Metrohm

Application Bulletin 241/2 e

Determination of cadmium and lead by anodic stripping voltammetry at a mercury film electrode

Summary

This Application Bulletin describes the determination of cadmium and lead at a mercury film electrode (MFE) by anodic stripping voltammetry (ASV). The mercury film is plated ex situ on a glassy carbon electrode and can be used for up to one day. With a deposition time of 30 s, the limit of detection is $\beta(Cd^{2+})$ = 0.02 µg/L and $\beta(Pb^{2+})$ = 0.05 µg/L. The linear working range for both elements goes up to approx. 50 µg/L using the same deposition time.

Samples

Surface water, ground water, sea water, waste water

Instruments

797 VA Computrace	2.797.0020
Accessories	
Driving belt	6.1244.020
Measuring vessel 5 mL	6.1415.150
Stopper	6.2709.040
Polishing set for solid-state electrodes	6.2802.000

Electrodes

WE	Glassy carbon electrode tip	6.1204.600
	Driving axle for RDE	6.1204.210
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L)	6.0728.020
	Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.1245.010
AE	Glassy carbon rod	6.1247.000
	Electrode holder	6.1241.020

Reagents

- Cd standard stock solution, $\beta(Cd^{2+})$ = 1 g/L
- Pb standard stock solution, $\beta(Pb^{2+})$ = 1 g/L
- Hg standard stock solution, $\beta(Hg^{2+})$ = 1 g/L
- Nitric acid, $w(HNO_3)$ = 65%, for trace analysis*, CAS 7697-37-2
- Hydrochloric acid, w(HCl) = 30%, for trace analysis*, CAS 7647-01-0
- Acetic acid, $w(CH_3COOH)$ = 100%, for trace analysis*, CAS 64-19-7
- Sulfuric acid, $w(H_2SO_4)$ = 96%, for analysis, CAS 7664-93-9
- Ammonium hydroxide solution, $w(NH_3)$ = 25%, for trace analysis*, CAS 1336-21-6
- Potassium chloride, KCl, for trace analysis*, CAS 7447-40-7
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

In addition, if UV digestion is required:

- Hydrogen peroxide solution, $w(H_2O_2)$ = 30%, for trace analysis*, CAS 7722-84-1

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

Solutions

Hg plating solution	$\beta(Hg^{2+})$ = 20 mg/L c(HCl) = 0.1 mol/L 0.4 mL mercury standard stock solution and 0.2 mL hydrochloric acid are diluted to 20 mL with ultrapure water.
Electrolyte	$c(CH_3COOH)$ = 2 mol/L $c(NH_3)$ = 1 mol/L c(KCl) = 1.5 mol/L 55.9 g KCl are dissolved in approx. 400 mL water. 55.5 mL acetic acid and 37 mL ammonium hydroxide solution are added and filled up to 500 mL with ultrapure water.

Standard solutions

Cd standard solution 1 mg/L	$\beta(Cd^{2+})$ = 1 mg/L Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL $w(HNO_3)$ = 65% and 0.05 mL Cd standard stock solution are added. The solution is made up to the mark with ultrapure water.
Cd standard solution 0.1 mg/L	$\beta(Cd^{2+})$ = 0.1 mg/L Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL $w(HNO_3)$ = 65% and 5 mL Cd standard solution 1 mg/L are added. The solution is made up to the mark with ultrapure water.
Pb standard solution 1 mg/L	$\beta(Pb^{2+})$ = 1 mg/L Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL $w(HNO_3)$ = 65% and 0.05 mL Pb standard stock solution are added. The solution is made up to the mark with ultrapure water.
Pb standard solution 0.1 mg/L	$\beta(Pb^{2+})$ = 0.1 mg/L Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL $w(HNO_3)$ = 65% and 5 mL Pb standard solution 1 mg/L are added. The solution is made up to the mark with ultrapure water.

Sample preparation

- Ground water, drinking water, sea water, and mineral water can usually be analyzed directly.
- Water that contains interfering organic substances is digested using the 909 UV Digester:

  10 mL acidified water sample (pH = 2) with 10 µL $w(HNO_3)$ = 65% and 100 µL $w(H_2O_2)$ = 30% are irradiated for 90 min at 90 °C.

Comments

- No platinum auxiliary electrode should be used in combination with a glassy carbon working electrode.
- Measuring vessel and reference electrode have to be free of platinum traces. Therefore it is recommended to have accessories dedicated to this application.

Mercury film plating

Preparation of the glassy carbon electrode

The glassy carbon electrode has to be clean and free of any insulating material before the mercury film can be plated. For cleaning the following procedure is recommended.

- With a soft tissue deposit, e.g. an old mercury film, is wiped off the electrode surface.
- For polishing the glassy carbon electrode a small amount of aluminum oxide (5 … 10 mg) is mixed with a few drops of water (0.2 … 0.5 mL) on the polishing cloth (part of the polishing set 6.2802.000) to form a slurry. The electrode is then polished with small 8-shaped movements on the polishing cloth.
- The slurry is rinsed off the electrode with ultrapure water.
- The electrode is then rinsed with ethanol and afterwards thoroughly with ultrapure water.

