Application Bulletin 220/4 e

Determination of platinum and rhodium in the ultratrace range by adsorptive stripping voltammetry

Summary

This Application Bulletin describes an analytical method for the determination of traces of Pt and Rh in the ng/L range by adsorptive stripping voltammetry. Interest in the determination of even minute quantities of platinum and rhodium in environmental materials has greatly increased in recent years. Their emission into the environment from automobile exhaust gas catalytic converters is of great interest. The same applies to the determination of platinum in body fluids and tissue samples following chemotherapeutic treatment for cancer.

Using the hanging mercury drop electrode (HMDE) and the DP (Differential Pulse) measuring mode, determination limits of approx. 0.1 ng/L Pt and 0.5 ng/L Rh can be achieved.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode	
909 UV Digester	2.909.0014

Electrodes

WE	Multi-Mode Electrode pro Mercury drop capillary	6.1246.120 6.1226.050
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Glassy Carbon rod Electrode holder	6.1247.000 6.1241.x20

Sample preparation

The determinations described are extremely sensitive to interference by organic substances, which is why all samples (even drinking water) must undergo digestion.

Water, aqueous solutions

In this case UV digestion (irradiation with UV light) has proved to be best.

10 mL sample is acidified with 10 µL w(HCl) = 30% (for trace analysis*) (approx. pH = 2), 50 µL w(H_2O_2) = 30% (for trace analysis*) is added and the solution irradiated in the 909 UV Digester for 90 min. After cooling down the digestion solution can be used directly for the voltammetric determination

Biological materials

There are two suitable digestion methods for materials with a high organic content:

- High-pressure ashing («High-Pressure Asher», HPA)
- Microwave digestion

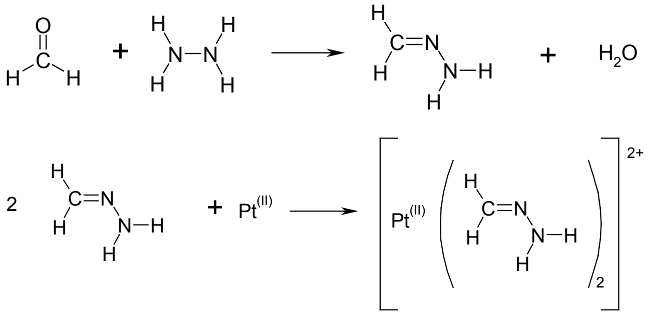
In both cases the sample is oxidized in sealed digestion vessels by a mixture of concentrated acids. The vessels are either heated conventionally (HPA) or by microwave irradiation.

* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

Method 1: Determination of platinum

Summary

Formaldehyde and hydrazine can be condensed to form the corresponding hydrazone, which forms a complex with Pt(II):



This complex is adsorbed on the surface of the HMDE, where it reduces the hydrogen overpotential. The measured signal of the hydrogen reduction is proportional to the concentration of the Pt complex. Owing to the catalytic effect of platinum the determination is extremely sensitive.

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Sulfuric acid, w(H_2SO_4) = 96%, for trace analysis*, CAS 7664-93-9
- Formaldehyde solution, w(HCHO) = 37%, CAS 50-00-0
- Hydrazine sulfate $N_2H_6SO_4$, for trace analysis*, CAS 10034-93-2
- Pt(IV) stock solution, β(Pt(IV)) = 1 g/L, commercially available
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

Solutions

Hydrazine sulfate solution	c($N_2H_6SO_4$) = 0.1 mol/L 0.13 g hydrazine sulfate is dissolved in 10 mL ultrapure water. This solution is stable for max. 1 week.
Electrolyte	c(H_2SO_4) = 0.72 mol/L c(HCHO) = $6.7 \cdot 10^{-3}$ mol/L c($N_2H_6SO_4$) = $3 \cdot 10^{-3}$ mol/L Approx. 15 mL ultrapure water and 0.8 mL w(H_2SO_4) = 96% are mixed in a 20 mL volumetric flask. After cooling down to room temperature, 0.6 mL c($N_2H_6SO_4$) = 0.1 mol/L and 10 µL w(HCHO) = 37% are added and the solution is filled to the mark with ultrapure water. This supporting electrolyte must be freshly prepared every day.

