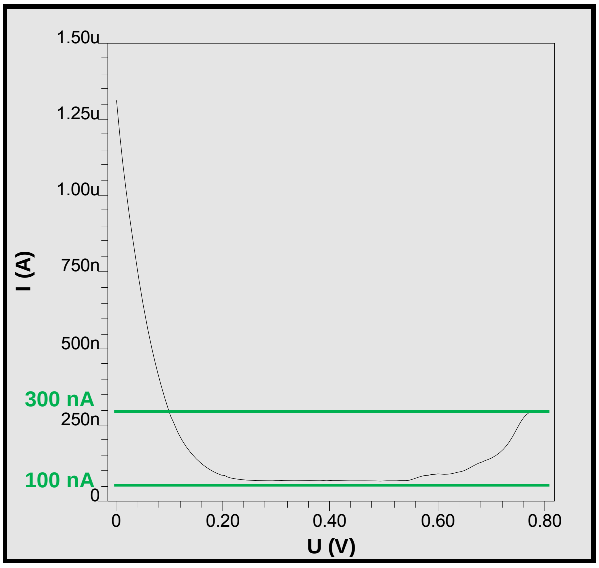
  In both methods the sample is oxidized in a closed vessel using a mixture of concentrated mineral acids.
  - An open wet digestion cannot be recommended because of the volatility of some mercury compounds.

Conditioning the gold electrode

In order to obtain reproducible curves, the gold electrode must be conditioned electrochemically. This should be carried out daily before the start of measurements, and also when the background current alters greatly from measurement to measurement.

The background current should normally be as low as possible. With a well-functioning gold electrode it has an approximate minimum value between 100 nA and 300 nA.

Example of the background current in the conditioning solution of a well-conditioned electrode



Reagents

- Perchloric acid, suprapur, w($HClO_4$) = 70%
- Ultrapure water type 1
  (electrical resistivity > 18.2 MΩ·cm, TOC < 10 ppb)

Conditioning

Conditioning solution

20 mL ultrapure water
+ 0.2 mL $HClO_4$

Voltammetric conditioning parameters

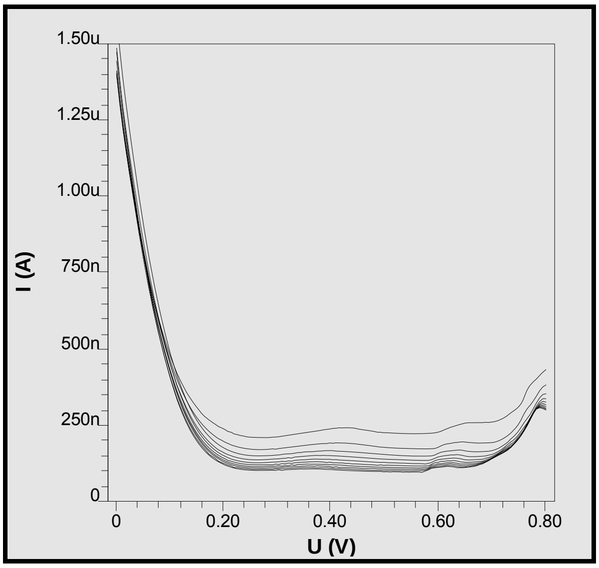
Working electrode	RDE
Stirrer speed (rpm)	2000
Mode	DP
Purge time	30 s
Pretreatment	
Hydrodynamic measurement	no
Cleaning potential	0 V
Cleaning time	10 s
Deposition potential	+1.5 V
Deposition time	30 s
Sweep	
Equilibration time	5 s
Start potential	0 V
End potential	+0.8 V
Voltage step	0.006 V
Voltage step time	0.1 s
Sweep rate	0.06 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
Cell off after measurement	yes
Determination	
No. of additions	0
No. of replications	10

Potentiostat

Highest current range	10 mA
Lowest current range	1 µA

Example

Changes in the background current of a gold electrode during the first 10 replications of conditioning.