This procedure should be carried out each time before plating the mercury film.

Plating the mercury film

20 mL Hg plating solution are transferred into the measuring vessel. The plating is carried out using the parameters given under «Parameters for mercury film plating».

Measuring solution

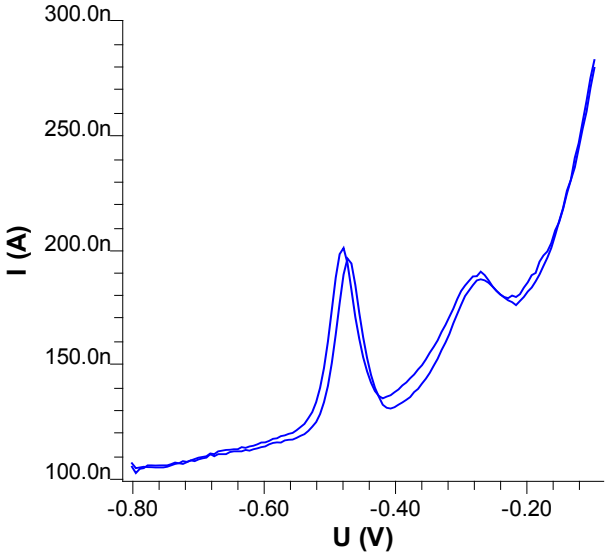
20 mL Hg plating solution

Parameters for mercury film plating

Determination	
No. of additions	0
No. of replications	2
Voltammetric	
Electrode	SSE/RDE
Measuring mode	DP
Stirring speed	2000 min^{-1}
Hydrodynamic measurement	No
Conditioning cycles	
Start potential	-1.2 V

End potential	-0.1 V
No. of cycles	50
Pretreatment	
Cleaning potential	-0.15 V
Cleaning time	2 s
Deposition potential	-1.3 V
Deposition time	180 s
Sweep	
Equilibration time	5 s
Start potential	-0.8 V
End potential	-0.1 V
Pulse amplitude	0.05 V
Pulse time	0.04 s
Potential step	0.006 V
Potential step time	0.1 s
Sweep rate	0.06 V/s

Example curves for mercury film plating



The peaks at -0.5 V and -0.3 V are related to lead and copper contamination of the Hg plating solution. These signals increase the more often the solution is used.

Comments

- The Hg plating solution can be reused several times (approx. 20 times). The solution itself is stable for at least one month. But with the number of plating processes the concentration of Hg in the solution decreases and the amount of contamination increases. Therefore the solution has to be replaced when no proper mercury film can be plated anymore.
- The waste Hg plating solution still contains hazardous amounts of mercury. Therefore, care has to be taken for an appropriate disposal, in accordance with the local legislation.

Assessment of the mercury film

To assess the quality of the mercury film it is recommended to run a blank determination. The measurement is carried out using the parameters given under «Parameters for mercury film assessment».

