Metrohm

Application Bulletin 243/2 e

Determination of chromium by adsorptive stripping voltammetry at the Ultra Trace graphite RDE

Summary

The method describes the determination of Cr traces in a range between 1 ... 250 µg/L. The method is based on the adsorption of a Cr(III)-diphenylcarbazonate complex on the Ultra Trace graphite rotating disk electrode (RDE). Organic compounds present in samples (e.g. natural waters) have a strong interfering effect. So they have to be removed by e.g. UV digestion. The determination is made by adsorptive stripping voltammetry in the DC (direct current) measuring mode. Purging with nitrogen is not necessary. The determinations work well also in high salt concentration solutions.

Chromium(VI) undergoes a redox reaction with 1,5-diphenylcarbazide forming a chromium(III) complex. This complex is adsorbed on the Ultra Trace graphite electrode and can be stripped from their surface. The corresponding DC current in the range between 1 ... 25 µg/L is proportional to the chromium(VI) concentration.

Instruments

VA instrument capable of operating a rotating disk electrode (RDE) and supporting direct current (DC) measuring mode	
909 UV Digester	2.909.0014

Electrodes

WE	Ultra Trace electrode tip Driving axle for RDE	6.1204.180 6.1204.x10
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

Reagents

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

- 1,5-Diphenylcarbazide, for analysis, CAS 140-22-7
- Acetone, for analysis, CAS 67-64-1
- Sulfuric acid, w(H_2SO_4) = 96%, for trace analysis*, CAS 7664-93-9
- Ammonium peroxodisulfate, for analysis, CAS 7727-54-0
- Cr(VI) standard solution, $\beta(Cr^{6+})$ = 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 sulfuric acid 3 mol/L 0.15 mol/L 0.015 mol/L	 c(H_2SO_4) = 3 mol/L c(H_2SO_4) = 0.15 mol/L c(H_2SO_4) = 0.015 mol/L Concentrated sulfuric acid is to be diluted with ultrapure water.
DPCI solution	c(DPCI) = 4 · 10^{-4} mol/L Weigh 10 mg of 1,5-diphenylcarbazide into a 100 mL volumetric flask and dissolve in 1 ... 3 mL acetone. Fill up to the mark with diluted sulfuric acid (0.015 mol/L). Store the solution in the dark. The solution is stable for 1 week. If diphenylcarbazide is not pure enough, it has to be purified before use by recrystallization from ethanol.
Peroxodisulfate solution (for sample preparation:	w(Ammonium peroxodisulfate) = 0.1% Ammonium peroxodisulfate is dissolved in ultrapure water.

oxidation Cr(III) → Cr(VI))	

Standard solutions

Cr(VI) standard solution	$\beta(Cr^{6+})$ = 0.5 mg/L Pipette 2.5 mL of diluted sulfuric acid (3 mol/L) and 0.025 mL Cr(VI) standard stock solution ($\beta(Cr^{6+})$ = 1 g/L) into a 50 mL volumetric flask. Fill up to the mark with ultrapure water.
Cr-DPCI standard solution	$\beta(Cr^{6+})$ = 0.5 mg/L (as Cr-DPCI complex) Pipette 2.5 mL of diluted sulfuric acid (3 mol/L) and 0.025 mL Cr(VI) standard stock solution ($\beta(Cr^{6+})$ = 1 g/L) into a 50 mL volumetric flask. Fill up to the mark with DPCI solution. Let it stand for 10 minutes. The solution is stable for 8 hours.

Sample preparation

It is recommended to determine chromium immediately after sampling and filtering through cellulose nitrate membrane filter of 0.45 µm pore size. In case the samples cannot be directly analyzed, an addition of HNO_3 to reach pH 2 is recommended [1]. The pH of the samples should be in the range of 2 to 7.

Sulfite-free and nearly organic-free natural waters (for example: sea water, drinking water)

Cr(VI): No special preparation is necessary, so that the samples can be analyzed directly as described under «Analysis», procedure a.