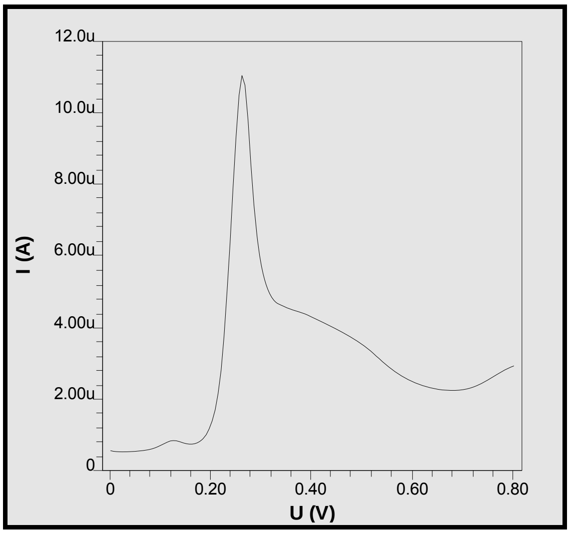
Remarks

- c(NaCl) = 3 mol/L must be used as the electrolyte in the electrolyte vessel (6.1245.010) of the reference electrode. If c(KCl) = 3 mol/L is used then sparingly soluble potassium perchlorate is formed which can then block the reference electrode diaphragm.
- Conditioning with the parameters given above should only be carried out in the electrolyte described. In electrolytes that contain chloride the gold electrode could be irreversibly damaged.
- Conditioning the electrode must be repeated so many times until the baseline no longer changes appreciably. Experience has shown that the background current will be below 400 nA at +0.6 V. If the electrode is in regular use then it is usually sufficient to condition it for about one hour directly before the start of work.
- If conditioning the electrode has to be repeated several times then it is advisable to replace the conditioning solution frequently, particularly at the start of conditioning.
- The increase in background current at approx. +0.35 V becomes smaller as conditioning proceeds. With intensively used electrodes it can disappear completely.
- For cleaning purposes the gold electrode can also be conditioned in c(NaOH) = 0.1 mol/L. In this case the following parameters should be used:

  Voltammetric parameters for cleaning in c(NaOH) = 0.1 mol/L

Working electrode	RDE
Stirrer speed (rpm)	2000
Mode	DP
Purge time	30 s
Pretreatment	
Hydrodynamic measurement	no
Cleaning potential	–1.5 V
Cleaning time	30 s
Deposition potential	+0.7 V
Deposition time	30 s
Sweep	
Equilibration time	5 s
Start potential	0 V
End potential	+0.8 V
Voltage step	0.006 V
Voltage step time	0.1 s
Sweep rate	0.06 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
Cell off after measurement	yes
Determination	
No. of additions	0
No. of replications	10

  Example of the background current in NaOH

  After cleaning in NaOH the electrode must always be thoroughly conditioned in the conditioning solution as described above.
- If the gold electrode is not to be used for more than one day then it is recommended that it is rinsed thoroughly with ultrapure water and stored in a dry condition.
- If after cleaning in NaOH and conditioning in conditioning solution the gold electrode can no longer be regenerated then it can be polished with aluminum oxide (Metrohm Order No. 6.2802.000). The electrode must then again be conditioned thoroughly as described above (time required approx. 0.5 to 1 day). However, after polished the performance of a new electrode can no longer be achieved (background current, detection limits).

Method 1: Determination of mercury in samples with a low chloride concentration

Theory

Mercury is determined by anodic stripping voltammetry (ASV) at the rotating gold electrode. Mercury ions are deposited on the gold electrode by reduction to Hg^0. In the stripping step the deposited Hg^0 is again oxidized to mercury ions.

This method is only suitable for samples with a low chloride concentration ($c(Cl^-) < 0.01$ mol/L). For samples with a higher chloride concentration or in the presence of other halides or pseudohalides the positive potential range of the method must be limited, as otherwise the gold electrode will be irreversibly damaged by oxidation.

Reagents

- Sulfuric acid, suprapur, $w(H_2SO_4) = 96\%$, CAS 7664-93-9
- Ethylenediaminetetraacetic acid disodium salt dihydrate, for analysis, $Na_2C_{10}H_{14}N_2O_8 \cdot 2H_2O$, CAS 6381-92-6
- Sodium chloride, suprapur, NaCl, CAS 7647-14-5
- Hg standard stock solution, $\beta(Hg^{2+}) = 1$ g/L (available commercially)
- Nitric acid, suprapur, $w(HNO_3) = 65\%$
- Ultrapure water type 1 (electrical resistivity > 18.2 MΩ·cm, TOC < 10 ppb)

Ready-to-use solutions:

Supporting electrolyte	$c(H_2SO_4) = 2$ mol/L $c(Na_2EDTA) = 0.02$ mol/L $c(NaCl) = 0.05$ mol/L
	0.372 g Na_2EDTA and 0.146 g NaCl are dissolved in approx. 40 mL ultrapure water and 5.56 mL H_2SO_4. After cooling down to room temperature they are made up to 50 mL with ultrapure water.
Hg standard solution	$\beta(Hg^{2+}) = 1$ mg/L
	0.1 mL Hg standard (1 g/L) and 0.1 mL HNO_3 (65%) are made up to 100 mL with ultrapure water.

