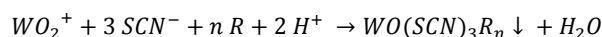
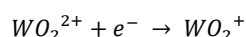


Determination of tungsten by anodic stripping voltammetry at the Ultra Trace graphite RDE

Summary

The method describes the determination of W(VI) traces in the range from 0.2 to 50 µg/L. Organic compounds present in the samples (e.g. natural waters) have an interfering effect. They have to be removed by UV digestion (e.g. 909 UV Digester). The interfering effect of Fe(III) up to a concentration of 100 mg/L is being eliminated by reduction to Fe(II) with ascorbic acid. When the amount of Cu(II) in the sample exceeds the amount of W(VI) 200 times or more, Cu ions have to be complexed with thiourea. The absolute concentration of Cu(II) should not exceed 5 mg/L. The determination is made by anodic stripping voltammetry (ASV) in DP mode.

W(VI) is deposited on the surface of the Ultra Trace graphite rotating disk electrode (RDE) as a result of electrochemical reduction of W(VI) and binding of the electrode reaction product W(V) into a low soluble ternary compound using antipyrine (ANT) or 4-dimethylaminoantipyrine (Pyramidon®, PYR) and thiocyanate ions: $WO(SCN)_3ANT_4$ or $WO(SCN)_3PYR_3$. The following equations can be used to describe the electrochemical reactions of W(VI):



with R being pyramidon or antipyrine. The maximal oxidation anodic current of the compound localized on the graphite electrode surface serves as the analytical response.

Instruments

VA instrument capable of operating a rotating disk electrode (RDE) and supporting differential pulse (DP) measuring mode	
909 UV Digester	2.909.0014

Electrodes

WE	Ultra Trace electrode tip	6.1204.180
	Driving axle for RDE	6.1204.x10
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L)	6.0728.x20

AE	Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.1245.010
	Glassy carbon rod	6.1247.000
	Electrode holder	6.1241.x20

Reagents

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

- Ammonium thiocyanate, NH_4SCN , for trace analysis*, CAS 1762-95-4
- Sodium hydroxide, for trace analysis*, CAS 1310-73-2
- Sulfuric acid, $w(H_2SO_4) = 96\%$, for trace analysis*, CAS 7664-93-9
- Antipyrine, (1,2-Dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one, phenazone), for analysis, CAS 60-80-0
- 4-dimethylaminoantipyrine, (Pyramidon®, 4-Dimethylamino-1,5-dimethyl-2-phenylpyrazol-3-one, aminophenazone), for analysis, CAS 58-15-1
- Ascorbic acid, (Vitamin C), for analysis, CAS 50-81-7
- Thiourea, CH_4N_2S , for analysis, CAS 62-56-6
- Sodium tungstate dihydrate, $Na_2WO_4 \cdot 2H_2O$, for trace analysis*, CAS 13472-45-2
- Ultrapure water, resistivity $>18 M\Omega \cdot cm$ (25 °C), type I grade (ASTM D1193)

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

Solutions

ANT solution	$w(ANT) = 20 \%$ An appropriate amount of antipyrine is dissolved in ultrapure water. The solution can be used for 1 week.
PYR	0.1 g 4-dimethylaminoantipyrine (dry weight, for 25 mL measuring solution)
Thiocyanate solution	$w(NH_4SCN) = 5 \%$ NH_4SCN is dissolved in ultrapure water.

Sodium hydroxide solution	c(NaOH) = 11 mol/L 440 g sodium hydroxide are dissolved and filled up to 1 L with ultrapure water.
Diluted sulfuric acid	c(H ₂ SO ₄) = 9 mol/L Concentrated sulfuric acid is diluted with ultrapure water.
Ascorbic acid solution	w(ascorbic acid) = 10 % An appropriate amount of ascorbic acid is dissolved in ultrapure water.
Thiourea	w(thiourea) = 5 % An appropriate amount of thiourea is dissolved in ultrapure water.

Standard solutions

W(VI) standard stock solution	$\beta(W^{6+}) = 1 \text{ g/L}$ Dissolve 1.7942 g of sodium tungstate dihydrate in 50 mL of ultrapure water. Add 50 mL of sodium hydroxide solution (c(NaOH) = 440 g/L) and transfer the solution into a 1 L measuring flask. Fill up to the mark with ultrapure water.
W(VI) standard solution	$\beta(W^{6+}) = 0.5 \text{ mg/L}$ Diluted solutions have to be prepared daily by dilution of the standard stock solution with ultrapure water.

