
Application Bulletin

Of interest to: General analytical laboratories, Waters, Metals B 1, 2, 6, 9, 10, 15, 16
Energy, Environmental protection, Trace analysis

Determination of titanium and uranium by voltammetry

Summary

This bulletin describes extremely sensitive methods for the determination of titanium and uranium. They are especially suitable for the analysis of ground, drinking, sea, surface and cooling waters, in which the concentration of these elements is of importance. The methods can, of course, also be used for the trace analysis in other matrices.

Titanium is determined by adsorptive stripping voltammetry (AdSV) with mandelic acid as complexing agent. The determination limit lies at 0.5 µg/L.

Also uranium is determined as chloranilic acid complex with adsorptive stripping voltammetry. Here the determination limit lies in low-chloride media at 50 ng/L, in seawater at 1 µg/L and in high-chloride media in a ppm range, after the chloride has been removed by means of a sulphate-loaded ion exchanger.

Apparatus and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
- 757 VA Computrace

Sample preparation

Organic matter often interferes with voltammetric determinations and therefore sample solutions usually have to be digested.

- Ground water, surface waters, mineral waters and drinking waters can usually be analysed without pre-treatment.
- Low polluted waste waters can be digested with the 705 UV-Digester. Add 50 - 100 µL w(H₂O₂) = 30% and 10 µL w(HCl) = 30% to 10 mL acidified sample (pH = 2) and irradiate for 1h at 90°C. After cooling to room temperature, the digested sample can be transferred directly to the polarographic vessel.
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
 - High-pressure asher
 - Microwave digestionBoth techniques oxidise the sample in a closed digestion vessel by means of a mixture of concentrated mineral acids.
 - According to AB 113, open wet digestion with H₂SO₄ and H₂O₂

Literature

- Henze G., Sander S.
Adsorption voltammetric techniques for the determination of uranium(VI) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone as complex forming reagent
Fresenius J Anal Chem (1994) 349:654-658
- Henze G., Sander S., Wagner W.
Direct Determination of Uranium Traces by Adsorptive Stripping Voltammetry
Universitäten Kaiserslautern und Trier 1994
- Henze G., Sander S.
Chloranilsäure als Komplexbildner für die Ultraspurenanalyse von Elementen durch Adsorptions-Stripping-Voltammetrie
GIT Fachz. Lab. 12/96
- Van den Berg, C.M.G.
Potentials and potentialities of cathodic stripping voltammetry of trace elements in natural waters.
Anal. Chim. Acta (1991) 250: 265-276
- Yokoi, K. Van den Berg, C.M.G.
Determination of titanium in sea water using catalytic cathodic stripping voltammetry
Anal. Chim. Acta (1991) 245: 2/ 167-176
- Li, H., Van den Berg, C.M.G.
Determination of Titanium in sea water using adsorptive cathodic stripping voltammetry
Anal. Chim. Acta (1989) 221/2 269-277
- Metrohm Application Bulletin 113

Method 1

Titanium determination

Theory

Titanium forms a complex with mandelic acid which can be determined by adsorptive stripping voltammetry.

Reagents

All of the used reagents must be of purest quality possible (analytical grade or suprapur). Only ultrapure water should be used.

- DL-mandelic acid, puriss p.a., CAS 611-72-3
- Ammonia solution, suprapur, $w(\text{NH}_3) = 25\%$
- Ti standard stock solution, $\beta(\text{Ti}) = 1 \text{ g/L}$ (commercially available)

Ready-to-use solutions

- Mandelic acid solution: $c(\text{mandelic acid}) = 0.4 \text{ mol/L}$
6.1 g mandelic acid are dissolved in 100 mL ultrapure water. The solution is stable for 1 week.
- diluted ammonia solution: $w(\text{NH}_3) = 10\%$
The ammonia solution is diluted with ultrapure water as appropriate.
- Ti Standard 1mg/L:
The standard stock solution is diluted with $c(\text{HCl}) = 0.1 \text{ mol/L}$. The standard has to be prepared anew daily.

