Application Bulletin 116/4 e

Determination of chromium in small quantities by polarography and adsorptive stripping voltammetry after digestion

Summary

This Application Bulletin describes methods for the polarographic and voltammetric determination of small quantities of chromium in water, effluent water and biological samples. Methods for the sample preparation for various matrices are given.

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 6.1226.030 or 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	Pt rod electrode	6.0343.x00

Sample preparation

Reagents

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

- Sulfuric acid, for trace analysis*, $w(H_2SO_4)$ = 96%, CAS 7664-93-9
- Hydrogen peroxide solution, for trace analysis*, $w(H_2O_2)$ = 30%, CAS 7722-84-1
- Hydrochloric acid, for trace analysis*, w(HCl) = 30%, CAS 7647-01-0
- Methyl isobutyl ketone (MIBK), for analysis, CAS 108-10-1
- Sodium diethyl dithiocarbamate trihydrate (NaDDTC), CAS 20624-25-3
- Potassium hydrogen phthalate, for analysis, CAS 877-24-7
- Sodium sulfite, for analysis, CAS 7757-83-7
- Potassium peroxodisulfate, for analysis, CAS 7727-21-1
- Potassium permanganate, for analysis, $KMnO_4$, CAS 7722-64-7
- Sodium hydroxide solution, for trace analysis*, w(NaOH) = 30%, CAS 1310-73-2
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)
- Water-repellent filter paper, diameter 9 cm

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

Solutions

Diluted sulfuric acid	$c(H_2SO_4)$ = 1.0 mol/L
Sodium diethyl dithiocarbamate solution	w(NaDDTC) = 2 % in water The solution should always be filtered before use.
Potassium hydrogen phthalate buffer (pH 4.0)	c(potassium hydrogen phthalate) = 0.05 mol/L
Potassium permanganate solution	$c(KMnO_4)$ = 0.02 mol/L
Diluted sodium hydroxide solution	c(NaOH) = 0.1 mol/L

Sample preparation

- For sulfite-free surface or drinking water no special preparation is necessary. The samples can be analyzed directly as described under «Analysis».
- With slightly contaminated waste water UV digestion has proved to be best. Add 10 µL conc. hydrochloric acid and 50 µL H_2O_2 to 10 mL of the sample solution and treat in the 909 UV Digester during 90 min at 90°C.

- Water containing also sulfite and Cr(III) next to Cr(VI): In acidic sulfite solution, Cr(VI) is reduced to Cr(III). Since one is primarily interested in the Cr(VI) fraction hexavalent chromium must first be extracted and determined separately.
    - Adjust the sample to pH = 4 with diluted sulfuric acid 1 mol/L.
    - Place 50 mL of this solution in a 100 mL separating funnel with 5 mL of pH 4.0 buffer solution, 2 mL NaDDTC and 10 mL MIBK. Shake vigorously for 2 minutes to extract the Cr(VI).
    - Allow to stand for 15 min, drain off the greater portion of the aqueous phase and filter the MIBK portion via a phase-separating filter into a 50 mL Kjeldahl flask. Rinse the separating funnel with a further 3 mL MIBK and pass this through the filter into the Kjeldahl flask. Add 10 mL distilled water, a glass boiling bead and 2 mL conc. sulfuric acid.
    - Place the Kjeldahl flask in a boiling water bath and drive off the MIBK with a strong stream of nitrogen. Rinse the gas inlet tip with distilled water and add 1.8 mL H_2O_2 to the still hot solution.
    - Heat over a Bunsen flame until the H_2O_2 starts to decompose. Stop heating until reaction is completed and the sulfuric acid is finally evaporated down to about 0.5 mL. Digestion is now completed, and the sample may be allowed to cool.
- Biological samples and waste water containing a high proportion of organic matter and chlorides proceed as follows: In the presence of sulfuric acid, Cr(VI) combines with chloride ions to form the volatile complex chromyl chloride (CrO_2Cl_2), whose boiling-point is 117 °C. To avoid loss of chromium owing to evaporation of chromyl chloride, add a spatula-tip of sodium sulfite to the sample before digestion. Digest as described in Application Bulletin 113: «Sample preparation».