Measuring solution

10 mL ultrapure water

1 mL electrolyte

Standard addition

0.1 mL $\beta(Cd^{2+})$ = 0.1 mg/L

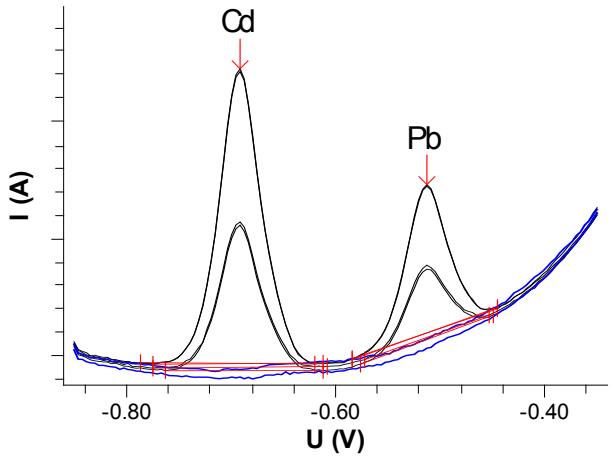
0.1 mL $\beta(Pb^{2+})$ = 0.1 mg/L

Parameters for mercury film assessment

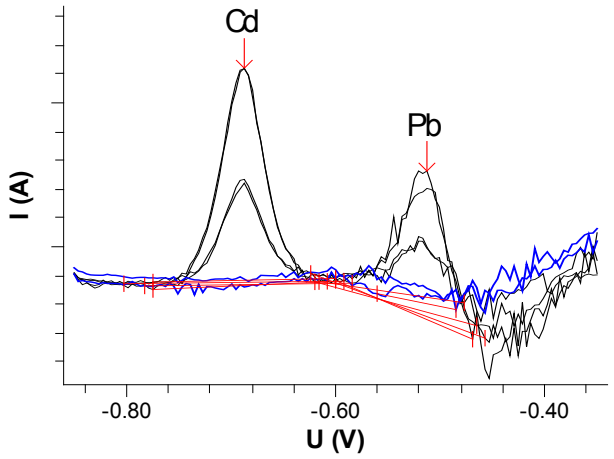
Determination	
No. of additions	2
No. of replications	2
Voltammetric	
Electrode	SSE/RDE
Measuring mode	DP
Stirring speed	2000 min^{-1}
Hydrodynamic measurement	No
Conditioning cycles	
Start potential	-0.8 V
End potential	-0.4 V
No. of cycles	25
Pretreatment	
Cleaning potential	-0.4 V
Cleaning time	2 s
Deposition potential	-1.0 V
Deposition time	90 s
Sweep	
Equilibration time	5 s
Start potential	-0.85 V

End potential	-0.35 V
Pulse amplitude	0.05 V
Pulse time	0.04 s
Potential step	0.004 V
Potential step time	0.1 s
Sweep rate	0.04 V/s
Substance + calibration	
Calibration	Standard addition
Name	Cd
Peak potential	-0.7 V
Name	Pb
Peak potential	-0.5 V

Example for a blank determination with a good mercury film



Example for a blank determination with a bad mercury film



Assessment criteria

- The curve of the background current should be smooth.
- With a proper mercury film the background current should be smaller than 200 nA.
- When the measuring solution contains equal mass concentrations of Cd and Pb, the Cd peak should have approximately double the height of the Pb peak.

If the background current is not smooth or too high it is recommended to remove the mercury film, carry out the cleaning and polishing procedure as described under «Preparation of the glassy carbon electrode» and plate a fresh mercury film.

If the ratio of Cd and Pb peak is not ok the reason is usually that the mercury film is too thin. Repeat the plating as described under «Plating the mercury film». If that does not improve the situation, remove the mercury film, carry out the cleaning and polishing procedure as described under «Preparation of the glassy carbon electrode» and plate a fresh mercury film.

Determination of Cd and Pb

10 mL (diluted) sample and 1 mL electrolyte are pipetted into the measuring vessel. The determination is carried out using the parameters given under «Parameters for determination of cadmium and lead».

The concentration of cadmium and lead is quantified by two additions of Cd and Pb standard solutions.

Measuring solution

10 mL (diluted) sample

1 mL electrolyte

Parameters for determination of cadmium and lead

Determination	
No. of additions	2
No. of replications	2
Voltammetric	
Electrode	SSE/RDE
Measuring mode	DP
Stirring speed	2000 min^{-1}
Hydrodynamic measurement	No
Conditioning cycles	
Start potential	-0.8 V

End potential	-0.4 V
No. of cycles	25
Pretreatment	
Cleaning potential	-0.4 V
Cleaning time	2 s
Deposition potential	-1.0 V
Deposition time	90 s
Sweep	
Equilibration time	5 s
Start potential	-0.85 V
End potential	-0.35 V
Pulse amplitude	0.05 V
Pulse time	0.04 s
Potential step	0.004 V
Potential step time	0.1 s
Sweep rate	0.04 V/s
Substance + calibration	
Calibration	Standard addition
Name	Cd
Peak potential	-0.7 V
Name	Pb
Peak potential	-0.5 V

Results

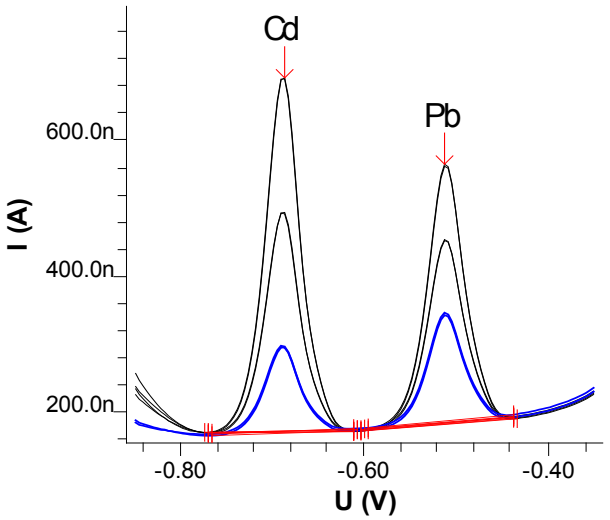
Average of 3 determinations with relative standard deviation.

Sample	β(Cd)	β(Pb)
Tap water	n/a	0.35 ± 9.1%
Ground water reference material BCR-609	0.19 µg/L ± 3.4%	1.36 µg/L ± 4.3%
Ground water reference material BCR-610	3.14 µg/L ± 1.3%	7.02 µg/L ± 1.3%
Sea water spiked with 1 µg/L Cd and Pb each	1.10 µg/L ± 3.4%	1.09 µg/L ± 1.0%

The following table shows the certified concentrations for the ground water reference materials and the measured result relative to the certified value.

