

Ready to use solutions

- Diluted sulphuric acid, $c(\text{H}_2\text{SO}_4) = 1.0 \text{ mol/L}$
- Sodium diethyl dithiocarbamate solution, $w(\text{NaDDTC}) = 2 \%$ in water
The solution should always be filtered before use.
- Potassium hydrogen phthalate buffer pH 4.0, $c(\text{potassium hydrogen phthalate}) = 0.05 \text{ mol/L}$
- Potassium permanganate solution, $c(\text{KMnO}_4) = 0.02 \text{ mol/L}$

Digestion**Sulphite-free surface water, drinking water**

No special preparation is necessary. The samples can be analysed directly as described under "Analysis".

Slightly contaminated waste water

Here the exposure to UV rays 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 705 UV Digester during 1 h at 90°C.

Water containing also sulphite and Cr(III) next to Cr(VI)

In an acidic sulphide 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 sulphuric 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. sulphuric 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 sulphuric acid is finally evaporated down to about 0.5 mL. Digestion is now completed, and the sample may be allowed to cool.

Biological matter and waste water containing a high proportion of organic matter and chlorides

In the presence of sulphuric 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 sulphite 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 sulphuric acid and heat to boiling-point.
- Continue adding KMnO_4 drop by drop until the pink colouring remains. While keeping the total volume constant by adding small amounts of water, allow the solution to boil approx. 5 min.
- Add NaOH 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 $\text{K}_2\text{S}_2\text{O}_8$:

Another possibility is the oxidation with the employment of $\text{K}_2\text{S}_2\text{O}_8$.

- Add 10 mL distilled water and a spatula-tip of $\text{K}_2\text{S}_2\text{O}_8$ to the cooled sulphuric 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 peroxodisulphate must be foiled off, otherwise traces of peroxide will interfere with the analysis.

Oxidation with UV in the 705 UV Digester:

Another possibility is the exposure to UV irradiation 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.

Literature

- 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

Method 1

Polarographic determination of Cr concentrations > 10 µg/L

Principle

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

Reagents

All of the used reagents must be of purest quality possible (p.a. or suprapur). Only high purity water should be used.

- Potassium hydroxide, w(KOH) = 45%
- Ammonia solution, w(NH₃) = 5%
- Acetic acid, puriss p.a., w(CH₃COOH) = 96 - 100 %
- Ethylene diamine, CAS 107-15-3
- Cr standard stock solution: β(Cr⁶⁺) = 1 g/L (commercially available)
- Working standard solutions:
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 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 polarogram is recorded with following parameters:

working electrode	SMDE
drop size	4
stirrer speed	2000 rpm
mode	DP
equilibration time	3 s
purge time	600 s
pulse amplitude	50 mV
start potential	+ 100 mV
end potential	- 170 mV
voltage step	4 mV
voltage step time	0.60 s
sweep rate	6.67 mV/s
peak potential	- 0.04 V

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

Remarks

- The solution has to be degassed for min. 10 min to prevent interferences from oxygen.
- The determination limit 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 analysed without digestion.

Figures

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===== 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	OPURGE			
2	OSTIR	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	OMEAS		U.standby mV	
8	REP)1			
9	PURGE			
10	STIR		Rot.speed 2000 /min	
11	END			

Method: AB116_1

 SUBSTANCES
CrVI - pol

Recognition

U.verify	-40 mV
U.tol (+/-)	30 mV
U.width min	10 mV
U.width max	200 mV
I.threshold	200 pA

Display / Plot

I.scale	auto
U.div	50.00 mV/cm
U.begin	80 mV
U.end	-160 mV

Baseline

Type	linear
Scope	whole
dU.front	auto
S.front	auto
dU.rear	auto
S.rear	auto

Evaluation

Mode	VA
Quantity	I.peak
Sign. digits	4

Calibration 1999-05-28 12:17:00

Technique	std.add.
Curve type	linear

Coefficients

Y.reg	-1.823e-08
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
Range max		g/L	g/L	g/L
M.conc./cm		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

Fig. 1 Method for the determination of Cr acc. to method 1 with the 746 VA Trace Analyzer