Determination

Measuring solution

10 mL sample
+ 1 mL supporting electrolyte

Voltammetric parameters

Working electrode	RDE
Stirrer speed (rpm)	2000
Mode	DP
Purge time	30 s
Pretreatment	
Hydrodynamic measurement	no
Cleaning potential	+0.9 V
Cleaning time	10 s
Deposition potential	+0.37 V
Deposition time	90 s
Sweep	
Equilibration time	5 s
Start potential	+0.4 V
End potential	+0.7 V
Voltage step	0.002 V
Voltage step time	0.1 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
Cell off after measurement	yes
Substances	
Peak position (Hg)	+0.6 V

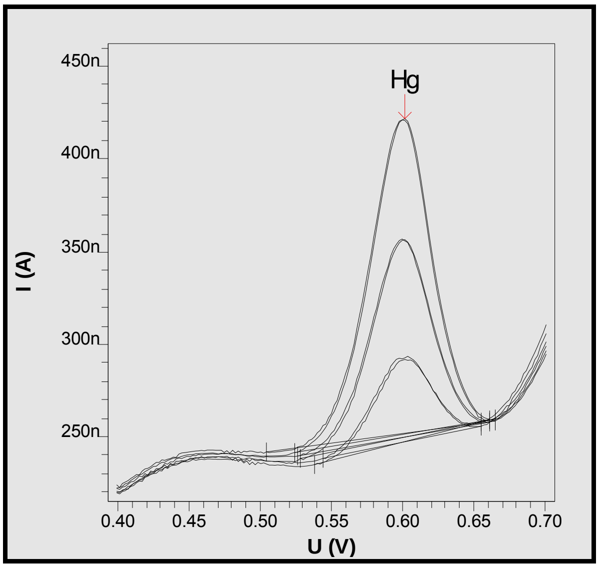
Potentiostat

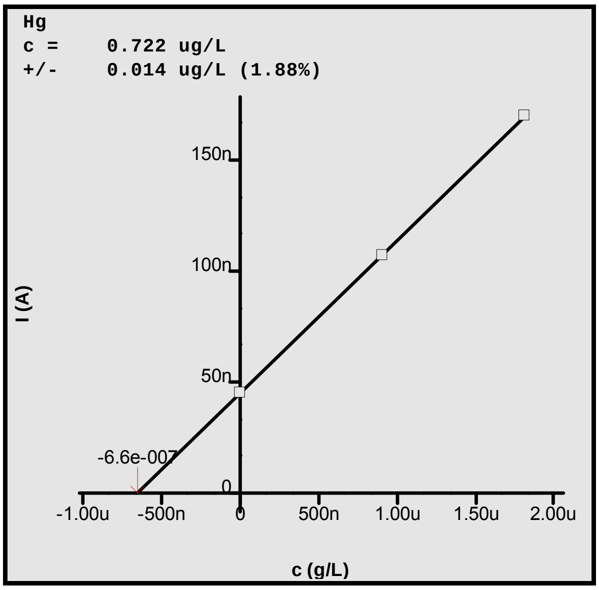
Highest current range	10 mA
Lowest current range	1 µA

The concentration in the sample is determined by standard addition.

Example

Determination of mercury in tap water (spiked sample)





```
Hg
c =     0.722 ug/L
+/-     0.014 ug/L (1.88%)
```

Sample volume	10 mL
Deposition time	90 s
Result	0.7 µg/L Hg

Remarks

- In order to obtain reproducible curves it is important that the gold electrode is first conditioned. See «Conditioning the gold electrode». Depending on the sample matrix, and if longer deposition times are used, it may be necessary to repeat this conditioning at regular intervals between the determinations.
- c(NaCl) = 3 mol/L must be used as the electrolyte in the electrolyte vessel (6.1245.010) of the reference electrode. If c(KCl) = 3 mol/L is used then sparingly soluble potassium perchlorate is formed which can then block the reference electrode diaphragm.
- If the gold electrode is not to be used for more than one day then it is recommended that it is rinsed thoroughly with ultrapure water and stored in a dry condition.
- The presence of oxygen does not interfere with the determination of mercury, as oxygen is only reduced at a potential of –0.1 V. The measuring solution does not need to be degassed for this reason.
- The pH of the measuring solution should be pH < 1. At pH > 1 the background current increases and from pH 2 completely hides the Hg peak.
- Determination limit and linear range apply under the assumption that a new, well-conditioned gold electrode and 10 mL sample are used, and that the sample matrix does not cause any interference:

	Deposition time		
	30 s	*90 s*	*180 s*
Limit of quantification	2 µg/L	0.4 µg/L	0.2 µg/L
Linear range up to	40 µg/L	15 µg/L	6 µg/L

- The supporting electrolyte described above can also be prepared using perchloric acid as an alternative to sulfuric acid. All other parameters remain unchanged.