Standard solutions

Pt(IV) standard solution	β(Pt(IV)) = 1 µg/L This solution is prepared from the Pt(IV) stock solution by dilution with c(HCl) = 0.1 mol/L. Dilutions with concentrations below 1 mg/L should be freshly prepared every day.

Analysis

Measuring solution

10 mL (diluted) digested sample

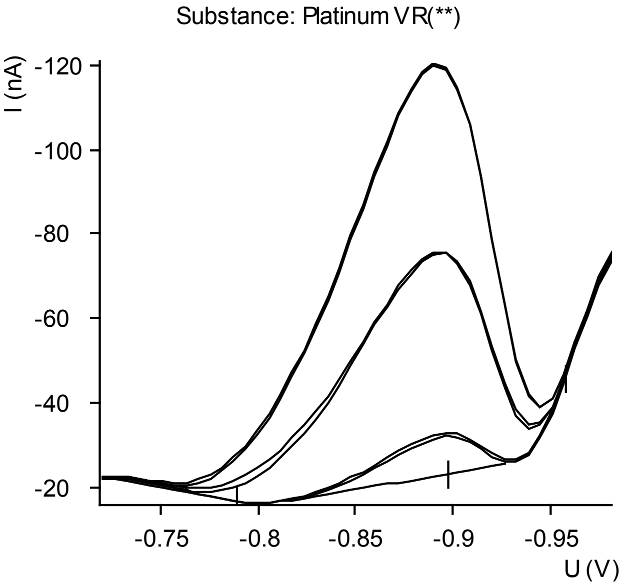
1.5 mL supporting electrolyte

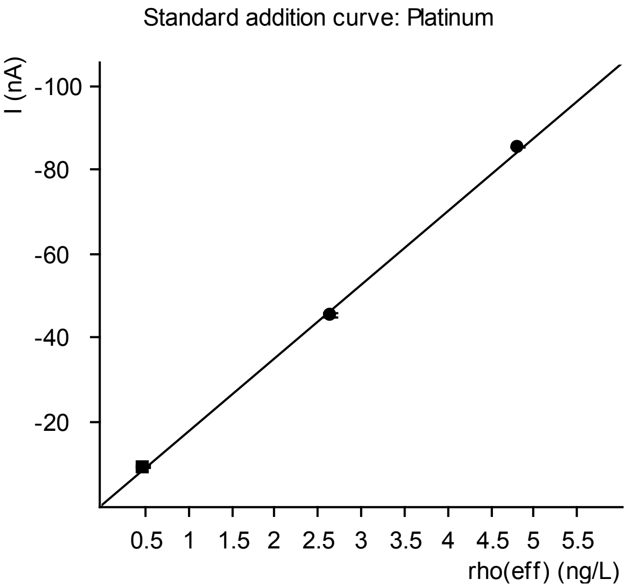
The concentration is determined by standard addition.

Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.6 V
Waiting time 1	120 s
Equilibration time	10 s
Sweep	
Start potential	-0.6 V
End potential	-1.1 V
Potential step	0.006 V
Potential step time	0.3 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V
Substance	
Name	Pt
Characteristic potential	-0.88 V

Example





Results

Sample	Tap water
Sample size	10.0 mL
β(Pt)	0.6 ng/L

Comments

- Under no circumstances the determination should be carried out with a Pt auxiliary electrode.
- A reference electrode that has already been used together with a Pt electrode should not be used.
- It is very advantageous if all vessels and electrodes are only used for this determination.
- If during the preparation of the supporting electrolyte the solution is not allowed to cool down to room temperature before the addition of the hydrazine sulfate and formaldehyde then an interfering peak will appear in the voltammogram at the peak potential of platinum.
- Pt(IV) is reduced to Pt(II) by the supporting electrolyte.
- With a deposition time of 120 s the limit of detection for Pt is approx. 0.1 ng/L.
- The sensitivity of the method could not be increased by using other measuring modes (square wave (SQW) and alternating current (AC)).
- With a deposition time of 60 s the working range is linear up to 200 ng/L Pt.
- With higher concentrations of nitrate the Pt peak is lost in the increase of the baseline. For example, 0.16 mol/L NO_3^- reduces the recovery of 5 ng/L Pt by 50%.