Sample	Certified value	Result / certified value
BCR-609	β(Cd) = 0.164 µg/kg β(Pb) = 1.63 µg/kg	115.8% 83.4%
BCR-610	β(Cd) = 2.94 µg/kg β(Pb) = 7.78 µg/kg	106.8% 90.2%

Example for Cd and Pb determination in ground water reference material BCR-610




```
Cd
c =     3.182 ug/L
+/-     0.023 ug/L (0.72%)
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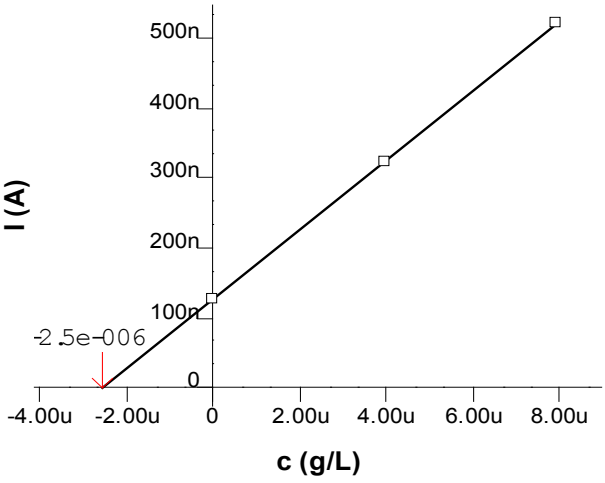

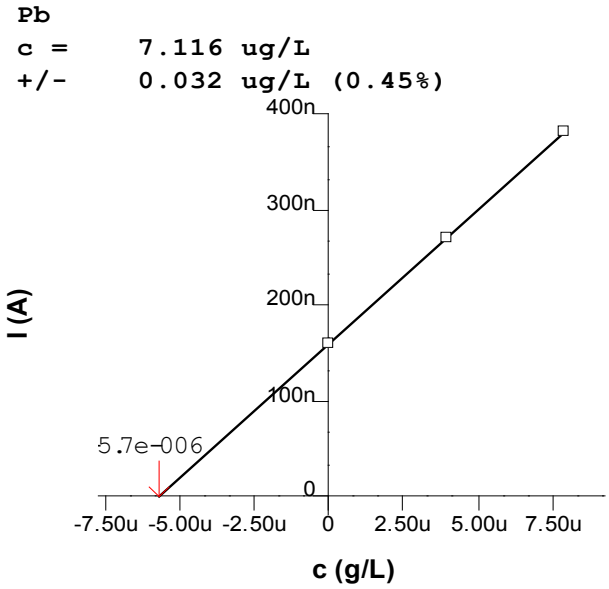

Limit of detection and linear working range

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.

The following table gives an overview over limit of detection depending on the deposition time.

Deposition time	*Limit of detection Cd*	*Limit of detection Pb*
30 s	0.02 µg/L	0.05 µg/L
90 s	0.007 µg/L	0.025 µg/L

The linear working range was read out from a calibration curve. With a deposition time of 30 s the linear working range for both elements goes up to approx. 50 µg/L. For concentrations above 50 µg/L the calibration curve gets slightly convex, why recoveries of < 90% have to be expected.

The limit of detection and linear working range were determined in standard solutions. Depending on the condition of the electrode or the sample matrix, these values can differ.

Interferences

Tl	Broad peak at approx. -0.6 V, mainly overlapping with the cadmium peak. Shows about 25% of the sensitivity of cadmium and 50% of the lead.
Sn(VI)	Peak at approx. -0.6 V. Shows about 5% of the sensitivity of cadmium and 10% of lead.
Pt, Rh	Platinum and other platinum metals reduce the overpotential for the hydrogen reduction at the mercury film. Therefore even concentrations in the µg/L range show an interfering background current caused by hydrogen formation.

Comments

- Deposition time and standard addition (volume and/or concentration of the standard solution) have to be adapted to the concentration of analyte in the measuring vessel. In this context it is important to consider the linear working range.
- The mercury film can be used for half a day up to one day. But effects from the sample matrix can reduce the lifetime of the mercury film. Indications for a fading mercury film are:
  - bad reproducibility of the replications
  - decreasing sensitivity of the additions (slope) by more than one third
  - increasing or noisy background current

  The mentioned indications can also be caused by matrix interferences. Therefore, in case of a suspicious mercury film, it is recommended to run a blank determination as described under «Assessment of the mercury film» and to decide based on these curves whether the film needs to be renewed.
- If the mercury film is not used it is recommended to keep either diluted electrolyte or diluted nitric acid ($c(HNO_3) \sim 0.05$ mol/L) in the measuring vessel. Storing the mercury film with ultrapure water is not recommended since it passivates the film.