Supporting electrolyte $HClO_4$	$c(HClO_4)$ = 1 mol/L $c(Na_2EDTA)$ = 0.02 mol/L c(NaCl) = 0.05 mol/L
	0.372 g Na_2EDTA and 0.146 g NaCl are dissolved in approx. 40 mL ultrapure water and 4.2 mL $HClO_4$[1] and made up to 50 ml with ultrapure water.

[1] Perchloric acid, suprapur, $w(HClO_4)$ = 70%

- If no interference or matrix effects occur during the determination (e.g. in a standard solution) then the background current at the start of the curve (potential range +0.4 V to +0.5 V) typically lies within the range 150 nA ... 400 nA (with a deposition time of 60 s).
- Possible interferences to the peak of $\beta(Hg^{2+})$ = 10 µg/L have been investigated under the conditions given above for the following ions. If nothing else is mentioned then the tests have been carried out up to an excess of 1000:1.

Interfering metals

Element	*Remarks*
Al^{3+}	Does not interfere.
Bi^{3+}	Does not interfere. Peaks at +0.17 V and +0.29 V
Ca^{2+}	Does not interfere, tested up to 10000:1.
Cd^{2+}	Does not interfere. Peak at –0.2 V
Co^{+2}	Does not interfere.
Cr^{3+}	Does not interfere.
Cr^{6+}	From a ratio of approx. 100:1 shoulder on the Hg peak. Peak at +0.49 V
Cu^{2+}	Does not interfere. Peak at +0.24 V
Fe^{3+}	Does not interfere. Peak at +0.44 V
Mg^{2+}	Does not interfere. From approx. 100 mg/L an increase in the background current becomes apparent in the range +0.4 V to +0.5 V.
Mn^{2+}	Does not interfere.
Ni^{2+}	Does not interfere.
Pb^{2+}	Does not interfere. Peak at –0.1 V
Sb^{3+}	Up to a ratio of approx. 100:1 the interfering peak at +0.56 V can be ignored. Peaks at +0.12 V (main signal), +0.4 V and +0.56 V.
Sb^{5+}	Does not interfere. Peak at +0.12 V
Se^{4+}	Does not interfere, but the Hg peak is slightly displaced to a more negative potential and the background current increases.
Se^{6+}	Does not interfere.
Sn^{2+}/Sn^{4+}	Does not interfere. Peak at –0.16 V
Zn^{2+}	Does not interfere.

Interfering non-metals

Element	*Remarks*
Halides, Pseudo-halides	Make oxidation easier and therefore destroy the gold electrode at positive potentials by the formation of gold halides. It may be necessary to adapt the voltammetric parameters. It is important that the positive potential range of the method is limited. This is done by displacing the parameters for «Cleaning potential» and «End potential» to more negative potentials. The size of this displacement depends on the type and concentration of the halide. If the Hg peak is greatly displaced then the «Deposition potential» must also be adapted. The rule is that the deposition potential must be at least 0.2 V more negative than the peak potential of mercury.
Cl^-	Displaces the Hg peak to more negative potentials. With $c(Cl^-)$ > 0.01 mol/L the voltammetric parameters must be adapted (see halides). In cases of doubt use the parameters given under «Determination of mercury in seawater».
I^-	Displaces the Hg peak to more negative potentials. At higher concentrations the voltammetric parameters must be adapted (see halides).
NO_2^-	Peak at +0.6 V. The peak generated by $c(NO_2^-)$ = 0.001 mol/L corresponds to a concentration of about $\beta(Hg^{2+})$ = 40 µg/L. At higher concentrations nitrous gases are formed.
NO_3^-	Does not interfere, tested up to 2 mol/L.
O_2	Does not interfere. Peak at –0.1 V.
PO_4^{3-}	Does not interfere up to a concentration of about 0.1 mol/L. At higher concentrations the increase in background current produced low-bias results.
SO_4^{2-}	Does not interfere, tested up to 2 mol/L.

Method 2:
Determination of mercury in seawater or other matrices containing chloride

Theory

The concentration of chloride in seawater is approx. 0.5 mol/L. This concentration is sufficient to oxidize and therefore destroy the gold electrode under the measuring conditions given in Method 1. This is why the voltammetric parameters must be adapted. The parameters given here can also be used for the determination of other samples with a similar chloride concentration.

Reagents + Determination

See «Method 1: Determination of mercury in samples with a low chloride concentration».