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===== 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
-----
    
```

```

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
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```

```

Substance : CrVI
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
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```

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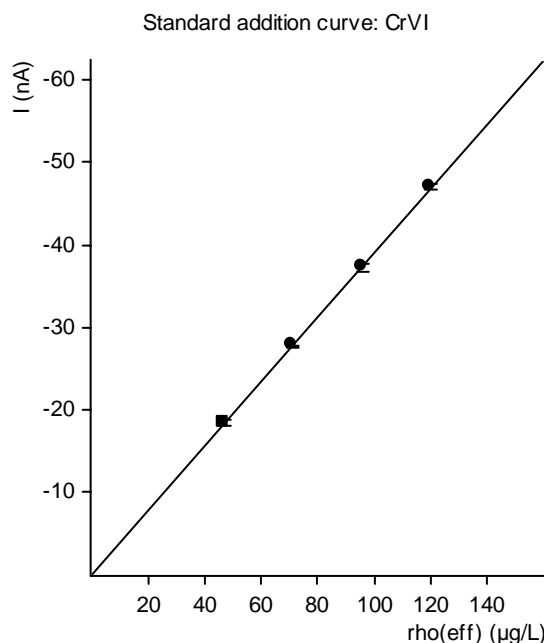
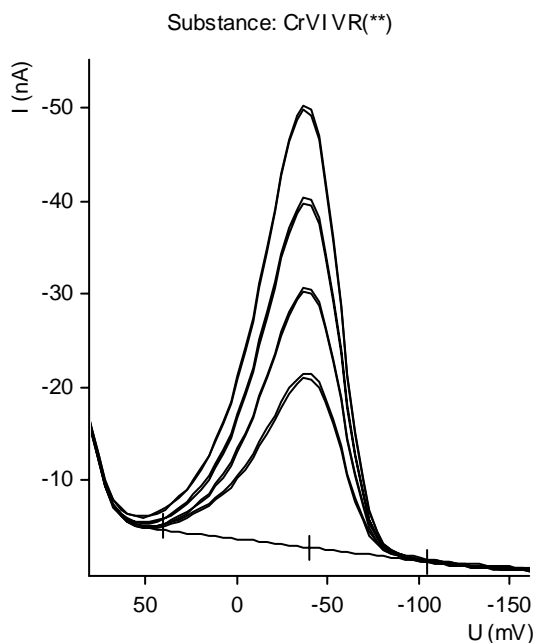


Fig. 2 Example of a determination of Cr according to method 1 with the 746 VA Trace Analyzer

Methods 2 + 3

Determination of Chromium Traces using Stripping Voltammetry

Principle

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 oxidised again catalytically into 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 (p.a. or suprapur). Only high purity water is to be used.

- Sodium acetate, suprapur
- Diethylenetriaminepentaacetate (DTPA), Titriplex™ V, puriss p.a., CAS 67-43-6
- Sodium nitrate, NaNO₃, suprapur
- Sodium hydroxide solution, suprapur, w(NaOH) = 30 %
- Cr standard stock solution: $\beta(\text{Cr}^{6+}) = 1 \text{ g/L}$ (commercially available)

Ready to use solutions

- Supporting electrolyte:
 - c(sodium acetate) = 0.2 mol/L
 - c(DTPA) = 0.05 mol/L
 - c(NaNO₃) = 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: for Cr concentrations between 0.02 and 1.5 µg/kg (ppb)

Standard addition solution

- Cr(VI) standard solution, $\beta(\text{Cr}^{6+}) = 0.02 \text{ mg/L}$
 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
 + 2.5 mL supporting electrolyte

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

The voltammogram is recorded using the following parameters:

working electrode	HMDE
stirrer speed	2000 rpm
drop size	7
mode	DP
purge time	300 s
deposition time	60 s
deposition potential	-1.0 V
equilibration time	10 s
pulse amplitude	50 mV
start potential	-1.0 V
end potential	-1.45 V
voltage step	10 mV
voltage step time	0.30 s