References

- Z. Zhao, H. Freiser
  Differential pulse polarographic determination of trace levels of platinum
  Anal. Chem. 58 (1986) 1498–1501.
- K. Hoppstock, F. Alt, K. Cammann, G. Weber
  Determination of platinum in biotic and environmental materials. Part II: A sensitive voltammetric method
  Fresenius Z. Anal. Chem. 335 (1989) 813–816.
- C. M. G. van den Berg, G. S. Jacinto
  The determination of platinum in sea water by adsorptive cathodic stripping voltammetry
  Anal. Chim. Acta. 211 (1988) 129–139.

Method 2: Determination of rhodium

Summary

In a hydrochloric acid solution rhodium forms a complex with formaldehyde that can be adsorbed on the HMDE. The adsorbed complex reduces the hydrogen overpotential at the mercury electrode and thus catalyzes the reduction of hydrogen. The signal of the hydrogen reduction is used for the determination; its size is proportional to the concentration of the Rh complex. The catalytic effect of the rhodium explains the extreme sensitivity of the method.

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Hydrochloric acid, w(HCl) = 30%, for trace analysis*, CAS 7647-01-0
- Formaldehyde solution, w(HCHO) = 37%, CAS 50-00-0
- Rh(III) stock solution, β(Rh(III)) = 1 g/L, commercially available
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

Standard solutions

Rh(III) standard-solution	β(Rh(III) = 1 µg/L This solution is prepared from the Rh(III) stock solution by dilution with c(HCl) = 0.1 mol/L. Dilutions with concentrations below 1 mg/L should be freshly prepared every day.

Analysis

Measuring solution

10 mL (diluted) digested sample

200 µL w(HCl) = 30%

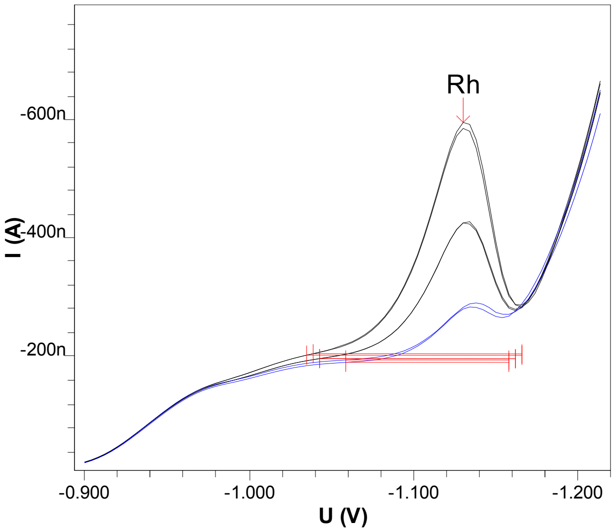
10 µL w(HCHO) = 37%

The concentration is determined by standard addition.

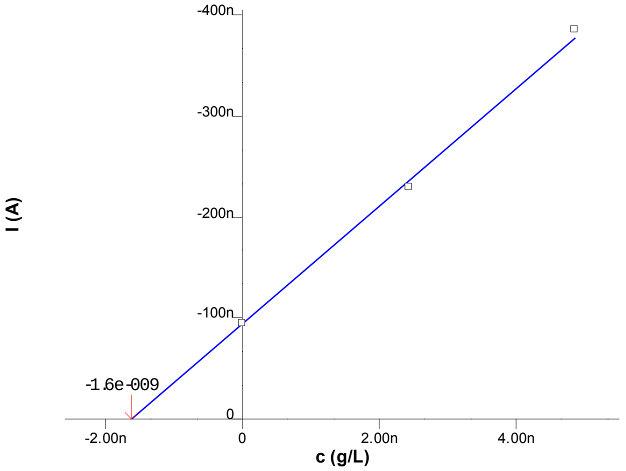
Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.7 V
Waiting time 1	60 s
Equilibration time	10 s
Sweep	
Start potential	-0.9 V
End potential	-1.23 V
Potential step	0.004 V
Potential step time	0.3 s
Sweep rate	0.013 V/s
Pulse amplitude	0.05 V
Substance	
Name	Rh
Characteristic potential	-1.15 V

Example



```
Rh
c =      1.655 ng/l
+/-      0.071 ng/l (4.31%)
```



Results

Sample	Tap water
Sample size	10.0 mL
β(Rh)	1.7 ng/L

Comments

- As the Rh peak lies in the hydrogen increase region it is recommended that only the front half of the peak is evaluated.