Sample preparation

Organic-free natural waters

No special pretreatment is needed. Samples can be analyzed directly, as described the analysis section.

Waste waters with organic compounds

Organic matrices have to be destroyed by means of UV digestion (909 UV Digester) under following conditions:

pH of the sample between	1 ... 2
Duration of the pretreatment	2 hours
Temperature	90 °C
H ₂ O ₂ volume	100 µL per 10 mL sample

Biological materials

Biological materials have to be dissolved by a wet digestion with sulfuric acid and H₂O₂ (see Application Bulletin 113 for details of the digestion procedure). The resulting acid solution (4 mL concentrated sulfuric acid to 100 mL aqueous solution) can be analyzed as described under «Analysis» without adding any sulfuric acid.

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 voltammogram clean the electrode by applying 9 - 10 linear potential scans in the range 0.5 - 1.0 V (for ANT) or in the range 0.5 - 0.7 V (for PYR) under stirring of the solution.

Method 1: W concentrations between 0.2 and 2.0 µg/L

Antipyrine (ANT) is used to analyze samples with a W concentration between 0.2 ... 2.0 µg/L.

Analysis

Transfer 20 mL of the sample solution to a 25 mL volumetric flask. Add 1.0 mL - 2.0 mL sulfuric acid, 1 mL thiocyanate solution, 1.0 mL ANT solution, 0.1 mL - 0.2 mL ascorbic acid solution and 0.1 - 0.2 mL of thiourea solution. Stir the solution after adding each reagent. Fill up the measuring flask to the mark with ultrapure water and mix thoroughly.

Measuring solution

20 mL sample solution

1.0 ... 2.0 mL diluted sulfuric acid

1.0 mL thiocyanate solution

1.0 mL ANT solution

0.1 ... 0.2 mL ascorbic acid solution

0.1 ... 0.2 mL thiourea solution

→ make up to 25 mL with ultrapure water

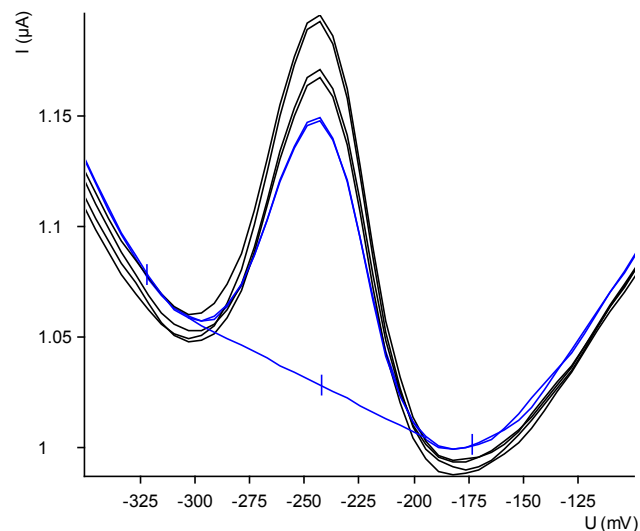
Pour the sample prepared into the polarographic vessel and run the voltammogram with the parameters specified below under «Parameters for the determination with ANT».

The tungsten content is determined by the standard addition method. Concentration and amounts of standard added depend on the W concentration in the sample.

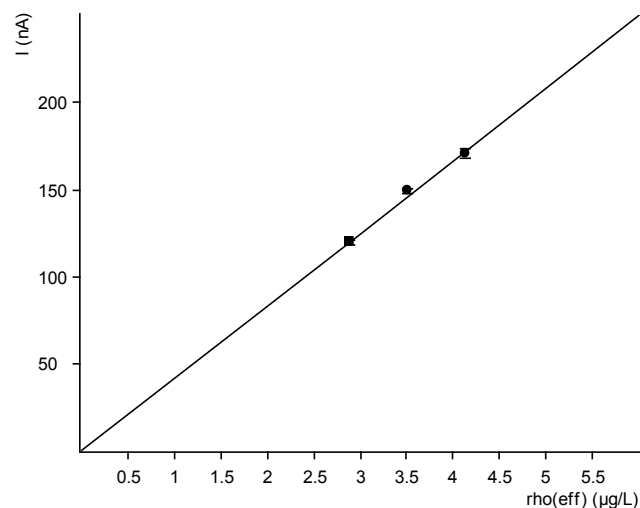
Parameters for the determination with ANT

Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min ⁻¹
<i>Cyclovoltammetric pretreatment</i>	
Start potential	0.5 V
Vertex potential	1.0 V
No. of cycles	10
<i>Potentiostatic pretreatment</i>	
Potential 1	-0.5 V
Waiting time 1	120 s
Equilibration time	10 s
<i>Sweep</i>	
Start potential	-0.4 V
End potential	-0.05 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	Tungsten
Characteristic potential	-0.23 V

Example



Standard addition curve: W6



Result

Sample size	20.0 mL
$\beta(\text{W}^{6+})$	2.89 $\mu\text{g/L}$

Comments

In case W(VI) is not present in the solution to be analyzed the reagent passivates the electrode surface. In case no analytical response is registered, proceed as following:

- Switch off the cell
- Clean the electrode surface mechanically
- Introduce standard additive to the sample
- Start the analyzing procedure from the beginning again

Method 2: W concentrations between 2 ... 50 µg/L

4-dimethylaminoantipyrine (PYP) is used to analyze samples with W concentration between 2.0 ... 50 µg/L.

Analysis

Transfer 20 mL of the sample solution to a 25 mL volumetric flask. Add 1.0 mL - 2.0 mL sulfuric acid, 1 mL ammonium thiocyanate, 0.1 g PYP, 0.1 mL - 0.2 mL ascorbic acid and 0.1 - 0.2 mL of thiourea. Stir the solution after adding each reagent. Fill up the measuring flask to the mark with high purity water and mix thoroughly.

Measuring solution

20 mL (diluted) sample solution
1.0 ... 2.0 mL diluted sulfuric acid
1.0 mL thiocyanate solution
0.1 g 4-dimethylaminoantipyrine (PYP)
0.1 ... 0.2 mL ascorbic acid solution
0.1 ... 0.2 mL thiourea solution
→ make up to 25 mL with ultrapure water

Pour the sample prepared into the polarographic vessel and run the voltammogram with the parameters specified below under «Parameters for the determination with PYP».

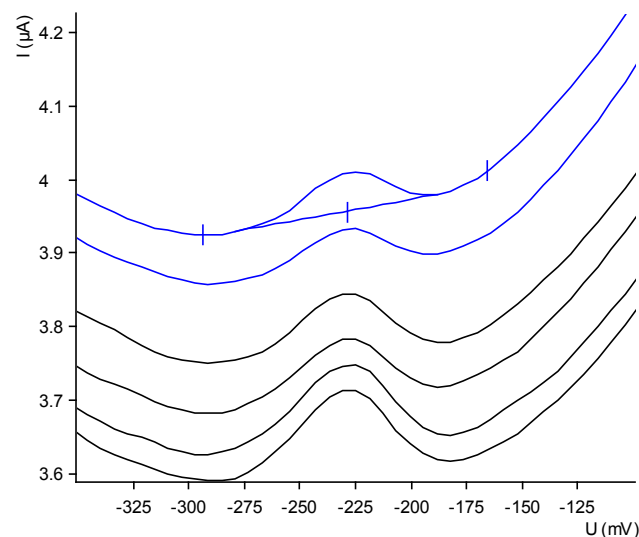
The tungsten content is determined by the standard addition method. Concentration and amounts of standard added depend on the W concentration in the sample.

Parameters for the determination with PYP

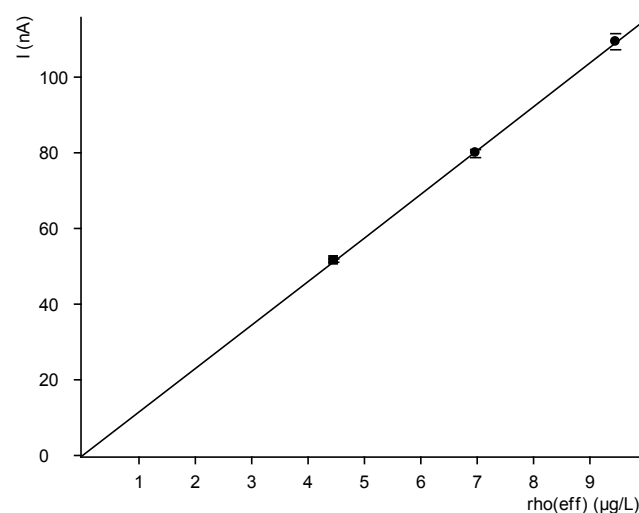
Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min ⁻¹
Cyclovoltammetric pretreatment	
Start potential	0.5 V
Vertex potential	0.7 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	-0.5 V
Waiting time 1	30 s
Equilibration time	10 s
Sweep	