- From time to time, electrodes and measuring vessel should be cleaned with sulfuric acid. For that, fill 1–2 mL concentrated sulfuric acid into the slightly wet measuring vessel. Attention, the solution gets hot! Carefully turn the measuring vessel to wet the entire surface with H_2SO_4. Then add 30–40 mL ultrapure water. Be very careful of splashing of the hot solution. Place the measuring vessel under the measuring head and turn on the stirring until the solution cooled down to room temperature. Empty the measuring vessel and rinse everything thoroughly with ultrapure water.
- Traces of metals can be removed with diluted nitric acid ($c(HNO_3) \sim 0.1$ mol/L). For cleaning, place 20–30 mL diluted nitric acid in the measuring vessel and switch on the stirrer for 10–30 min. Empty the measuring vessel and rinse everything thoroughly with ultrapure water.

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] A. M. Bond, Modern Polarographic Methods in Analytical Chemistry, Marcel Dekker, 1980.

[3] K. Brainina and E. Neyman, Electroanalytical Stripping Methods, John Wiley & Sons, 1993.

[4] H. Nürnberg, Electroanalytical Chemistry, John Wiley & Sons, 1974.

[5] M. Smyth and J. Vos, Analytical Voltammetry, Elsevier Science Publishers, 1992.

Appendix

Method print «Parameters for mercury film plating»

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--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB 241_Plating of mercury film.mth
Title           : Plating Hg film on GC electrode 6.1204.600
Remark1         : 20 mL Hg plating solution
Remark2         : Plating solution: c(Hg) = 20 mg/L, c(HCl) = 0.1 mol/L

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Hg film plating
Sample amount (mL): 20.000
Cell volume (mL): 20.000

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

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

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

Initial electr. conditioning      : No

No. of additions                  : 0
No. of replications               : 2

Measure blank                     : No
Addition purge time (s)           : 20

Initial purge time (s)            :       60

Conditioning cycles
Start potential (V)               :   -1.200
End potential (V)                 :   -0.100
No. of cycles                     :       50

Hydrodynamic (measurement)        :      No
Cleaning potential (V)            :   -0.150
Cleaning time (s)                 :    2.000
Deposition potential (V)          :   -1.300
Deposition time (s)               :  180.000

Sweep
Equilibration time (s)            :    5.000
Start potential (V)               :   -0.800
End potential (V)                 :   -0.100
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)      : 10
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 «Parameters for determination of cadmium and lead»

These parameters are identical to «Parameters for mercury film assessment»

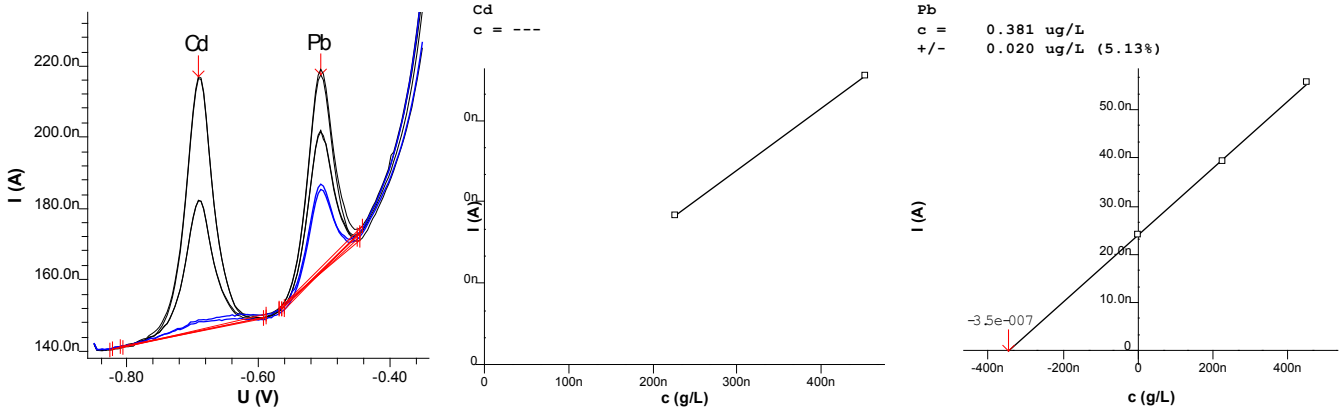
```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB 241_Determination of Cd Pb at MFE.mth
Title           : Determination of Cd Pb at mercury film electrode (MFE)
Remark1         : 10 mL sample + 1 mL electrolyte
Remark2         : Electrolyte: c(HAC) = 2 mol/L, c(NH3) = 1 mol/L, c(KCl) =  1.5 mol/L