Voltammetric parameters

Working electrode	RDE
Stirrer speed (rpm)	2000
Mode	DP
Purge time	30 s
Pretreatment	
Hydrodynamic measurement	no
Cleaning potential	+0.7 V
Cleaning time	10 s
Deposition potential	0 V
Deposition time	60 s
Sweep	
Equilibration time	5 s
Start potential	+0.15 V
End potential	+0.6 V
Voltage step	0.002 V
Voltage step time	0.1 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
Stand-by potential	no
Substances	
Peak position (Hg)	+0.4 V

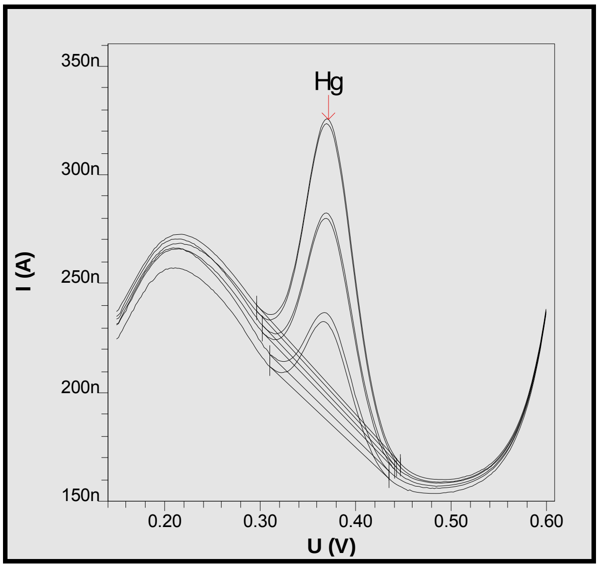
Potentiostat

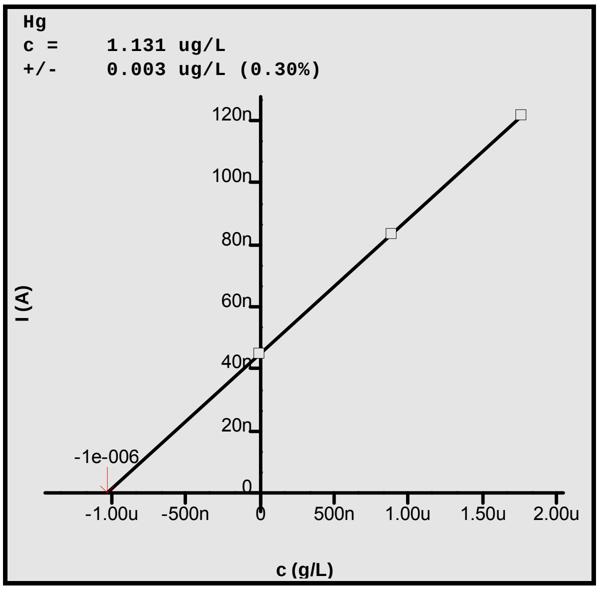
Highest current range	10 mA
Lowest current range	1 µA

The concentration in the sample is determined by standard addition.

Example

Determination of mercury in low-nutrient seawater (spiked sample)





```
Hg
c =     1.131 ug/L
+/-     0.003 ug/L (0.30%)
```

Sample volume	10 mL
Deposition time	60 s
Result	1.1 µg/L Hg

Remarks

- Under certain circumstances even higher chloride concentrations or the presence of other halides or pseudohalides may make a further adaptation of the parameters necessary (see also the remarks about under «interfering halides» under «Method 1: Determination of mercury in samples with a low chloride concentration»).

Literature

- Sipos L., Golimowski J., Valenta P., Nürnberg H.W.
  New voltammetric procedure for the simultaneous determination of copper and mercury in environmental samples
  Fresenius Z Anal Chem 298(1979) 1-8
- Kapel M., Komaitis M.E.
  Polarographic determination of trace elements in food from a single digest.
  Analyst 104(1979) 124-135
- Nürnberg H.W., Valenta P. Sipos L., Branica M.
  The reliable determination of mercury traces in sea water by subtractive differential pulse voltammetry at the twin gold electrode
  Anal Chim Acta 115(1980) 25-42
- Ahmed R., Valenta P. Nürnberg H.W.
  Voltammetric determination of mercury levels in tuna fish
  Mikrochim Acta (1981) 171-184
- Ireland-Ripert J., Bermond A., Ducauze C.
  Determination of methylmercury in the pressure of inorganic mercury by anodic stripping voltammetry
  Anal Chim Acta 143(1982) 249-254
- Golimowski J., Gustavsson I.
  Determination of mercury in fish using differential pulse anodic stripping voltammetry
  Fresenius Z Anal Chem 317(1984) 481
- Leu M., Seiler H.
  AC2 Inversvoltammetrische Bestimmung von Quecksilber in Harn
  Fresenius Z Anal Chem 321(1985) 479-482
- Seritti A., Morelli E., Orsini F., Nannicini L.
  Heavy metals in seawater in front of chlor-alkali plant
  Marine Pollution Bulletin 18/8(1987) 461-463