- With a deposition time of 120 s the determination limit for Rh is approx. 0.5 ng/L.
- With a deposition time of 60 s the working range is linear up to 500 ng/L Rh.
- The presence of nitrate does not interfere with the determination but displaces the potential of the Rh peak towards more negative values.

References

- E. Helmers, N. Mergel
  Platinum and rhodium in a polluted environment: Studying the emissions of automobile catalysts with emphasis on the application of CSV rhodium analysis
  Fresenius J. Anal. Chem. 362 (1998) 522–528
- C. León, H. Emons, P. Ostapczuk, K. Hoppstock
  Simultaneous ultratrace determination of platinum and rhodium by cathodic stripping voltammetry
  Anal. Chim. Acta. 336 (1997) 99–104

Method 3: Simultaneous determination of rhodium and platinum

Summary

Rhodium and platinum can also be determined if they are both present in the same solution. As hydrazine interferes with the Rh determination, rhodium is first determined in hydrochloric acid solution without hydrazine sulfate. Afterwards the hydrazine sulfate solution and dilute sulfuric acid are added and the Pt determination is carried out.

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*). Only high purity water should be used.

- Hydrochloric acid, w(HCl) = 30%, for trace analysis*, CAS 7647-01-0
- Sulfuric acid, w(H_2SO_4) = 96%, for trace analysis*, CAS 7664-93-9
- Formaldehyde solution, w(HCHO) = 37%, CAS 50-00-0
- Hydrazine sulfate, $N_2H_6SO_4$, for trace analysis*, CAS 10034-93-2
- Rh(III) stock solution, β(Rh(III)) = 1 g/L, commercially available
- Pt(IV) stock solution, β(Pt(IV)) = 1 g/L, commercially available
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

Solutions

Hydrazine sulfate solution	c($N_2H_6SO_4$) = 0.1 mol/L 0.13 g hydrazine sulfate is dissolved in 10 mL ultrapure water. This solution is stable for max. 1 week.
Diluted sulfuric acid	c(H_2SO_4) = 2 mol/L The diluted sulfuric acid is prepared from w(H_2SO_4) = 96% by dilution with ultrapure water.

Standard solutions

Rh(III) standard solution	β[Rh(III)] = 1 µg/L The solution is prepared from the Rh(III) standard stock solution by dilution with c(HCl) = 0.1 mol/L. Dilutions with concentrations below 1 mg/L should be freshly prepared every day.
Pt(IV) standard solution	β[Pt(IV)] = 1 µg/L The solution is prepared from the Pt(IV) standard stock solution by dilution with c(HCl) = 0.1 mol/L. Dilutions with concentrations below 1 mg/L should be freshly prepared every day.

Analysis

Measuring solution for the Rh determination

10 mL (diluted) digested sample

200 µL w(HCl) = 30%

10 µL w(HCHO) = 37%

The concentration of Rh is determined by standard addition using the parameters specified in method 2.