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              : 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)           : 20

Initial purge time (s)            :      300

Conditioning cycles
Start potential (V)               :   -0.800
End potential (V)                 :   -0.400
No. of cycles                     :       25

Hydrodynamic (measurement)        :      No
Cleaning potential (V)            :   -0.400
Cleaning time (s)                 :    2.000
Deposition potential (V)          :   -1.000
Deposition time (s)               :   90.000

Sweep
Equilibration time (s)            :    5.000
Start potential (V)               :   -0.850
End potential (V)                 :   -0.350
Voltage step (V)                  :    0.004
Voltage step time (s)             :    0.100
Sweep rate (V/s)                  :    0.040
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                     : 2
Eliminate spikes                  : Yes

Substances
--------------------------------------------------------------------------------
Cd                      : -0.700 V   +/- 0.050 V

Standard solution       : 1   0.100 mg/L
Addition volume (mL)    : 0.100

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

Pb                      : -0.500 V   +/- 0.050 V
```

```
Standard solution        : 1   0.100 mg/L
Addition volume (mL)     : 0.100

Lead                     : Final result (Pb) =
                           Conc * (11 / 10) * (1e+006 / 1) + 0 - 0
```

Baseline

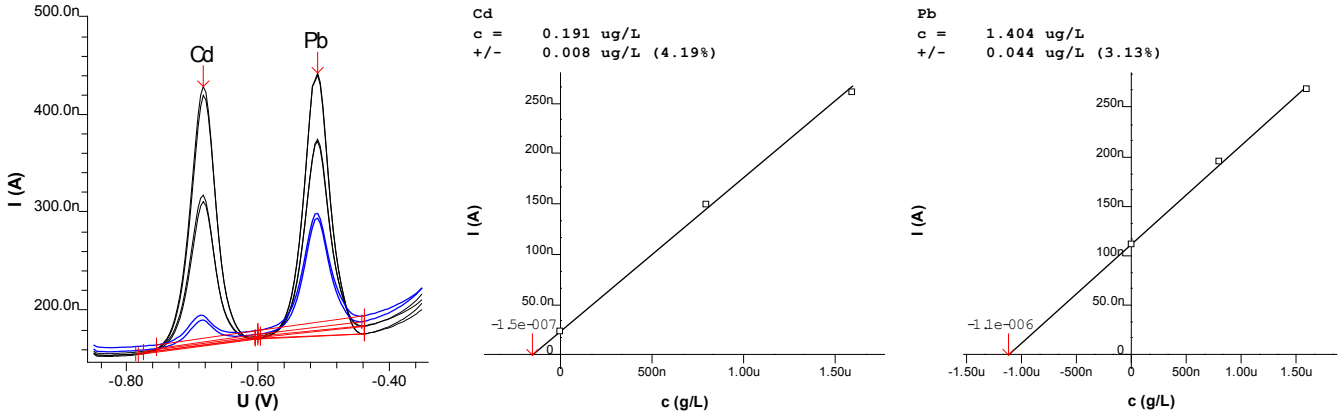
Substance	Addition	automatic	start (V)	end (V)	type	scope
Cd	Sample	yes	---	---	linear	wholePeak
	Addition 1	yes	---	---	linear	wholePeak
	Addition 2	yes	---	---	linear	wholePeak
Pb	Sample	yes	---	---	linear	wholePeak
	Addition 1	yes	---	---	linear	wholePeak
	Addition 2	yes	---	---	linear	wholePeak

Example for the determination of cadmium and lead in tap water



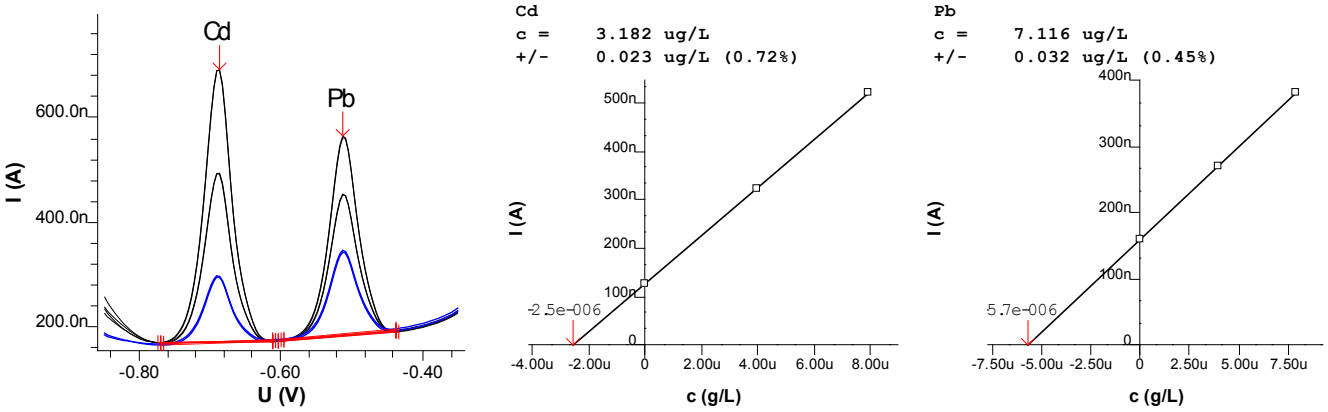