Oxidation from Cr(III) to Cr(VI)

Oxidation with $KMnO_4$

- Add 10 mL distilled water and 2 drops $KMnO_4$ solution to the cooled sulfuric acid and heat to boiling-point.
- Continue adding $KMnO_4$ drop by drop until the pink color remains. While keeping the total volume constant by adding small amounts of water, allow the solution to boil approx. 5 min.
- Add diluted NaOH solution to the still hot solution to bring the pH value to 5-9.
- Now the solution can be cooled and rinsed into the polarography vessel with distilled water.

Oxidation with $K_2S_2O_8$

Another possibility is the oxidation with $K_2S_2O_8$.

- Add 10 mL distilled water and a spatula-tip of $K_2S_2O_8$ to the cooled sulfuric acid digestion solution
- Boiling slightly, allow solution to boil down to approx. 0.5 mL, then cool and afterwards fill up to 10 mL.
- The surplus of peroxodisulfate must be boiled off, otherwise traces of peroxide will interfere with the analysis.

Oxidation with UV in the 909 UV Digester at pH 4-6

- To do this, adjust 10 mL of the sample solution to pH 4-6, then add 50 µL H_2O_2. Afterwards expose the sample solution to treatment in the UV Digester at 90°C for 30 min.

Method 1: Polarographic determination of Cr concentrations >10 µg/L

Summary

Higher chromium concentrations are determined at the dropping mercury electrode. Cr(III) must first be wet chemically oxidized. The Cr(IV) content is determined by means of DP polarography.

Reagents

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

- Potassium hydroxide, for trace analysis* w(KOH) = 30%, CAS 1310-58-3
- Ammonia solution, for trace analysis*, w(NH_3) = 25%, CAS 1336-21-6
- Acetic acid, for trace analysis*, w(CH_3COOH) = 96 - 100 %, CAS 64-19-7
- Ethylene diamine, for analysis, CAS 107-15-3
- Cr standard stock solution: ß(Cr^{6+}) = 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

Diluted ammonia solution	w(NH_3) = 5%

Standard solutions

Cr(VI) standard solution	β(Cr^{6+}) = 1 mg/L The diluted standard solutions (e.g. 1 mg/L Cr) are prepared from a standard stock solution by dilution in water. They are freshly prepared daily.

Analysis

Measuring solution

10 mL (diluted) sample or digestion solution

10 µL ethylene diamine

150 µL acetic acid

200 µL diluted ammonia solution

Adjust the pH value of the solution with KOH or acetic acid to pH 6.8 ± 0.1. If necessary, allow to cool. The solution is purged with nitrogen for 600 s.

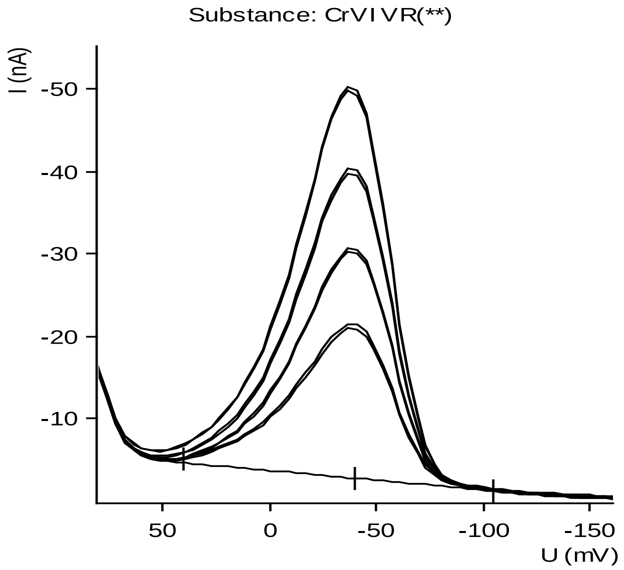
The chromium concentration is determined by means of the standard addition method.