Measuring solution for the Pt determination

Measuring solution from the Rh determination

15 µL $c(N_2H_6SO_4)$ = 0.1 mol/L

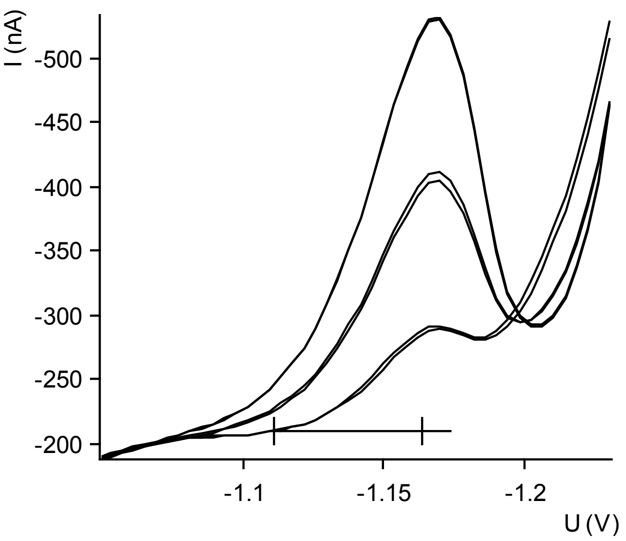
0.675 mL $c(H_2SO_4)$ = 2 mol/L

After the addition of the hydrazine sulfate solution the mixture is stirred for 60 s. The diluted sulfuric acid is then added and the platinum is determined under the conditions given in method 1.

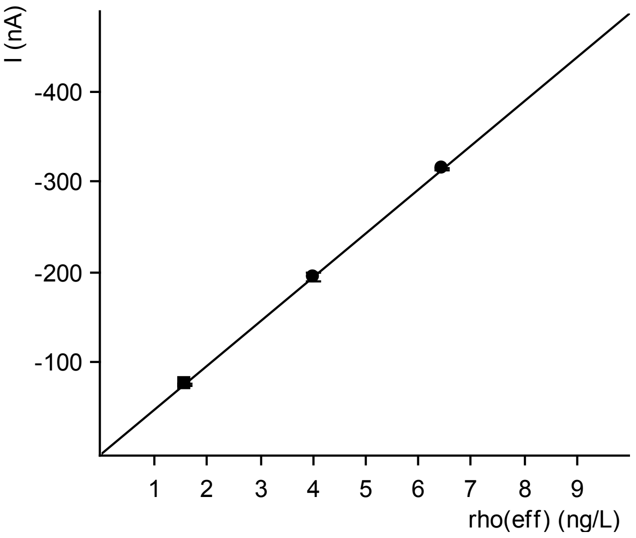
The Pt concentration is determined by standard addition.

Examples

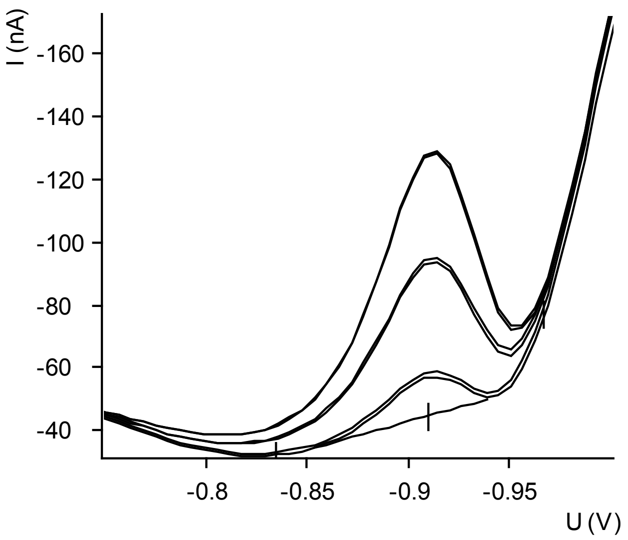
Substance: Rhodium VR(**)



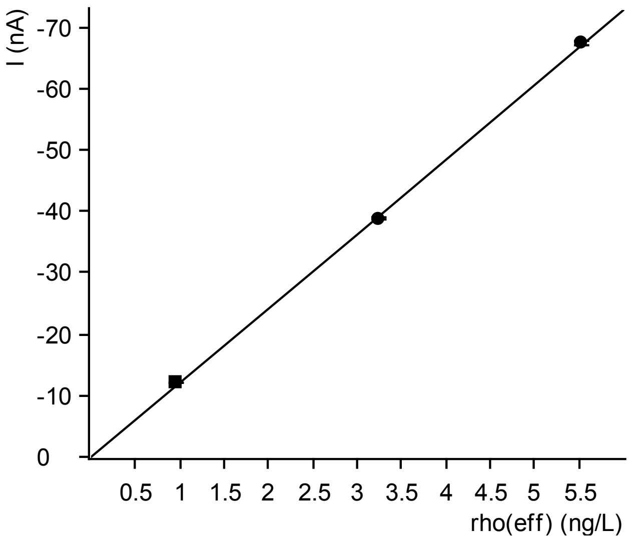
Standard addition curve: Rhodium



Substance: Platinum VR(**)