sweep rate	33.3 mV/s
peak potential	-1.25 V

The concentrations are determined by standard addition.

Figures

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
 Method: AB116_2 .mth OPERATION SEQUENCE
 Title : Chromium Determination. AB116 Part 2

	Instructions	t/s	Main parameters	Auxiliary parameters
1	DOS/M		V.added 2.500 mL	
2	SMPL/M		V.fraction mL	V.total L
3	STIR		Rot.speed 2000 /min	
4	PURGE	300.0		
5	(ADD			
6	PURGE			
7	STIR	10.0	Rot.speed 2000 /min	
8	SEGMENT		Segm.name DPCSV	
9	ADD>M		Soln.name Cr-Std	V.add 0.100 mL
10	ADD)2			
11	END			

Method: AB116_2 SEGMENT DPCSV

	Instructions	t/s	Main parameters	Auxiliary parameters
1	OPURGE			
2	(REP			
3	STIR	5.0	Rot.speed 2000 /min	
4	HMDE		Drop size 7	Meas.cell normal
5	DPMODE		U.ampl -50 mV	t.meas 20.0 ms
			t.step 0.30 s	t.pulse 40.0 ms
6	MEAS	60.0	U.meas -1000 mV	
7	OSTIR	10.0		
8	FSWEEP	14.7	U.start -1000 mV	U.step 10 mV
			U.end -1450 mV	Sweep rate 33.33 mV/s
9	OMEAS		U.standby mV	
10	STIR		Rot.speed 2000 /min	
11	REP)1			
12	PURGE			
13	END			

Method: AB116_2 SUBSTANCES CrVI - DPCSV

Recognition	Display / Plot
U.verify -1250 mV	I.scale auto
U.tol (+/-) 50 mV	U.div 50.00 mV/cm
U.width min 10 mV	U.begin -1050 mV
U.width max 400 mV	U.end -1450 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	Coefficients
1997-01-10 11:36:07	
Technique std.add.	Y.reg -4.639e-08
Curve type linear	Slope -0.1139
	Nonlin.
	Mean dev. 7.16e-09

Additions			
Soln.name	Cr-Std		
Mass conc.	20 ug/L	g/L	g/L
Range min	0 g/L	g/L	g/L
Range max	g/L	g/L	g/L
M.conc./cm	g/L	g/L	g/L

Method: AB116_2 CALCULATION max. 15 lines

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

Fig.3 Method for the determination of chromium acc. to method 2 with the 746 VA Trace Analyzer

===== METROHM 757 VA COMPUTRACE (5.757.0010) =====

Determ. : 11271032_tap water.dth
 Date : 2000-11-27 Time: 09:32:35
 Modified : 2000-11-29 13:42:17 User: Cell volume: 12.500 ml

Ident tap water Sample volume 10.000 ml

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