Analysis

Measuring solution

10 mL (diluted) sample
+ 1 mL mandelic acid solution

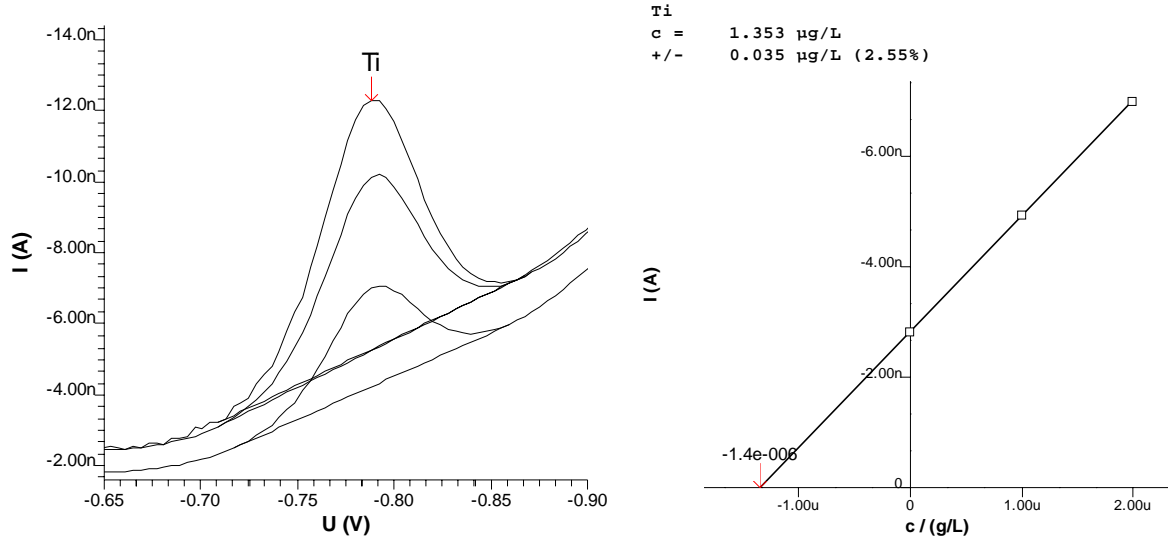
Adjust the pH value to 3.0 with $w(\text{NH}_3) = 10\%$.

The voltammogram is recorded with the following parameters:

Working electrode	HMDE
Stirrer/RDE	2000 rpm
Drop size	4
Measurement mode	DP
Purge time	300 s
Pulse amplitude	0.05 V
Deposition potential	- 0.57 V
Deposition time	30 s
Equilibration time	5 s
Start potential	- 0.57 V
End potential	- 0.95 V
Voltage step	0.004 V
Voltage step time	0.2 s
Sweep rate	0.02 V/s
Peak potential (Ti)	- 0.79 V

The concentration is determined by standard addition.

Figures



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===== METROHM 757 VA COMPUTRACE (5.757.0020) =====
Determ.      : 11021144_Sea Water Ti.dth
Sample ID    : Sea Water Ti
Creator      : ---
Date         : 1999-11-02
Time        : 11:44:42
Modified by  : zu
Date        : 2001-07-05
Time        : 08:43:10
User        : zu
Date        : 2001-07-05
Time        : 08:43:11
    
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Cell volume: 11.000 mL
Sample amount: 10.000 mL
    
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Method : Ti Determination.mth
Title  : Ti i n Sea Water
Remark1 : 10 mL Seawater + 1mL Mandelic Acid 0.4 mol/L
Remark2 : NH3 10% --->pH 3
    
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Substance : Ti
Mass conc.: 1.230 ug/L
MC.dev.   : 0.031 ug/L ( 2.55%)
Mass      : 13.534 ng
Add.mass  : 10.000 ng
Comments  : -----
    