Standard addition curve: Platinum



Results

Sample	Tap water
Sample size	10.0 mL
β(Rh)	1.6 ng/L
β(Pt)	1.1 ng/L

Comments

- Under no circumstances should the determination be carried out with a Pt auxiliary electrode.
- A reference electrode that has already been used together with a Pt electrode should not be used.

- It is very advantageous if all vessels and electrodes are only used for this determination.
- In order to avoid heating the measuring solution and the enlargement of the interference peak at the Pt potential associated with this, the sulfuric acid is added in dilute form.

References

- E. Helmers, N. Mergel
  Platinum and rhodium in a polluted environment: Studying the emissions of automobile catalysts with emphasis on the application of CSV rhodium analysis
  Fresenius J. Anal. Chem. 362 (1998) 522–528.
- C. León, H. Emons, P. Ostapczuk, K. Hoppstock
  Simultaneous ultratrace determination of platinum and rhodium by cathodic stripping voltammetry
  Anal. Chim. Acta. 336 (1997) 99–104

Appendix

Report for the example determination of Pt in tap water (spiked sample) after UV digestion according to method 1

```
================= METROHM 746 VA TRACE ANALYZER (5.746.0101) =================
 Determ.     : 11221602             User:                      Date: 2000-11-22
 Modified    : 2000-11-22 16:38:04  Run :  0                   Time: 16:02:51
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
  6     Auf221100_2                                                      10 mL
--------------------------------------------------------------------------------
 Method  :  AB220_Pt
 Title   :  Determination of Platinum with DPCSV. AB220
 Remark1 :  10 mL sample + 1.5 mL electrolyte
 Remark2 :  tap water (digestion 22.11.2000/2 pos.6)
--------------------------------------------------------------------------------

  Substance : Platinum                                       Comments
  Mass conc.:    551.8 pg/L            Mass     : 5.518 pg   ------------------
  MC.dev.   :     63.7 pg/L (11.5%)    Add.mass :    25 pg
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -897   -8.897  -9.055   0.2229            front overlapping
              01   -896   -9.212                             front overlapping
              10   -897   -45.44  -45.10   0.4846   -36.04   front overlapping
              11   -897   -44.76                             front overlapping
              20   -897   -84.78  -84.87   0.1349   -39.77   crit. rear ovlp.
              21   -896   -84.97                             crit. rear ovlp.

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Platinum     std.add.     -8.407e-09       -17.52                 1.160e-09


 Final results                         +/- Res.dev.   %      Comments
 ---------------------------------     -----------------     ------------------
   Platinum =   551.78 pg/L                63.7    11.5
```

Method print for the determination of Pt according to method 1

```
================= METROHM 746 VA TRACE ANALYZER (5.746.0101) =================
 Method: AB220_Pt.mth         OPERATION SEQUENCE
 Title : Determination of Platinum with DPCSV. AB220
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    SMPL>M               V.fraction          mL     V.total              L
 2    DOS>M                Soln.name   electrol       V.add         1.500 mL
 3    PURGE
 4    STIR          300.0  Rot.speed      2000 /min
 5    (ADD
 6      PURGE
 7      STIR        30.0   Rot.speed      2000 /min
 8      (REP
 9        SEGMENT          Segm.name   DPCSV
10      REP)1
11      ADD>M              Soln.name   Pt_Std         V.add         0.025 mL
12    ADD)2
13    END
Method: AB220_Pt              SEGMENT
                                  DPCSV
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    0PURGE
 2    STIR           5.0   Rot.speed      2000 /min
 3    HMDE                 Drop size         4        Meas.cell   normal
 4    DPMODE               U.ampl          -50 mV     t.meas         20.0 ms
                           t.step         0.30 s      t.pulse        40.0 ms
 5    MEAS          120.0  U.meas         -600 mV
 6    0STIR         10.0
 7    FSWEEP        26.1   U.start        -600 mV     U.step            6 mV
                           U.end         -1100 mV     Sweep rate       20 mV/s
 8    0MEAS                U.standby           mV
 9    END
```