Start potential	-0.4 V
End potential	-0.05 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	Tungsten
Characteristic potential	-0.23 V

Example



Standard addition curve: W6



Result

Sample size	20.0 mL
$\beta(W^{6+})$	5.57 µg/L

Comments

- In case W(VI) is not present in the solution to be analyzed the reagent passivates the electrode surface. In case no analytical response is registered, proceed as following:
 - Switch off the cell
 - Clean the electrode surface mechanically
 - Introduce standard additive to the sample
 - Start the analyzing procedure from the beginning again
- Samples with W concentration higher than 50 µg/L should be diluted with ultrapure water. The sample solution in the measuring vessel should contain maximum 1 µg W. If it contains more, the electrode surface will be overloaded.

References

Malakhova, N. A., Popkova, G. N., Wittmann, G., Kalnichevskaja, L. N., Brainina, Kh. Z., Anodic stripping voltammetry of tungsten at graphite electrodes, *Electroanalysis*, 1996 (8), 375 - 380

Appendix

Report for the example determination of tungsten according to method 1 with antipyrine (ANT)

```
===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Determ.      : 04271103      User:      Date: 1993-04-27
Modified     : 1994-05-11 15:29:23 Run : 0      Time: 11:03:09
Sample table: -
```

```
-----
Pos.  Ident.1/S1  Ident.2/S2  Ident.3/S3  Method.call  Sample size/S0
-----
Method : AB242EAN
Title  : Tungsten at Ultra Trace Graphite Electr.by ASV/ANT
Remark1 : 2N sulf+1mlCNS- +1ml anti20%/Depora Ref/UV pH2 2h 90 C
Remark2 : tel=4+2 min, add W(VI)=0.5ppb/0.1 ml asc,thio/3 min boiling
-----
```

```
Substance : W6
Mass conc.: 2.890 ug/L      Mass      : 57.8 ng
MC.dev.   : 0.198 ug/L (6.84%) Add.mass   : 12.5 ng
Cal.dev.  : -              V0.sample: 20 mL
Comments  -----
```

```
-----
VR  U/mV  I/nA  I.mean  Std.dev.  I.delta  Comments
-----
00 -242  118.9  119.7   1.168
01 -243  120.6
10 -242  149.9  149.0   1.334  29.23
11 -242  148.0
20 -242  172.7  170.6   3.006  21.63
21 -242  168.5
```

```
Substance  Techn.  Y.reg/offset  Slope  Nonlin.  Mean deviat.
-----
W6          std.add.  1.205e-07    0.04171  -----  2.601e-09
```

```
Final results      +/- Res.dev.  %  Comments
-----
W6 = 2.8900 ug/L    0.198  6.84
```

Method print for the determination of tungsten according to method 1 with antipyrine (ANT)

```
===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB242EAN.mth      OPERATION SEQUENCE
Title : Tungsten at Ultra Trace Graphite Electr.by ASV/ANT
-----
```

```
-----
Instructions  t/s  Main parameters  Auxiliary parameters
-----
1  SMPL/M      V.fraction      mL  V.total      L
2  RDE          Rot.speed      3000 /min
3  (REP
4  SEGMENT      Segm.name      dummy
5  SEGMENT      Segm.name      sweep
6  REP)1
7  (ADD
8  (REP
9  SEGMENT      Segm.name      sweep
10 SEGMENT      Segm.name      dummy
11 REP)1
12 (REP
13 SEGMENT      Segm.name      sweep
14 SEGMENT      Segm.name      W-seg
15 STIR          Rot.speed      3000 /min
16 REP)1
17 ADD>M        Soln.name      w.std      V.add      0.025 mL
18 ADD)2
19 END

Method: AB242EAN      SEGMENT
                        dummy
-----
```

```
-----
Instructions  t/s  Main parameters  Auxiliary parameters
-----
1  DPMODE      U.ampl      50 mV  t.meas      20.0 ms
2  MEAS        240.0      t.step      0.30 s  t.pulse      40.0 ms
3  DSWEEEP     23.4      U.meas      -500 mV
U.start      -500 mV  U.step      6 mV
U.end        -50 mV   Sweep rate  20 mV/s
```

4 END

Method: AB242EAN

SEGMENT

sweep

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	DCTMODE		t.step	0.10 s	t.meas	40.0 ms
2	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
3	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
4	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
5	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
6	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
7	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
8	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
9	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
10	DSWEEP	4.6	U.start	500 mV	U.step	12 mV
			U.end	1000 mV	Sweep rate	120 mV/s
11	END					