Cr(VI) + Cr(III): As the chromium must be in the Cr(VI) state, samples have to be oxidized before analysis: to 100 mL of the sample, add 1 mL of $c(H_2SO_4)$ = 0.15 mol/L and 10 mL ammonium peroxodisulfate solution. Heat up and boil for 30-35 minutes to reduce the volume to the half until complete decomposition of the ammonium peroxodisulfate. Allow to cool, rinse into a 100 mL volumetric flask and fill up to .the mark with high purity water. Analyze as described under «Analysis», procedure a.

Organic-free natural waters with inorganic reducing agents

Cr(VI) + Cr(III): Analyze after oxidation with ammonium peroxodisulfate as described under «Analysis», procedure a.

Sulfite containing water and Cr(III) as well as Cr(VI)

In an acid sulfite solution, Cr(VI) is reduced to Cr(III). Since Cr(VI) fraction appears to be of primary interest, hexavalent chromium must first be extracted and determined separately. For a more detailed procedure, refer to Application Bulletin 116.

Waste waters with organic compounds

Cr(VI) + Cr(III): Cr determination is only possible after the elimination of organic matrix and oxidation of Cr(III) to Cr(VI). Organic matrices have to be destroyed through UV digestion under the following conditions:

Duration of the pretreatment	1 … 2 hours
Temperature	90 °C
H_2O_2 volume	100 µL per 10 mL sample

When UV photolysis is done the sample has to be oxidized with ammonium peroxodisulfate. Further on, let the sample cool down and bring the solution up to the previous volume by adding ultrapure water. Analyze as described in «Analysis», procedure a or b.

Biological materials

Cr(VI) + Cr(III): Biological materials have to be be transformed to a solution by wet digestion with H_2SO_4 and H_2O_2.

Resulting acid solution has to be neutralized with NaOH (w = 30%) up to pH = 8 - 10 and brought up to the exact volume with ultrapure water. Kept with this level of pH for 1 hour, acidified with 0.15 mol/L sulfuric acid to approximately pH ≈ 3 and then boiled down for 10 minutes together with 10 mL of ammonium peroxodisulfate in a 250 mL flask in order to prevent the concentrated solution from being lost. Cool down the solution prepared for the analysis, pour it into the measuring flask and bring it up to the exact volume with ultra-pure water. Analyze as described in «Analysis», procedure a.

Electrode preparation

Before starting the analysis, rinse the electrode with ultrapure water and dry it with a filter paper. Remove a thin layer from the electrode surface using the polishing set 6.2802.020 acc.

to the instructions. After each voltammogramm clean the electrode surface voltammetrically by applying 2-5 linear potential scans between 0.35 V and -0.05 V under stirring of the solution.

An electrode which has been used as mercury film electrode, cannot be used for other applications. Nor can an electrode be used as mercury film electrode, which has before been used for other applications (especially organics).

Analysis

The Cr concentration is determined by the standard addition method. Concentrations and amounts of the standards are depending on the concentration of Cr in the samples.

Procedure a (with solution exchange)

Take three 20 mL volumetric flasks and pipette 15.0 mL of the sample in each one. Add 1.0 mL diluted sulfuric acid (3.0 mol/L) and 0.2 - 1.0 mL DPCI solution. Add also Cr(VI) standard solution to the 2nd and 3rd flask. Bring all the solutions to the mark by ultrapure and mix thoroughly. Let them stand for 15 min so that the complex can be formed. Put the solution from the first flask into the measuring vessel. Instead of standard additions, change these solutions during analysis.

Measuring solution procedure a

Sample (flask 1)

15.0 mL (diluted) sample solution

1 mL c(H_2SO_4) = 3 mol/L

0.2 … 1 mL DPCI solution

→ make up to 20 mL with ultrapure water and wait for 15 min

Standard (flask 2 and 3)

15.0 mL (diluted) sample solution

x mL Cr(VI) standard solution

1 mL c(H_2SO_4) = 3 mol/L

0.2 … 1 mL DPCI solution

→ make up to 20 mL with ultrapure water and wait for 15 min

Pour the prepared sample or standard into the polarographic vessel, install the Ultra Trace graphite electrode and run the voltammogram under the conditions specified under «Parameters».