Substance : Cr(VI) Comments
 Mass conc.: 257.352 ng/l
 MC.dev.: 13.540 ng/l (5.26%)
 Mass : 3.217 ng
 Add.mass : 2.000 ng

VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
1-1	-1.208	-74.9	-73.7	1.795		
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	Nonlin.	Mean deviat.
Cr(VI)	std.add.	-7.383e-008	-2.874e-001		1.674e-009

Solutions

No.	Content	Vol. (ml)	Predose (ml)
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Final results	+/-	Res. dev.	%	Comments
Cr(VI) =	0.322 ug/l	0.017	5.261	

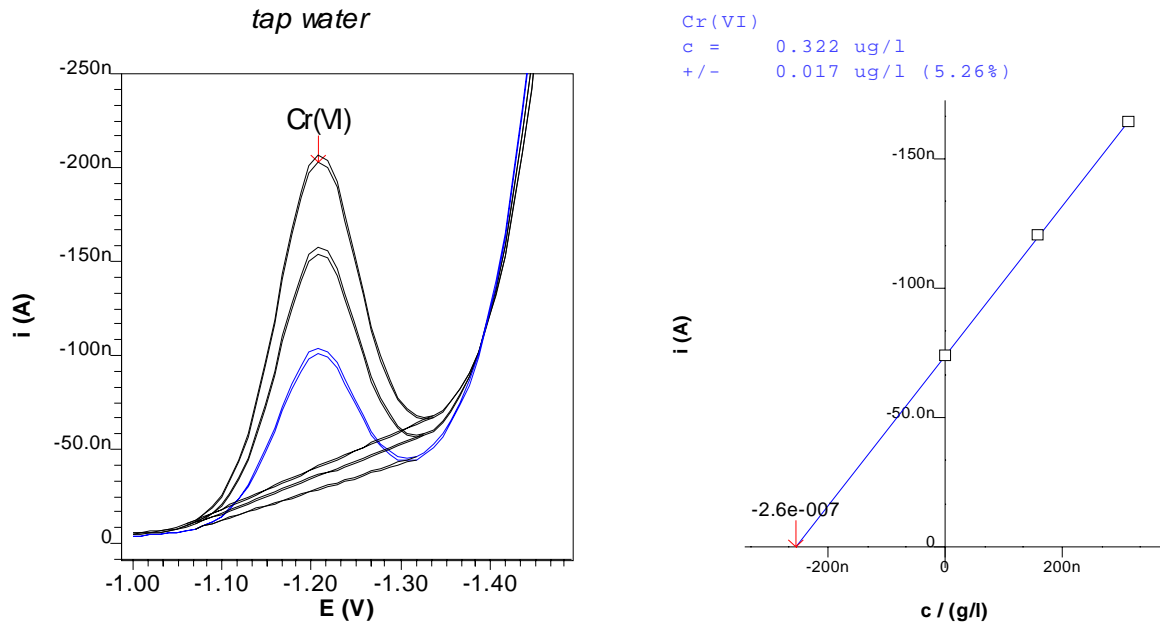


Fig. 4 Determination of chromium with the 757 VA Computrace

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

Standard addition solution

Cr(VI) standard solution, $\beta(\text{Cr}^{6+}) = 0.25 \text{ mg/L}$

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

+ 2.5 mL supporting electrolyte

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

The voltammogram is recorded using the following parameters:

working electrode	HMDE
stirrer speed	2000 rpm
drop size	7
mode	DP
purge time	300 s
equilibration time	10 s
pulse amplitude	50 mV
start potential	-1.0 V
end potential	-1.5 V
voltage step	10 mV
voltage step time	0.30 s
sweep rate	33.3 mV/s
peak potential	-1.25 V

The concentrations are determined by standard addition.

Remarks

- For methods 2+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.

Figures

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB116_3 .mth          OPERATION SEQUENCE
Title : Chromium Determination. AB116 Part 3
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	Instructions	t/s	Main parameters		Auxiliary parameters	
1	SMPL/M		V.fraction		V.total	L
2	DOS/M		V.added	2.500	mL	
3	PURGE					
4	STIR	300.0	Rot.speed	2000	/min	
5	(ADD					
6	PURGE					
7	STIR	30.0	Rot.speed	2000	/min	
8	OPURGE					
9	(REP					
10	STIR	5.0	Rot.speed	2000	/min	
11	OSTIR	5.0				
12	SEGMENT		Segm.name	DPCSV		
13	REP)1					
14	ADD>M		Soln.name	CrStd	V.add	0.050 mL
15	ADD)2					
16	END					