Method: AB242EAN

SEGMENT

W-seg

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	DPMODE		U.ampl	50 mV	t.meas	20.0 ms
			t.step	0.30 s	t.pulse	40.0 ms
2	MEAS	120.0	U.meas	-500 mV		
3	OSTIR					
4	MEAS	10.0	U.meas	-500 mV	U.step	6 mV
5	SWEEP	18.6	U.start	-400 mV	Sweep rate	20 mV/s
			U.end	-50 mV		
6	END					

Report for the example determination of tungsten according to method 2 with 4-dimethylaminoantipyrine (PYR)

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====

Determ. : 04261815

User:

Date: 1994-04-26

Modified : 1994-05-16 07:56:50 Run : 0

Time: 18:15:25

Sample table: -

Pos.	Ident.1/S1	Ident.2/S2	Ident.3/S3	Method.call	Sample size/S0
					20 mL

Method : AB242EPY

Title : Tungsten at Ultra Trace Graphite electr.by ASV/PYR

Remark1 : 2N sulf+1 mlCNS- +0.1g pyra/Lough Swilly N3/UV pH2+5ppb W 6+

Remark2 : tel = 90+30 sec, add W(VI)=2 ppb/0.1 ml asc,0.1 ml thio/boil

Substance : W6

Mass conc.: 4.458 ug/L

Mass : 89.16 ng

Comments

MC.dev. : 0.127 ug/L (2.85%)

Add.mass : 50 ng

Cal.dev. : -

V0.sample: 20 mL

VR	U/mV	I/nA	I.mean	Std.dev.	I.delta	Comments
00	-229	51.88	51.58	0.4158		
01	-229	51.29				
10	-230	78.79	79.53	1.036	27.94	
11	-228	80.26				
20	-228	107.1	108.6	2.141	29.05	
21	-228	110.1				

Substance	Techn.	Y.reg/offset	Slope	Nonlin.	Mean deviat.
W6	std.add.	5.149e-08	0.01155		9.372e-10

Final results

+/- Res.dev. %

Comments

W6 = 5.5722 ug/L

0.159 2.85

Method print for the determination of tungsten according to method 2 with 4-dimethylaminoantipyrine (PYR)

```
===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB242EPY.mth          OPERATION SEQUENCE
Title : Tungsten at Ultra Trace Graphite electr.by ASV/PYR
-----
```

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	SMPL/M		V.fraction	20.000 mL	V.total	25.0 mL
2	RDE		Rot.speed	3000 /min		
3	(REP					
4	SEGMENT		Segm.name	dummy		
5	SEGMENT		Segm.name	sweep		
6	REP)1					
7	(ADD					
8	SEGMENT		Segm.name	dummy		
9	SEGMENT		Segm.name	sweep		
10	(REP					
11	SEGMENT		Segm.name	sweep		
12	SEGMENT		Segm.name	W-seg		
13	STIR		Rot.speed	3000 /min		
14	REP)1					
15	ADD>M		Soln.name	w.std	V.add	0.100 mL
16	ADD)2					
17	END					

```
Method: AB242EPY          SEGMENT
                           dummy
-----
```

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	DPMODE		U.ampl	50 mV	t.meas	20.0 ms
			t.step	0.30 s	t.pulse	40.0 ms
2	MEAS	90.0	U.meas	-500 mV		
3	DSWEEP	23.4	U.start	-500 mV	U.step	6 mV
			U.end	-50 mV	Sweep rate	20 mV/s
4	END					

```
Method: AB242EPY          SEGMENT
                           sweep
-----
```

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	DCTMODE		t.step	0.10 s	t.meas	40.0 ms
2	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
3	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
4	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
5	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
6	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
7	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
8	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
9	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
10	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
11	DSWEEP	2.1	U.start	500 mV	U.step	12 mV
			U.end	700 mV	Sweep rate	120 mV/s
12	END					

```
Method: AB242EPY          SEGMENT
                           W-seg
-----
```

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	DPMODE		U.ampl	50 mV	t.meas	20.0 ms
			t.step	0.30 s	t.pulse	40.0 ms
2	MEAS	30.0	U.meas	-500 mV		
3	OSTIR					
4	MEAS	10.0	U.meas	-500 mV	U.step	6 mV
5	SWEEP	18.6	U.start	-400 mV	Sweep rate	20 mV/s
			U.end	-50 mV		
6	END					