Procedure b

Take a 20 mL volumetric flasks, pour about 15 mL of the sample. Add 1.0 mL sulfuric acid 3.0 mol/L and 0.2 - 1.0 mL DPCI solution. Bring the solution to the mark by adding ultrapure water and mix thoroughly. Let it stand for 15 min and put the solution nto the measuring vessel. Standard additions are done with the Cr complex solution.

Measuring solution procedure b

15.0 mL (diluted) sample solution

1 mL c(H_2SO_4) = 3 mol/L

0.2 … 1 mL DPCI solution

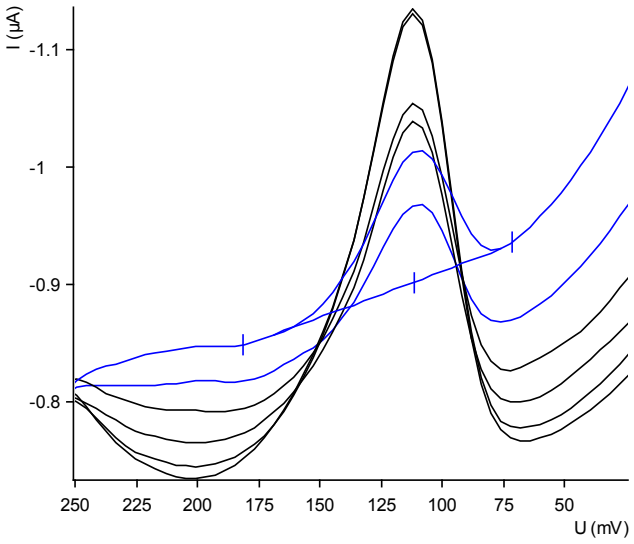
→ make up to 20 mL with ultrapure water and wait for 15 min

Pour the prepared sample into the polarographic vessel, install the Ultra Trace graphite electrode and run the voltammogram under the conditions specified under «Parameters». The concentration is quantified by addition of Cr-DPCI standard solution.

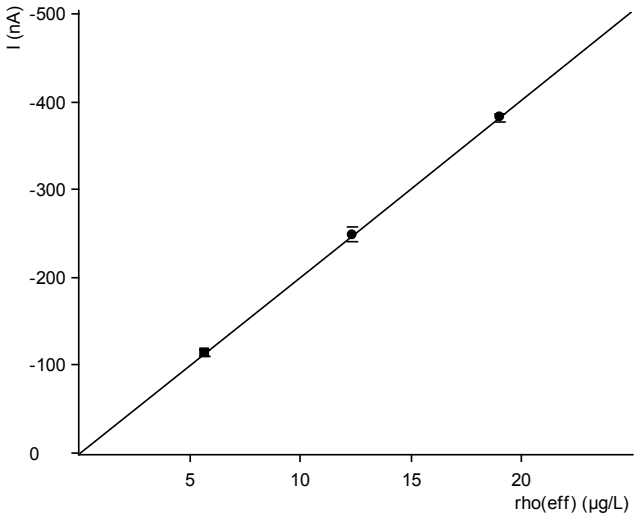
Parameters

Voltammetric	
Measuring mode	DC – Direct current
Stirring rate	2000 min^{-1}
Cyclovoltammetric pretreatment	
Start potential	0.35 V
Vertex potential	-0.05 V
No. of cycles	5
Potentiostatic pretreatment	
Potential 1	0.35 V
Waiting time 1	60 s
Equilibration time	10 s
Sweep	
Start potential	0.35 V
End potential	-0.05 V
Potential step	0.004 V
Potential step time	0.1 s
Sweep rate	0.04 V/s
Substance	
Name	Cr
Characteristic potential	0.1 V

Example



Standard addition curve: Cr(VI)



Result

Sample	Waste water
Sample size	15.0 mL
β(Cr)	5.68 µg/L

Comments

- The total Cr concentration in the measuring vessel should not be higher than 50 µg/L including the standard additions. If the amount is higher, the electrode surface will be overloaded and the analyses are not reproducible.
- The method is suitable for samples with Cr concentrations between 1 and 25 µg/L. Samples with Cr concentrations between 25 and 250 µg/L must be diluted 1:10 with ultrapure water.