```
======= METROHM 797 VA COMPUTRACE (Version 1.3.2.85) (Serial No. 18154) ========
 Determination  : 1410170922_Tap water.dth
 Sample ID      : Tap water
 Creator method : zu               Date : 2014-07-10          Time:  11:30:05
 Creator determ.: zu               Date : 2014-10-17          Time:  09:22:23
 Modified by    : ---              Date :                     Time:
--------------------------------------------------------------------------------
 Method         : Determination Cd Pb on MFE auto.mth
 Title          : Determination of Cd Pb on mercury film electrode
 Remark1        : 5mL sample
 Remark2        : + 0.5 mL acetate buffer / KCl
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  11.000 mL
--------------------------------------------------------------------------------
 Substance      : Cd
 Conc.          : ---
 Conc.dev.      : ---
 Add.amount     :   2.500 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1    ---     ---     ---       ---             No peak found
 1 - 2    ---     ---                               No peak found
 2 - 1  -0.691   36.41   36.63     0.314
 2 - 2  -0.691   36.86
 3 - 1  -0.691   71.46   70.99     0.654     34.36
 3 - 2  -0.691   70.53

 Substance      : Pb
 Conc.          : 346.173 ng/L
 Conc.dev.      :  17.744 ng/L     ( 5.13%)
 Amount         :   3.808 ng
 Add.amount     :   2.500 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.505   24.90   24.07     1.174      0.00
 1 - 2  -0.505   23.24
 2 - 1  -0.505   39.15   39.28     0.185     15.20
 2 - 2  -0.505   39.41
 3 - 1  -0.505   55.63   55.65     0.031     16.37
 3 - 2  -0.505   55.67


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Cd           std.add.       2.119e-009   1.522e-001   5.793e-010      0.99978
 Pb           std.add.       2.400e-008   6.932e-002   1.230e-009      0.99905


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

 Cd:
 Cadmium          =      ---  ug/L                          No result found

 Pb:
 Lead             =    0.381  ug/L    0.020        5.126
```

Example for the determination of cadmium and lead in groundwater reference material BCR-609



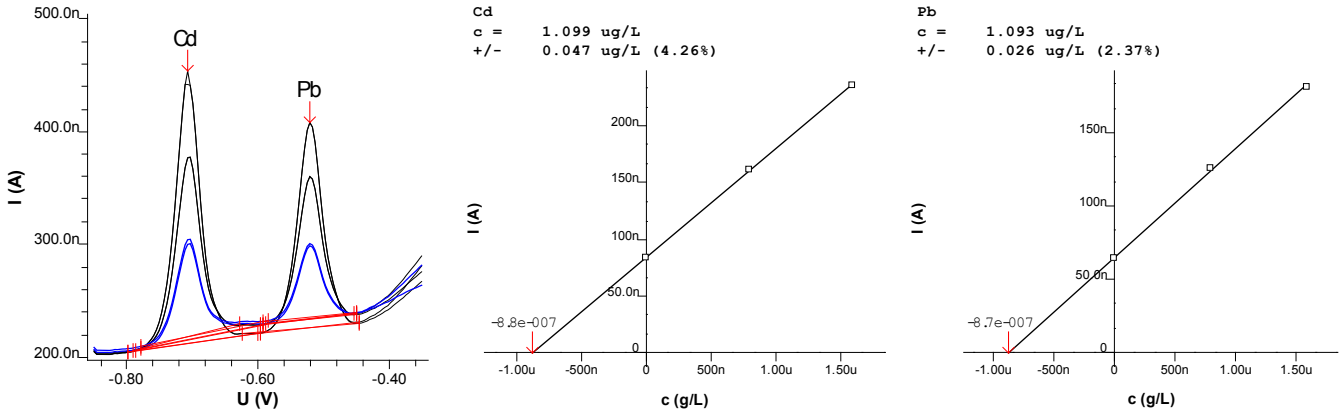

```
======== METROHM 797 VA COMPUTRACE (Version 1.3.2.85) (Serial No. 2173) ========
 Determination  : 1405200849_BCR-609_direkt.dth
 Sample ID      : BCR-609_direkt
 Creator method : ka                Date : 2014-04-07          Time:  12:59:42
 Creator determ.: ka                Date : 2014-05-20          Time:  08:49:24
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : GC_Hg-ex situ.mth
 Title          : GC 61204600   Electrode
 Remark1        : BCR-609_Direkt
 Remark2        :  10 mL_BCR-609_direkt
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.500 mL
--------------------------------------------------------------------------------
 Substance      : Cd
 Conc.          : 153.061 ng/L
 Conc.dev.      :   6.417 ng/L     ( 4.19%)
 Amount         :   1.913 ng
 Add.amount     :  10.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.687    24.0    23.3     1.025       0.0
 1 - 2  -0.683    22.6
 2 - 1  -0.683   151.7   149.2     3.540     125.9
 2 - 2  -0.683   146.7
 3 - 1  -0.683   264.6   260.6     5.703     111.4
 3 - 2  -0.683   256.5