Annex

Report for example on «Determination of Hg in tap water»

```
======== METROHM 797 VA COMPUTRACE (Version 1.3.0.77) (Serial No. 5195) ========
 Determination  : 0808141410_Tap water spiked.dth
 Sample ID      : Tap water spiked
 Creator method : zu                Date : 2008-05-09          Time:  14:20:13
 Creator determ.: zu                Date : 2008-08-14          Time:  14:10:51
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : AB096_1_Det of Hg with Au RDE.mth
 Title          : Determination of Mercury with Gold RDE
 Remark1        : 10 mL  sample + 1 mL electrolyte
 Remark2        : Electrolyte: c(H2SO4) = 2 M, c(EDTA) = 0.02 M, c(NaCl) = 0.05 M
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  11.000 mL
--------------------------------------------------------------------------------
 Substance      : Hg
 Conc.          : 656.190 ng/L
 Conc.dev.      :  12.338 ng/L     ( 1.88%)
 Amount         :   7.218 ng
 Add.amount     :  10.000 ng


 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1   0.600    44.2    45.0     1.087       0.0
 1 - 2   0.604    45.8
 2 - 1   0.602   106.5   106.8     0.437      61.8
 2 - 2   0.600   107.1
 3 - 1   0.602   170.2   169.7     0.672      62.9
 3 - 2   0.600   169.2
```

```
 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Hg           std.add.       4.497e-008   6.853e-002   1.259e-009      0.99993


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

 Hg:
 Mercury           =    0.722  ug/L    0.014        1.880
```

Report for example on «Determination of Hg in low-nutrient seawater»

```
======== METROHM 797 VA COMPUTRACE (Version 1.3.1.84) (Serial No. 5195) ========
 Determination  : 0808130959_Low nutrient seawater spiked.dth
 Sample ID      : Low nutrient seawater spiked
 Creator method :                   Date : 2008-08-12          Time:  16:44:54
 Creator determ.: zu                Date : 2008-08-13          Time:  09:59:52
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : AB096_2 Det of Hg in sea water with Au RDE.mth
 Title          : Determination of Mercury in sea water with Gold RDE
 Remark1        : 10 mL  seawater + 1 mL electrolyte
 Remark2        : Electrolyte: c(H2SO4) = 2 M, c(EDTA) = 0.02 M, c(NaCl) = 0.05 M
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  11.000 mL
--------------------------------------------------------------------------------
 Substance      : Hg
 Conc.          :   1.028 ug/L
 Conc.dev.      :   0.003 ug/L     ( 0.30%)
 Amount         :  11.311 ng
 Add.amount     :  10.000 ng


 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1   0.370    44.7    44.7     0.027       0.0
 1 - 2   0.372    44.7
 2 - 1   0.372    83.3    83.3     0.041      38.6
 2 - 2   0.372    83.3
 3 - 1   0.372   121.4   121.6     0.259      38.3
 3 - 2   0.372   121.8



 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Hg           std.add.       4.469e-008   4.346e-002   1.625e-010      0.99999



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

 Hg:
 Mercury           =    1.131  ug/L    0.003        0.304
```

Method printout for «Conditioning the gold electrode» at the 797 VA Computrace

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB096_Conditioning of Au electrode for Hg determination.mth
Title           : Conditioning of Au electrode for Hg determination
Remark1         : 20 mL H2O + 0.2 mL HClO4 (70%)
Remark2         :

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Cond Au electrode
Sample amount (mL): 20.000
Cell volume (mL): 20.200

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                               : DP - Differential Pulse

Highest current range              : 10  mA
Lowest current range               : 1   uA

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

Initial electr. conditioning       : No

No. of additions                   : 0
No. of replications                : 10

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

Initial purge time (s)             :       30

Conditioning cycles
Start potential (V)                :   -1.200
End potential (V)                  :   -0.100
No. of cycles                      :        0

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :    0.000
Cleaning time (s)                  :   10.000
Deposition potential (V)           :    1.500
Deposition time (s)                :   30.000

Sweep
Equilibration time (s)             :    5.000
Start potential (V)                :    0.000
End potential (V)                  :    0.800
Voltage step (V)                   :    0.006
Voltage step time (s)              :    0.100
Sweep rate (V/s)                   :    0.060
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040

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 printout for «Cleaning the gold electrode in NaOH» at the 797 VA Computrace

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB096_Cleaning of Au electrode in NaOH.mth
Title           : Cleaning of Au electrode in NaOH
Remark1         : 20 mL NaOH
Remark2         : c(NaOH) = 0.1 mol/L

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Cleaning Au-RDE
Sample amount (mL): 20.000
Cell volume (mL): 20.000

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                               : DP - Differential Pulse

Highest current range              : 10  mA
Lowest current range               : 1   uA

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

Initial electr. conditioning       : No

No. of additions                   : 0
No. of replications                : 10

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

Initial purge time (s)             :       30

Conditioning cycles
Start potential (V)                :   -1.200
End potential (V)                  :   -0.100
No. of cycles                      :        0