References

[1] Golimowski, P., Valenta, H. W., Nürnberg, F. W., Trace Determination of Chromium in various waters by adsorption differential Pulse Voltammetry, Fresenius Z. Anal. Chem., 322 (1985) 315 - 322

[2] Malakhova, N. A., Chernysheva, A. V., Brainina, Kh. Z., Adsorptive Stripping Voltammetry of Chromium 1,5-diphenylcarbazonate, Electroanalysis, 3 (1991) 803 - 814

[3] Malakhova, N. A., Chernysheva, A. V., Brainina Kh. Z., Adsorption and electrochemical transformations of diphenylcarbazide and diphenylcarbazone on graphite electrodes, Electroanalysis, 3 (1991) 691 - 698

Appendix

Report for the example determination of Cr according to procedure b

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 04181906             User:                      Date: 1994-04-18
 Modified    : no                   Run :  0                   Time: 19:06:28
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
                                                                      15 mL
--------------------------------------------------------------------------------
 Method  :  AB_243
 Title   :  Determination of Chromium on epoxy graphite el.RDE
 Remark1 :  0.15 M sulf+1.0 ml DPCI 4x10-4 M+waste water Pal.Plengen
 Remark2 :  tel = 1 min,add = 5 ppb Cr-complex
--------------------------------------------------------------------------------

  Substance : Cr(VI)                                          Comments
  Mass conc.:    5.681 ug/L            Mass     : 85.22 ng   ------------------
  MC.dev.   :    0.307 ug/L (5.4%)     Add.mass :   100 ng
  Cal.dev.  :    -                     V0.sample:    15 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   111    -110.9  -114.0    4.449           front overlapping
              01   111    -117.2                            front overlapping
              10   112    -239.2  -245.1    8.270   -131.1   front overlapping
              11   111    -250.9                            front overlapping
              20   112    -368.5  -372.0    4.941   -126.9   front overlapping
              21   112    -375.5                            front overlapping

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Cr(VI)       std.add.     -1.141e-07     -0.02009                 5.381e-09


 Final results                        +/- Res.dev.   %      Comments
 ---------------------------------    -----------------     ------------------
       CrVI =   5.681 ug/L               0.307    5.4
```

Method print for the determination of Cr according to procedure b

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB_243  .mth         OPERATION SEQUENCE
 Title : Determination of Chromium on epoxy graphite el.RDE
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    SMPL/M               V.fraction          mL    V.total             mL
 2    DOS/M                V.add         5.000 mL
 3    RDE                  Rot.speed      3000 /min
 4    SEGMENT              Segm.name   dumming
 5    (ADD
 6      (REP
 7        SEGMENT          Segm.name   regener
 8        SEGMENT          Segm.name   regener
 9        SEGMENT          Segm.name   regener
10        SEGMENT          Segm.name   regener
11        SEGMENT          Segm.name   regener
12        SEGMENT          Segm.name   swp
13        STIR             Rot.speed      3000 /min
14        0MEAS            U.standby           mV
15      REP)1
16      ADD>M              Soln.name   Cr_std          V.add         0.200 mL
17    ADD)2
18    END

 Method: AB_243               SEGMENT
                               regener
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    DCTMODE              t.step         0.10 s     t.meas         40.0 ms
 2    MEAS                 U.meas          350 mV
 3    DSWEEP         3.7   U.start         350 mV     U.step          12 mV
                           U.end           -50 mV     Sweep rate     120 mV/s
 4    END
 Method: AB_243               SEGMENT
```

swp

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	DCTMODE		t.step	0.10 s	t.meas	40.0 ms
2	MEAS	60.0	U.meas	350 mV		
3	0STIR					
4	MEAS	10.0	U.meas	350 mV		
5	SSWEEP	10.3	U.start	350 mV	U.step	4 mV
			U.end	-50 mV	Sweep rate	40 mV/s
6	END					

Method: AB_243 SEGMENT dumming

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	DCTMODE		t.step	0.10 s	t.meas	40.0 ms
2	MEAS	60.0	U.meas	350 mV		
3	DSWEEP	10.3	U.start	350 mV	U.step	4 mV
			U.end	-50 mV	Sweep rate	40 mV/s
4	END					