Report for the example determination of Rh in tap water (spiked sample) after UV digestion according to method 2

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination   : 11221804_20001122_2_9.dth
 Sample ID       : 20001122_2_9
 Creator method :                  Date :                     Time:
 Creator determ.:                  Date : 2000-11-22          Time:  18:04:05
 Modified by     : ---             Date :                     Time:
--------------------------------------------------------------------------------
 Method          : AB 220_2 Det of Rh.mth
 Title           : Determination of Rhodium
 Remark1         : 10 mL sample + 200 uL HCl (30 %) + 10 uL Formaldehyd
 Remark2         : tap water (22.11.2000/2 pos. 9)
--------------------------------------------------------------------------------
 Sample amount   :  10.000 mL
 Cell volume     :  10.210 mL
--------------------------------------------------------------------------------
 Substance       : Rh
 Conc.           :   1.621 ng/L
 Conc.dev.       :   0.070 ng/L     ( 4.31%)
 Amount          :  16.547 pg
 Add.amount      :  25.000 pg

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -1.138   -96.2   -94.8     1.945       0.0
 1 - 2  -1.134   -93.4
 2 - 1  -1.130  -229.0  -229.8     1.152    -135.0
 2 - 2  -1.134  -230.6
 3 - 1  -1.130  -392.3  -386.0     8.820    -156.2
 3 - 2  -1.130  -379.8


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Rh           std.add.      -9.425e-008  -5.815e+001   6.243e-009      0.99858


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

 Rh:
 default           =    1.655  ng/l    0.071        4.314
```

Method print for the determination of Rh according to method 2

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method           : AB 220_2 Det of Rh.mth
Title            : Determination of Rhodium
Remark1          : 10 mL sample + 200 uL HCl (30 %) + 10 uL Formaldehyd
Remark2          : tap water (22.11.2000/2 pos. 9)

Calibration      : Standard addition
Technique        : Batch
Addition         : Manual

Sample ID        : 20001122_2_9
Sample amount (mL): 10.000
Cell volume (mL): 10.210

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

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

Electrode                          : HMDE
Drop size (1..9)                   : 4
Stirrer speed (rpm)                : 2000

Initial electr. conditioning       : No

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

Measure blank                      : No
Addition purge time (s)            : 30

Initial purge time (s)             :      300
```

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

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :   -0.100
Cleaning time (s)                  :    0.000
Deposition potential (V)           :   -0.700
Deposition time (s)                :   60.000

Sweep
Equilibration time (s)             :    5.000
Start potential (V)                :   -0.900
End potential (V)                  :   -1.210
Voltage step (V)                   :    0.004
Voltage step time (s)              :    0.300
Sweep rate (V/s)                   :    0.013
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                      : 1
Eliminate spikes                   : Yes

Substances
--------------------------------------------------------------------------------
Rh                       : -1.180 V   +/- 0.050 V

Standard solution        : 1   1.000 ug/L
Addition volume (mL)     : 0.025

default                  : Final result (Rh) =
                           Conc * (10.21 / 10) * (1e+009 / 1) + 0 - 0

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

Report for the example determination of Rh and Pt in tap water (spiked sample) after UV digestion according to method 3

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 11221713              User:                      Date: 2000-11-22
 Modified    : no                    Run :  0                   Time: 17:13:37
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
  8     Auf221100_2                                                      10 mL
--------------------------------------------------------------------------------
 Method  :  AB220R+P
 Title   :  Determination of Rhodium and Platinum. AB 220
 Remark1 :  Aufschluss 22.11.2000/2 Pos.8
 Remark2 :  tap water
--------------------------------------------------------------------------------