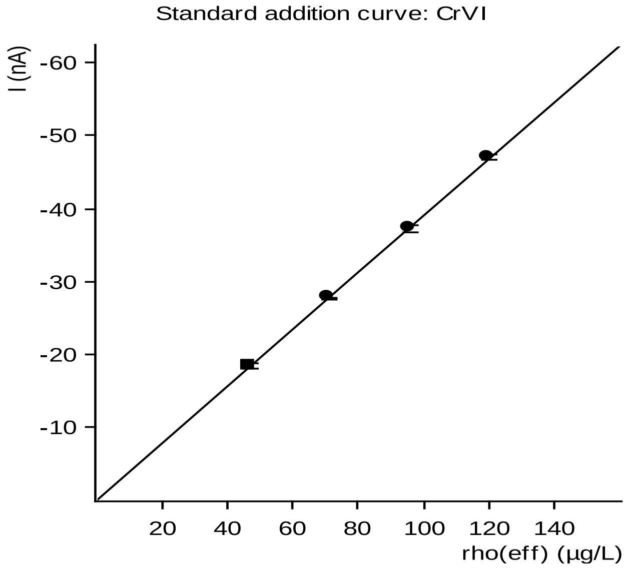
Parameters

Voltammetric	
Electrode operating mode	SMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	3 s
Sweep	
Start potential	0.10 V
End potential	-0.17 V
Potential step	0.004 V
Potential step time	0.6 s
Sweep rate	0.0067 V/s
Pulse amplitude	0.05 V

Substance	
Name	Cr
Characteristic potential	-0.04 V

Example





Result

Sample	Waste water
Sample size	10 mL
β(Cr)	47.7 µg/L

Comments

- The solution has to be degassed for min. 10 min to prevent interferences from oxygen.

- The limit of detection in samples is 10 µg/L, the upper limit of the linear range is 1 mg/L Cr. Samples of higher concentrations must be diluted.
- We recommend an evaluation of the curves using the „linear“ or „exponential“ baseline.
- Weak organically contaminated waste water can be analyzed without digestion.

Methods 2 + 3: Determination of chromium traces using adsorptive stripping voltammetry

Summary

Cr(III) ions or Cr(IV) ions after „in situ“ reduction at the mercury electrode, build a complex with DTPA. In this complex the Cr(III) is reduced to Cr(II) and oxidized again catalytically to Cr(III) by nitrate ions. The current flowing during this process can be used for the quantitative determination of Cr.

Reagents

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

- Sodium acetate, for trace analysis*, CAS 127-09-3
- Diethylenetriaminepentaacetic acid (DTPA), Titriplex™ V, for analysis, CAS 67-43-6
- Sodium nitrate, $NaNO_3$, for trace analysis*, CAS 7631-99-4
- Sodium hydroxide solution, for trace analysis*, w(NaOH) = 30 %, CAS 1310-73-2
- Cr standard stock solution: $ß(Cr^{6+})$ = 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

Supporting electrolyte	c(sodium acetate) = 0.2 mol/L c(DTPA) = 0.05 mol/L $c(NaNO_3)$ = 2.5 mol/L 1.64 g sodium acetate, 1.96 g DTPA and 21.3 g sodium nitrate are dissolved in ultrapure water and filled up to 100 mL.

Method 2: Cr concentrations between 0.02 and 1.5 µg/kg

Standard solution

Cr(VI) standard solution	$ß(Cr^{6+})$ = 0.02 mg/L Diluted standard solutions are prepared from a standard stock solution by dilution in water. They are freshly prepared daily.

Analysis

Measuring solution

10 mL (diluted) sample

2.5 mL supporting electrolyte

Adjust the pH value of this solution to 6.2 ± 0.1, using diluted NaOH solution.