 Substance      : Pb
 Conc.          :   1.123 ug/L
 Conc.dev.      :   0.035 ug/L     ( 3.13%)
 Amount         :  14.037 ng
 Add.amount     :  10.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.509   111.4   111.4     0.071       0.0
 1 - 2  -0.509   111.5
 2 - 1  -0.509   193.3   194.9     2.256      83.5
 2 - 2  -0.509   196.5
 3 - 1  -0.509   266.4   267.9     2.053      73.0
 3 - 2  -0.509   269.3


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Cd           std.add.       2.333e-008   1.524e-001   2.096e-009      0.99899
 Pb           std.add.       1.120e-007   9.970e-002   3.719e-009      0.99907


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

 Cd:
 Cadmium           =    0.191  ug/L    0.008        4.192

 Pb:
 Lead              =    1.404  ug/L    0.044        3.131
```

Example for the determination of cadmium and lead in groundwater reference material BCR-610




```
======== METROHM 797 VA COMPUTRACE (Version 1.3.2.85) (Serial No. 2173) ========
 Determination  : 1405221026_BCR-610_direkt.dth
 Sample ID      : BCR-610_direkt
 Creator method : ka                Date : 2014-04-07          Time:  12:59:42
 Creator determ.: zu                Date : 2014-10-10          Time:  12:52:10
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : GC_Hg-ex situ.mth
 Title          : GC 61204600   Electrode
 Remark1        : BCR-610_direkt
 Remark2        :  10 mL_BCR-610_direkt
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.500 mL
--------------------------------------------------------------------------------
 Substance      : Cd
 Conc.          :   2.546 ug/L
 Conc.dev.      :   0.018 ug/L     ( 0.72%)
 Amount         :  31.820 ng
 Add.amount     :  50.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.691   126.4   126.6     0.250       0.0
 1 - 2  -0.691   126.7
 2 - 1  -0.691   321.4   322.9     2.127     196.3
 2 - 2  -0.687   324.4
 3 - 1  -0.687   519.7   521.2     2.180     198.4
 3 - 2  -0.687   522.8

 Substance      : Pb
 Conc.          :   5.693 ug/L
 Conc.dev.      :   0.026 ug/L     ( 0.45%)
 Amount         :  71.161 ng
 Add.amount     :  50.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.513   159.7   159.7     0.126       0.0
 1 - 2  -0.513   159.6
 2 - 1  -0.513   269.5   270.1     0.836     110.5
 2 - 2  -0.513   270.7
 3 - 1  -0.513   381.6   381.3     0.439     111.2
 3 - 2  -0.513   381.0


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Cd           std.add.       1.265e-007   4.969e-002   1.427e-009      0.99996
 Pb           std.add.       1.596e-007   2.803e-002   7.512e-010      0.99998


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

 Cd:
 Zinc             =    3.182  ug/L    0.023        0.719

 Pb:
 Cadmium          =    7.116  ug/L    0.032        0.450
```

Example for the determination of cadmium and lead in spiked sea water




```
======== METROHM 797 VA COMPUTRACE (Version 1.3.2.85) (Serial No. 2173) ========
 Determination  : 1405271451_Meerwasser_dot 1ppb_direkt.dth
 Sample ID      : Meerwasser_dot 1ppb_direkt
 Creator method : ka                Date : 2014-04-07          Time:  12:59:42
 Creator determ.: ka                Date : 2014-05-27          Time:  14:51:48
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : GC_Hg-ex situ.mth
 Title          : GC 61204600   Electrode
 Remark1        : Meerwasser_pH 2 _dot 1ppb_direkt
 Remark2        : 10 mL _Meerwasser__dot 1ppb Ac_KCl_DIREKT
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.510 mL
--------------------------------------------------------------------------------
 Substance      : Cd
 Conc.          : 878.253 ng/L
 Conc.dev.      :  37.375 ng/L     ( 4.26%)
 Amount         :  10.987 ng
 Add.amount     :  10.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.707    85.8    83.7     2.952       0.0
 1 - 2  -0.703    81.6
 2 - 1  -0.703   160.9   161.0     0.070      77.3
 2 - 2  -0.703   161.0
 3 - 1  -0.707   240.7   235.0     7.948      74.1
 3 - 2  -0.711   229.4

 Substance      : Pb
 Conc.          : 873.709 ng/L
 Conc.dev.      :  20.666 ng/L     ( 2.37%)
 Amount         :  10.930 ng
 Add.amount     :  10.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.520    65.0    64.6     0.516       0.0
 1 - 2  -0.520    64.2
 2 - 1  -0.520   126.2   126.0     0.370      61.4
 2 - 2  -0.520   125.7
 3 - 1  -0.520   181.3   181.3     0.001      55.3
 3 - 2  -0.520   181.3


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Cd           std.add.       8.384e-008   9.546e-002   4.339e-009      0.99837
 Pb           std.add.       6.485e-008   7.422e-002   1.876e-009      0.99955


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

 Cd:
 Cadmium           =    1.099  ug/L    0.047        4.256

 Pb:
 Lead              =    1.093  ug/L    0.026        2.365
```