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :   -1.500
Cleaning time (s)                  :   30.000
Deposition potential (V)           :    0.700
Deposition time (s)                :   30.000

Sweep
Equilibration time (s)             :    5.000
Start potential (V)                :    0.000
End potential (V)                  :    0.800
Voltage step (V)                   :    0.006
Voltage step time (s)              :    0.100
Sweep rate (V/s)                   :    0.060
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040

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 printout for «Determination of mercury in samples with a low chloride concentration » at the 797 VA Computrace

```
-------------------------------------------------------------------------------
 Method parameters
-------------------------------------------------------------------------------
Method          : AB096_1 Det of Hg with Au RDE.mth
Title           : Determination of Mercury with Gold RDE
Remark1         : 10 mL  sample + 1 mL electrolyte
Remark2         : Electrolyte: c(H2SO4) = 2 M, c(EDTA) = 0.02 M, c(NaCl) = 0.05 M

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : sample
Sample amount (mL): 10.000
Cell volume (mL): 11.000

Voltammetric parameters
-------------------------------------------------------------------------------
Mode                               : DP - Differential Pulse
Highest current range              : 10  mA
Lowest current range               : 1   uA
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)            : 20
Initial purge time (s)             :       30

Conditioning cycles
Start potential (V)                :    0.300
End potential (V)                  :    0.700
No. of cycles                      :        0

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :    0.900
Cleaning time (s)                  :   10.000
Deposition potential (V)           :    0.370
Deposition time (s)                :   90.000
Sweep
Equilibration time (s)             :   10.000
Start potential (V)                :    0.400
End potential (V)                  :    0.700
Voltage step (V)                   :    0.002
Voltage step time (s)              :    0.100
Sweep rate (V/s)                   :    0.020
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040
Cell off after measurement         :      Yes

Peak evaluation
-------------------------------------------------------------------------------
Regression technique               : Linear Regression
Peak evaluation                    : Height
Minimum peak width (V.steps)       : 10
Minimum peak height (A)            : 1.000e-010
Reverse peaks                      : No
Smooth factor                      : 1
Eliminate spikes                   : Yes

Substances
-------------------------------------------------------------------------------
Hg                       : 0.600 V   +/- 0.050 V

Standard solution        : 1   1.000 mg/L
Addition volume (mL)     : 0.010

Mercury                  : Final result (Hg) =
                           Conc * (11 / 10) * (1e+006 / 1) + 0 - 0

Baseline
-------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
-------------------------------------------------------------------------------
Hg        Sample      yes       ---       ---     linear      wholePeak
          Addition 1  yes       ---       ---     linear      wholePeak
          Addition 2  yes       ---       ---     linear      wholePeak
-------------------------------------------------------------------------------
```

Method printout for «Conditioning the gold electrode» at the 746 VA Trace Analyzer

```
================= METROHM 746 VA TRACE ANALYZER (5.746.0101) =================
 Method: AB96_CON.mth         OPERATION SEQUENCE
 Title : Conditioning of Au electrode for Hg determination
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters           Auxiliary parameters
      ------------- -----  -------------------------  ------------------------
 1    DOS>M                Soln.name   H2O            V.add        20.000 mL
 2    DOS>M                Soln.name   HClO4          V.add         0.200 mL
 3    STIR          30.0   Rot.speed      2000 /min
 4    (REP
 5      SEGMENT            Segm.name   COND_Au
 6      SEGMENT            Segm.name   COND_Au
 7    REP)8
 8    0MEAS                U.standby           mV
 9    END

 Method: AB96_CON              SEGMENT
                                COND_Au
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters           Auxiliary parameters
      ------------- -----  -------------------------  ------------------------
 1    RDE            3.0   Rot.speed      2000 /min
 2    DPMODE               U.ampl           50 mV     t.meas         20.0 ms
                           t.step         0.10 s      t.pulse        40.0 ms
 3    MEAS          10.0   U.meas            0 mV
 4    MEAS          30.0   U.meas         1500 mV
 5    0STIR          5.0
 6    SWEEP         13.6   U.start           0 mV     U.step            6 mV
                           U.end           800 mV     Sweep rate       60 mV/s
 7    0MEAS                U.standby           mV
 8    END


Method: AB96_CON                 DOCUMENTATION
--------------------------------------------------------------------------------

COPY  Reports, Curves                                  TO Destination
 ---------------------------------------------------    --------------------
 Curve Smth Sgmt:COND_Au VR:**                           Printer
```