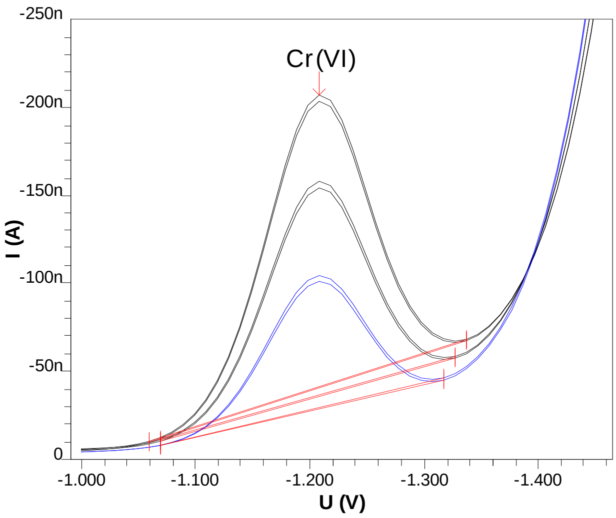
The chromium concentration is determined by means of the standard addition method.

Parameters

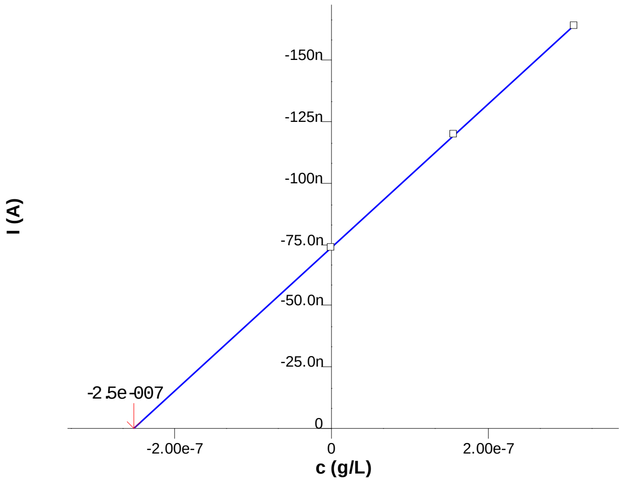
Voltammetric	
Electrode operating mode	HMDE
Drop size	7
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-1.0 V
Waiting time 1	60 s
Equilibration time	10 s
Sweep	
Start potential	-1.0 V
End potential	-1.45 V
Potential step	0.01 V
Potential step time	0.3 s
Sweep rate	0.033 V/s
Pulse amplitude	0.05 V

Substance	
Name	Cr
Characteristic potential	-1.25 V

Example



```
Cr(VI)
c =     0.316 ug/l
+/-     0.010 ug/l (3.26%)
```



Result

Sample	Tap water
Sample size	10 mL
β(Cr)	0.32 µg/L

Method 3: Cr concentrations between 1 and 5 µg/L

Standard addition solution

Cr(VI) standard solution	β(Cr^{6+}) = 0.25 mg/L Diluted standard solutions are prepared from a standard stock solution by dilution in water. They are freshly prepared daily.

Analysis

Measuring solution

10 mL (diluted) sample

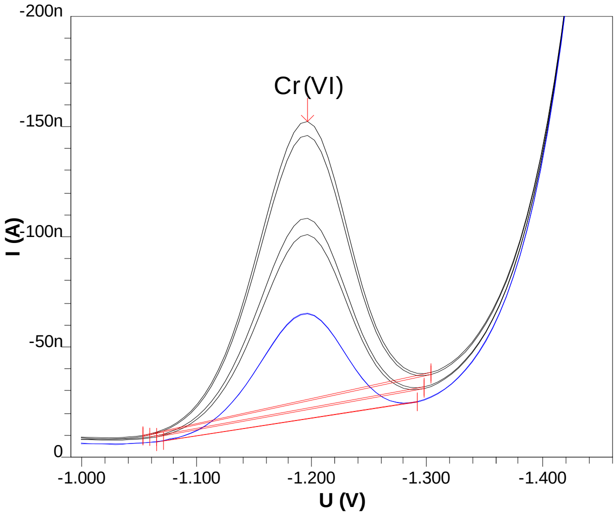
2.5 mL supporting electrolyte

Adjust the pH value of this solution to 6.2 ± 0.1, using diluted NaOH solution. The chromium concentration is determined by means of the standard addition method.