```

Method: AB116_3          SEGMENT
                        DPCSV
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	Instructions	t/s	Main parameters		Auxiliary parameters	
1	HMDE		Drop size	7	Meas.cell	normal
2	DPMODE		U.ampl	-50	t.meas	20.0 ms
			t.step	0.30	t.pulse	40.0 ms
3	SWEEP	14.7	U.start	-1000	U.step	10 mV
			U.end	-1450	Sweep rate	33.33 mV/s
4	END					

```

Method: AB116_3          SUBSTANCES
                        CrVI - DPCSV
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Recognition		Display / Plot	
U.verify	-1250 mV	I.scale	auto
U.tol (+/-)	50 mV	U.div	50.00 mV/cm
U.width min	10 mV	U.begin	mV
U.width max	200 mV	U.end	mV
I.threshold	200 pA		

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

Calibration		Coefficients	
Technique	std.add.	Y.reg	-1.575e-08
Curve type	linear	Slope	-0.01386
		Nonlin.	
		Mean dev.	7.335e-10

Additions				
Soln.name	CrStd			
Mass conc.	1.00	mg/L	g/L	g/L
Range min		g/L	g/L	g/L
Range max		g/L	g/L	g/L
M.conc./cm		g/L	g/L	g/L

```

Method: AB116_3          CALCULATION
                        max. 15 lines
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Quantity	Formula (R##, C##, A##)	Res.unit	Sig.dig.
CrVI	R1000=MC:CrVI	#g/L	5

Fig. 5 Method for the determination of chromium acc. to method 3 with the 746 VA Trace Analyzer

===== METROHM 757 VA COMPUTRACE (5.757.0010) =====

Determ. : 11271458_sea water.dth
 Date : 2000-11-27 Time: 13:58:48
 Modified : 2000-11-27 14:12:03 User: Cell volume: 12.500 ml

Ident : sea water Sample volume : 10.000 ml

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

Substance : Cr(VI) Comments
 Mass conc.: 1.272 ug/l
 MC.dev.: 0.072 ug/l (5.69%)
 Mass : 15.898 ng
 Add.mass : 12.500 ng

VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
1-1	-1.196	-47.5	-47.8	0.372		
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	Nonlin.	Mean deviat.
Cr(VI)	std.add.	-4.775e-008	-3.765e-002		3.719e-010

Solutions

No. Content Vol. (ml) Predose (ml)

Final results +/- Res. dev. % Comments
 Cr(VI) = 1.590 ug/l 0.090 5.688

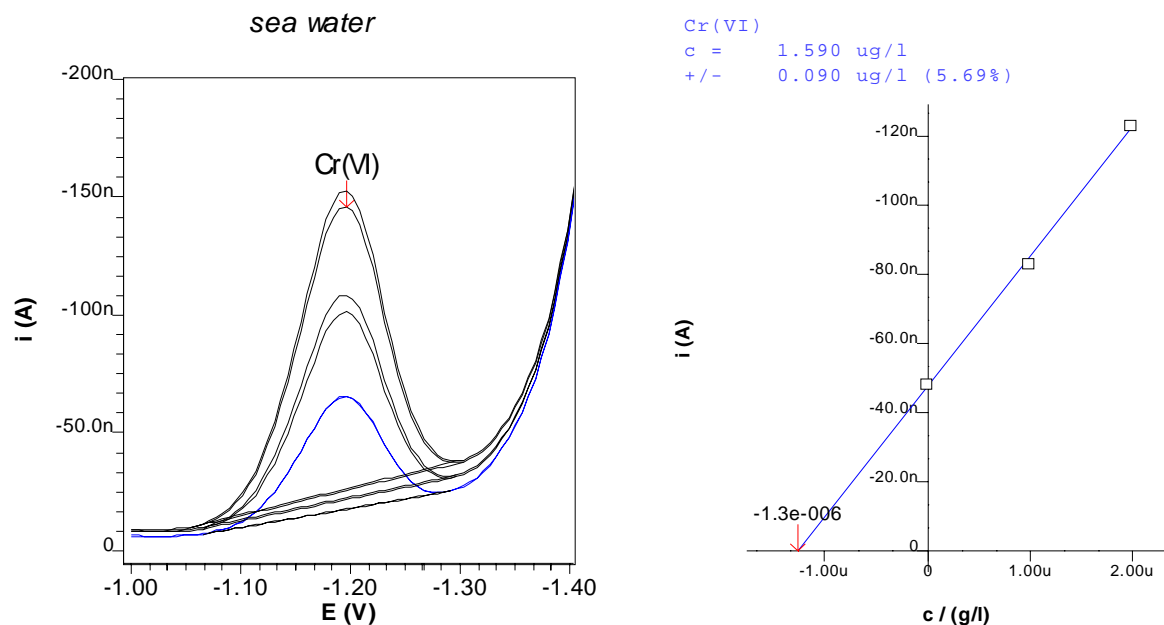


Fig. 6 Determination of chromium with the 757 VA Computrace