Method printout for «Cleaning the gold electrode in NaOH» at the 746 VA Trace Analyzer

```
================= METROHM 746 VA TRACE ANALYZER (5.746.0101) =================
 Method: AB96_cle.mth         OPERATION SEQUENCE
 Title : Cleaning of Au electrode in NaOH
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters           Auxiliary parameters
      ------------- -----  -------------------------  ------------------------
 1    DOS>M                Soln.name   NaOH           V.add        20.000 mL
 2    STIR          30.0   Rot.speed      2000 /min
 3    (REP
 4      SEGMENT            Segm.name   Clean_Au
 5      SEGMENT            Segm.name   Clean_Au
 6    REP)8
 7    0MEAS                U.standby           mV
 8    END

 Method: AB96_cle              SEGMENT
                               Clean_Au
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters           Auxiliary parameters
      ------------- -----  -------------------------  ------------------------
 1    RDE            3.0   Rot.speed      2000 /min
 2    DPMODE               U.ampl           50 mV     t.meas         20.0 ms
                           t.step         0.10 s      t.pulse        40.0 ms
 3    MEAS          30.0   U.meas        -1500 mV
 4    MEAS          30.0   U.meas          700 mV
 5    0STIR          5.0
 6    SWEEP         13.6   U.start           0 mV     U.step            6 mV
                           U.end           800 mV     Sweep rate       60 mV/s
 7    0MEAS                U.standby           mV
 8    END


Method: AB96_cle                 DOCUMENTATION
--------------------------------------------------------------------------------

COPY  Reports, Curves                                  TO Destination
 ---------------------------------------------------    --------------------
 Curve Smth Sgmt:Clean_Au VR:**                          Printer
```

Method printout for «Determination of mercury in samples with a low chloride concentration » at the 746 VA Trace Analyzer

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB96_1  .mth         OPERATION SEQUENCE
 Title : Determination of Mercury with Gold RDE
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    SMPL>M               V.fraction          mL     V.total              L
 2    DOS>M                Soln.name   electrol       V.add         1.000 mL
 3    STIR          20.0   Rot.speed      2000 /min
 4    (ADD
 5      STIR        10.0   Rot.speed      2000 /min
 6      (REP
 7        SEGMENT          Segm.name   ASV_Hg
 8      REP)1
 9      ADD>M              Soln.name   Hg_std         V.add         0.010 mL
10    ADD)2
11    0MEAS                U.standby           mV
12    END

 Method: AB96_1                SEGMENT
                                 ASV_Hg
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    RDE            3.0   Rot.speed      2000 /min
 2    DPMODE               U.ampl           50 mV     t.meas         20.0 ms
                           t.step         0.10 s      t.pulse        40.0 ms
 3    MEAS          10.0   U.meas          900 mV
 4    MEAS          90.0   U.meas          370 mV
 5    0STIR         10.0
 6    SWEEP         15.3   U.start         400 mV     U.step            2 mV
                           U.end           700 mV     Sweep rate       20 mV/s
 7    0MEAS                U.standby           mV
 8    END


 Method: AB96_1                   DOCUMENTATION
--------------------------------------------------------------------------------

COPY  Reports, Curves                                 TO Destination
 --------------------------------------------------   --------------------
 Report Full                                           Printer
 Curve Smth Sbst:Mercury VR:**                         Printer
 Curve Cal Sbst:Mercury                                Printer


  Method: AB96_1                   SUBSTANCES
                               Mercury  - ASV_Hg
--------------------------------------------------------------------------------

      Recognition                               Display / Plot
      -------------------------                 ---------------------------
      U.verify           600 mV                 I.scale       auto
      U.tol (+/-)         50 mV                 U.div          50.00 mV/cm
      U.width min         10 mV                 U.begin              mV
      U.width max        200 mV                 U.end                mV
      I.threshold        200 pA

      Baseline                                  Evaluation
      -------------------------                 ---------------------------
      Type           linear                     Mode          VA
      Scope          whole                      Quantity      I.peak
      dU.front       auto                       Sign. digits     4
       S.front       auto
      dU.rear        auto
       S.rear        auto

  Calibration   2008-09-30 09:57:01             Coefficients
  ---------------------------------             -------------------------
  Technique     std.add.                        Y.reg         5.976e-08
  Curve type    linear                          Slope           0.08036
                                                Nonlin.
                                                Mean dev.      8.48e-10

                Additions
                ------------------------------------------------------------
  Soln.name       Hg_std
  ----------
  Mass conc.          1 mg/L             g/L             g/L             g/L
  Range min              g/L             g/L             g/L             g/L
  Range max              g/L             g/L             g/L             g/L
  M.conc./cm             g/L             g/L             g/L             g/L


 Method: AB96_1                CALCULATION
                              max. 15 lines
--------------------------------------------------------------------------------

 Quantity        Formula (R##, C##, A##)                    Res.unit   Sig.dig.
 ------------    ----------------------------------------   --------   --------
 Mercury         R1000=MC:Mercury                           #g/L          5
```