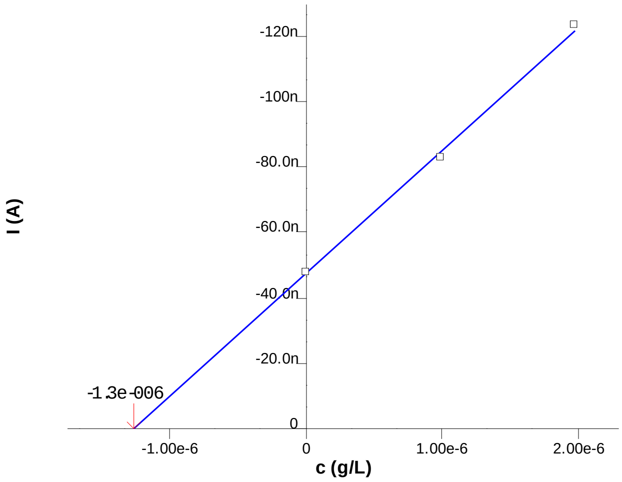
Parameters

Voltammetric	
Electrode operating mode	HMDE
Drop size	7
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	10 s
Sweep	
Start potential	-1.0 V
End potential	-1.5 V
Potential step	0.01 V
Potential step time	0.3 s
Sweep rate	0.033 V/s
Pulse amplitude	0.05 V
Substance	
Name	Cr
Characteristic potential	-1.25 V

Example



```
Cr(VI)
c =     1.585 ug/l
+/-     0.110 ug/l (6.92%)
```



Result

Sample	Sea water
Sample size	10 mL
β(Cr)	1.6 µg/L

Comments

- For methods 2 and 3 chromium should be present as Cr(VI), since with pure Cr(III) solutions peak heights constantly diminish. Sensitivity with the Cr(VI) solutions is far greater than with the Cr(III) solutions.
- Higher Mg concentrations (>100 mg/L) interfere with the Cr(VI) determination. The background current greatly increases. It is recommended to dilute the sample solutions, e.g. seawater.

References

- Golimowski J., Valenta P., Nürnberg H. W.
  Trace determination of chromium in various water types by adsorption differential pulse voltammetry
  Fresenius Z. Anal. Chem. 322, (1985) 315-322
- Scholz F., Lange B., Draheim M., Pelzer J.
  The catalytic adsorptive stripping voltammetric determination of chromium
  with DTPA and nitrate
  Fresenius Z. Anal.Chem. 388, (1990) 627-629

Appendix

Report for the example determination of chromium according to method 1

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 05281203             User:                      Date: 1999-05-28
 Modified    : 2000-12-04 11:59:21  Run :  0                   Time: 12:03:14
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        waste water                                                      10 mL
--------------------------------------------------------------------------------
 Method  :  AB116_1
 Title   :  Chromium Determination. AB116 Part 1
 Remark1 :  10 mL sample + 10 µL ethylene diamine + 150 µL acetic acid
 Remark2 :  + 200 µL NH3 + NaOH --> pH 6.8
--------------------------------------------------------------------------------

  Substance : CrVI                                           Comments
  Mass conc.:    47.68 ug/L            Mass     : 476.8 ng   ------------------
  MC.dev.   :    0.952 ug/L (2%)       Add.mass :   250 ng
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -40    -18.17  -18.36   0.2621
              01   -40    -18.54
              10   -40    -27.49  -27.57   0.1061   -9.210
              11   -40    -27.64
              20   -40    -36.77  -37.07   0.4113   -9.499
              21   -40    -37.36
              30   -39    -46.40  -46.67   0.3835   -9.605
              31   -39    -46.94