  Substance : Rhodium                                        Comments
  Mass conc.:    1.600 ng/L          Mass     :    16 pg     ------------------
  MC.dev.   :    0.059 ng/L (3.66%)  Add.mass :    25 pg
  Cal.dev.  :    -                   V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -1163  -75.84  -76.76    1.309            front overlapping
              01   -1162  -77.69                             front overlapping
              10   -1167  -197.2  -193.9    4.652   -117.2
              11   -1167  -190.6
              20   -1168  -312.6  -313.6    1.417   -119.6
              21   -1168  -314.6
```

```
  Substance : Platinum                                       Comments
  Mass conc.:    1.062 ng/L            Mass     : 10.62 pg   ------------------
  MC.dev.   :    0.050 ng/L (4.7%)     Add.mass :    25 pg
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------- -------   ------------------
              00   -910   -12.01  -12.09   0.1041            front overlapping
              01   -910   -12.16                             front overlapping
              10   -912   -38.77  -38.68   0.1339   -26.59   front overlapping
              11   -912   -38.58                             front overlapping
              20   -913   -66.97  -67.13   0.2241   -28.45   front overlapping
              21   -913   -67.29                             front overlapping

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Rhodium      std.add.     -7.626e-08       -48.67                 2.673e-09
 Platinum     std.add.     -1.176e-08       -12.12                 5.902e-10


 Final results                         +/- Res.dev.   %      Comments
 ---------------------------------     -----------------     ------------------
    Rhodium =   1.5997 ng/L               0.059    3.66
   Platinum =   1.0621 ng/L               0.050    4.70
```

Method print for the determination of Rh and Pt according to method 3

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB220R+P.mth         OPERATION SEQUENCE
 Title : Determination of Rhodium and Platinum. AB 220
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    SMPL>M               V.fraction          mL     V.total              L
 2    DOS>M                Soln.name                  V.add         0.210 mL
 3    REM                  +200 uL HCl (30%), 10 uL Formaldehyde (36.5%)
 4    PURGE
 5    STIR          300.0  Rot.speed      2000 /min
 6    (ADD
 7      PURGE
 8      STIR        30.0   Rot.speed      2000 /min
 9      (REP
10        SEGMENT          Segm.name   DPCSV_Rh
11      REP)1
12      ADD>M              Soln.name   Rh_Std         V.add         0.025 mL
13    ADD)2
14    STIR                 Rot.speed      2000 /min
15    DOS>M                Soln.name   Hydrazin       V.add         0.015 mL
16    STIR          60.0   Rot.speed      2000 /min
17    DOS>M                Soln.name   2M H2SO4       V.add         0.675 mL
18    PURGE         30.0
19    (ADD
20      PURGE
21      STIR        30.0   Rot.speed      2000 /min
22      (REP
23        SEGMENT          Segm.name   DPCSV_Pt
24      REP)1
25      ADD>M              Soln.name   Pt_Std         V.add         0.025 mL
26    ADD)2
27    END

 Method: AB220R+P              SEGMENT
                               DPCSV_Rh
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    0PURGE
 2    STIR           5.0   Rot.speed      2000 /min
 3    HMDE                 Drop size         4        Meas.cell   normal
 4    DPMODE               U.ampl          -50 mV     t.meas         20.0 ms
                           t.step         0.30 s      t.pulse        40.0 ms
 5    MEAS          60.0   U.meas         -700 mV
 6    0STIR         10.0
 7    FSWEEP        25.8   U.start        -900 mV     U.step            4 mV
                           U.end         -1230 mV     Sweep rate    13.33 mV/s
 8    0MEAS                U.standby           mV
 9    END


Method: AB220R+P              SEGMENT
```

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                               DPCSV_Pt
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      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  ------------------------
 1    0PURGE
 2    STIR           5.0   Rot.speed      2000 /min
 3    HMDE                 Drop size         4         Meas.cell   normal
 4    DPMODE               U.ampl          -50 mV      t.meas         20.0 ms
                           t.step         0.30 s       t.pulse        40.0 ms
 5    MEAS          60.0   U.meas         -600 mV
 6    0STIR
 7    FSWEEP        26.1   U.start        -600 mV      U.step            6 mV
                           U.end         -1100 mV      Sweep rate       20 mV/s
 8    0MEAS                U.standby           mV
 9    END
```