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------
---------   ------------
 CrVI         std.add.     -1.823e-08   -3.960e-04                 2.948e-10


 C#  Workg.com.var  Remark
 --  -------------  ----------------

 Final results                         +/- Res.dev.   %      Comments
 ---------------------------------     -----------------     ------------------
       CrVI =   47.683 ug/L               0.952    2.00
```

Method print for the determination of chromium according to method 1

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB116_1 .mth         OPERATION SEQUENCE
 Title : Chromium Determination. AB116 Part 1
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    DOS/M                V.added       0.360 mL
 2    SMPL/M               V.fraction          mL     V.total              L
 3    STIR                 Rot.speed      2000 /min
 4    PURGE         600.0
 5    (ADD
 6      PURGE
 7      STIR        10.0   Rot.speed      2000 /min
 8      SEGMENT            Segm.name   pol
 9      ADD>M              Soln.name   Cr-Std         V.add         0.050 mL
10    ADD)3
11    END

 Method: AB116_1               SEGMENT
                                    pol
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    0PURGE
 2    0STIR          3.0
 3    (REP
 4      SMDE               Drop size         4
 5      DPMODE             U.ampl          -50 mV     t.meas         20.0 ms
                           t.step         0.60 s      t.pulse        40.0 ms
 6      SWEEP       42.6   U.start         100 mV     U.step            4 mV
                           U.end          -170 mV     Sweep rate    6.667 mV/s
```

```
 7      0MEAS             U.standby           mV
 8    REP)1
 9    PURGE
10    STIR                Rot.speed      2000 /min
11    END

  Method: AB116_1                  SUBSTANCES
                               CrVI      - pol
--------------------------------------------------------------------------------

      Recognition                               Display / Plot
      -------------------------                 ---------------------------
      U.verify           -40 mV                 I.scale       auto
      U.tol (+/-)         30 mV                 U.div          50.00 mV/cm
      U.width min         10 mV                 U.begin           80 mV
      U.width max        200 mV                 U.end           -160 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   1999-05-28 12:17:00             Coefficients
  ---------------------------------             -------------------------
  Technique     std.add.                        Y.reg        -1.823e-08
  Curve type    linear                          Slope        -0.0003892
                                                Nonlin.
                                                Mean dev.      2.95e-10

                Additions
                ------------------------------------------------------------

Soln.name       Cr-Std
  ----------
  Mass conc.         10 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: AB116_1               CALCULATION
                              max. 15 lines
--------------------------------------------------------------------------------

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

Report for the example determination of chromium according to method 2

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 11271032_tap water.dth
 Sample ID      : tap water
 Creator method :                   Date :                     Time:
 Creator determ.:                   Date : 2000-11-27          Time:   10:32:35
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : AB 116 M2.mth
 Title          : AB 116/3 Determination of Cr (Method 2)
 Remark1        : 10 mL sample + 2.5 mL supporting electrolyte
 Remark2        :
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.500 mL
--------------------------------------------------------------------------------
 Substance      : Cr(VI)
 Conc.          : 252.741 ng/L
 Conc.dev.      :   8.247 ng/L     ( 3.26%)
 Amount         :   3.159 ng
 Add.amount     :   2.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -1.208   -74.9   -73.7     1.795       0.0
 1 - 2  -1.208   -72.4
 2 - 1  -1.208  -121.3  -119.9     2.053     -46.2
 2 - 2  -1.208  -118.4
 3 - 1  -1.208  -165.6  -164.1     2.045     -44.3
```

```
 3 - 2  -1.208  -162.7


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Cr(VI)       std.add.      -7.375e-008  -2.918e-001   2.362e-009      0.99929


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

 Cr(VI):
 default           =    0.316  ug/l    0.010        3.263
```

Method print for the determination of chromium according to method 2

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB116_2_Det of CrVI with HMDE.mth
Title           : Determination of Chromium(VI). AB116 part 2
Remark1         : 10ml sample + 2.5ml buffer --> pH 6.2 ± 0.1 with NaOH
Remark2         : buffer.: 0.2mol/l sodium acetate + 0.05mol/l DTPA + 2.5 mol/l NaNO3

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : oxydized sample
Sample amount (mL): 10.000
Cell volume (mL): 12.500

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)            : 10

Initial purge time (s)             :      300

Conditioning cycles
Start potential (V)                :    0.000
End potential (V)                  :    0.000
No. of cycles                      :        0

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :    0.000
Cleaning time (s)                  :    0.000
Deposition potential (V)           :   -1.000
Deposition time (s)                :   60.000

Sweep
Equilibration time (s)             :   10.000
Start potential (V)                :   -1.000
End potential (V)                  :   -1.450
Voltage step (V)                   :    0.010
Voltage step time (s)              :    0.300
Sweep rate (V/s)                   :    0.033
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
--------------------------------------------------------------------------------
Cr(VI)                   : -1.250 V   +/- 0.050 V

Standard solution        : 1   20.000 ug/L
Addition volume (mL)     : 0.100

default                  : Final result (Cr(VI)) =
                           Conc * (12.5 / 10) * (1e+006 / 1) + 0 - 0

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

Report for the example determination of chromium according to method 3

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 11271458_sea water.dth
 Sample ID      :
 Creator method :                   Date :                     Time:
 Creator determ.:                   Date : 2000-11-27          Time:  14:58:48
 Modified by    :                   Date : 2017-07-10          Time:  13:37:11
--------------------------------------------------------------------------------
 Method         : AB 116 M3.mth
 Title          :
 Remark1        : 10 mL sample + 2.5 mL supporting electrolyte
 Remark2        :
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.500 mL
--------------------------------------------------------------------------------
 Substance      : Cr(VI)
 Conc.          :   1.268 ug/L
 Conc.dev.      :   0.088 ug/L     ( 6.92%)
 Amount         :  15.849 ng
 Add.amount     :  12.500 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -1.196   -47.5   -47.8     0.372       0.0
 1 - 2  -1.196   -48.0
 2 - 1  -1.196   -79.5   -82.8     4.691     -35.1
 2 - 2  -1.190   -86.1
 3 - 1  -1.196  -126.1  -123.3     3.956     -40.5
 3 - 2  -1.196  -120.5


 Substance     Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Cr(VI)       std.add.      -4.746e-008  -3.743e-002   3.655e-009      0.99582


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

 Cr(VI):
 default          =    1.585  ug/l    0.110        6.923
```

Method print for the determination of chromium according to method 3

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB116_3_Det of CrVI with HMDE.mth
Title           : Determination of Chromium(VI). AB116 part 3
Remark1         : 10ml sample + 2.5ml buffer --> pH 6.2 ± 0.1 with NaOH
Remark2         : buffer.: 0.2mol/l sodium acetate + 0.05mol/l DTPA + 2.5 mol/l
NaNO3

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual
```

```
Sample ID       : oxydized sample
Sample amount (mL): 10.000
Cell volume (mL): 12.500

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)            : 10

Initial purge time (s)             :      300

Conditioning cycles
Start potential (V)                :    0.000
End potential (V)                  :    0.000
No. of cycles                      :        0

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :    0.000
Cleaning time (s)                  :    0.000
Deposition potential (V)           :   -1.000
Deposition time (s)                :    0.000

Sweep
Equilibration time (s)             :   10.000
Start potential (V)                :   -1.000
End potential (V)                  :   -1.450
Voltage step (V)                   :    0.010
Voltage step time (s)              :    0.300
Sweep rate (V/s)                   :    0.033
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
--------------------------------------------------------------------------------
Cr(VI)                   : -1.250 V   +/- 0.050 V

Standard solution        : 1   1.000 mg/L
Addition volume (mL)     : 0.100

default                  : Final result (Cr(VI)) =
                           Conc * (12.5 / 10) * (1e+006 / 1) + 0 - 0

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