```

VR	V	nA	I.mean	Std.Dev.	I.delta	Comments
1-1	-0.788	-2.785	-2.824	0.055		
1-2	-0.788	-2.863				
2-1	-0.788	-4.916	-4.954	0.053	-2.130	
2-2	-0.788	-4.992				
3-1	-0.788	-7.024	-7.003	0.050	-2.049	
3-2	-0.788	-6.982				

Substance	Calibr.	Y.reg/offset	Slope	Std.Dev.
Ti	std.add.	-2.837e-009	-2.305e-003	5.214e-011

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Final results
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Ti:
Titanium = 1.353 µg/L 0.035 2.554
    
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Fig. 1 Titanium determination in seawater with the 757 VA Computrace

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB266_1 .mth OPERATION SEQUENCE
Title : Determination of Titanium. AB266 Method 1
    
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	Instructions	t/s	Main parameters	Auxiliary parameters
1	SMPL>M		V.fraction mL	V.total L
2	DOS>M		Soln.name mandelic	V.add 1.000 mL
3	PURGE			
4	STIR	30.0	Rot.speed 2000 /min	
5	(ADD			
6	PURGE			
7	STIR	10.0	Rot.speed 2000 /min	
8	OPURGE			
9	(REP			
10	SEGMENT		Segm.name Ti_AdSV	
11	REP)2			
12	PURGE			
13	ADD>M		Soln.name Ti_Std	V.add 0.010 mL
14	ADD)1			
15	END			

Method: AB266_1 SEGMENT Ti_AdSV

	Instructions	t/s	Main parameters	Auxiliary parameters
1	STIR	5.0	Rot.speed 2000 /min	
2	HMDE		Drop size 4	Meas.cell normal
3	DPMODE		U.ampl -50 mV	t.meas 20.0 ms
			t.step 0.20 s	t.pulse 40.0 ms
4	MEAS	30.0	U.meas -570 mV	
5	OSTIR	5.0		
6	SWEEP	19.6	U.start -570 mV	U.step 4 mV
			U.end -950 mV	Sweep rate 20 mV/s
7	OMEAS		U.standby mV	
8	END			

Fig. 2 Parameters for the determination of titanium with the 746 VA Trace Analyzer

Method 2

Uranium determination

Theory

Uranium forms a complex with chloranilic acid which can be determined by adsorptive stripping voltammetry.

Reagents

All of the used reagents must be of purest quality possible (analytical grade or suprapur). Only ultrapure water should be used.

- Chloranilic acid (2,5- dichloro-3,6-dihydro-1,4-benzoquinone), puriss p.a. CAS 87-88-7
- Sulfuric acid, suprapur, w(H₂SO₄) = 96 %
- Sodium hydroxide solution, suprapur, w(NaOH) = 30 %
- U standard stock solution, β(U) = 1 g/L (commercially available)

Ready-to-use solutions

- CAA solution: $c(\text{chloranilic acid}) = 5 \cdot 10^{-3} \text{ mol/L}$
0.104 g chloranilic acid are dissolved in 100 mL ultrapure water.
- diluted sulfuric acid: $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$
Sulfuric acid is diluted with ultrapure water as appropriate.
- U standard solution: $\beta(\text{U}) = 1 \text{ mg/L}$
The standard stock solution is diluted with $c(\text{H}_2\text{SO}_4) = 0.002 \text{ mol/L}$.

Analysis
Measuring solution

10 mL (diluted) sample
+ 0.1 mL CAA solution

Adjust the pH value to 2.5 ± 0.1 with $w(\text{NaOH}) = 30 \%$ or $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$.

The voltammogram is recorded with the following parameters:

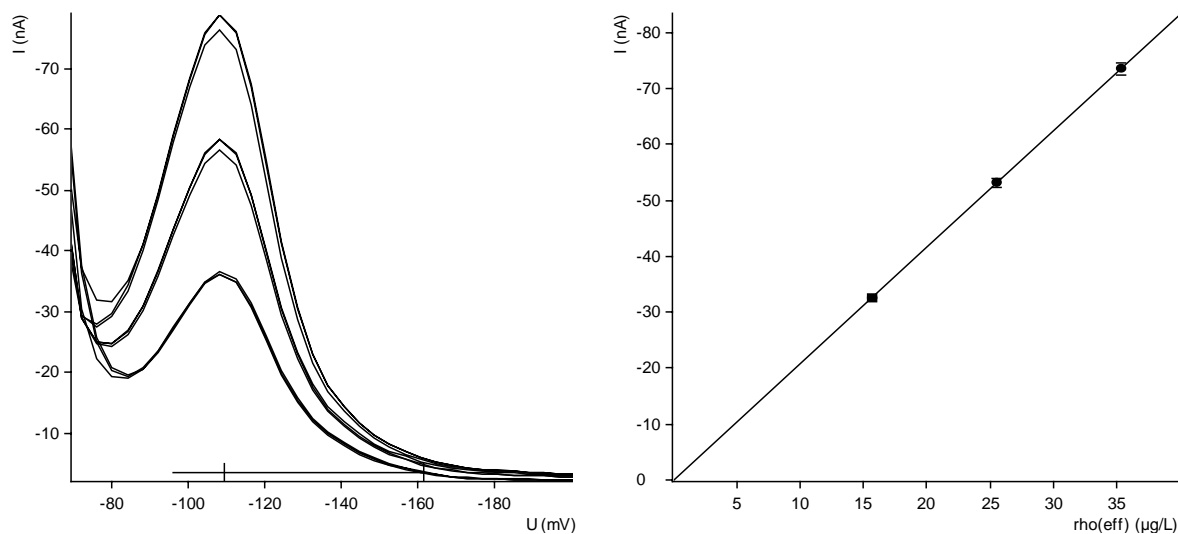
Working electrode	HMDE
Stirrer/RDE	2000
Drop size	7
Measurement mode	DP
Purge time	300 s
Pulse amplitude	0.05 V
Deposition potential	- 0.04 V
Deposition time	15 s
Equilibration time	5 s
Start potential	- 0.04 V
End potential	- 0.3 V
Voltage step	0.004 V
Voltage step time	0.1 s
Sweep rate	0.04 V/s
Peak potential (U)	- 0.11 V

The concentration is determined by standard addition.

Remarks

- The uranium concentration in the vessel should not exceed 500 ng absolute (with standard additions). If concentrations are higher, either the sample must be diluted or the analysis must be done at the SMDE.
- Higher uranium concentrations also require more CAA.
- Mo, Sb, Sn and V form CAA complexes as well. These do not interfere with the determination, do, however, perhaps require more CAA solution.

Figures



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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Determ.      : 06091533          User: zu          Date: 1998-06-09
Modified     : no                Run : 0            Time: 15:33:20
Sample table: -
    
```

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Pos.  Ident.1/S1  Ident.2/S2  Ident.3/S3  Method.call  Sample size/S0
-----
      Seawater   pH2.47
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Method : U_AdSV
Title  : Determination of Uranium
Remark1 : 50 uL seawater + 9.95 mL H2O + 0.1 mL CAA solution -> pH 2.47
Remark2 :
    
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Substance : Uranium
Mass conc.: 3.179 mg/L          Mass      : 158.9 ng
MC.dev.   : 0.092 mg/L (2.91%) Add.mass   : 100 ng
Cal.dev.  : -                  V0.sample: 50 uL
Comments  : -----
    
```

VR	U/mV	I/nA	I.mean	Std.dev.	I.delta	Comments
00	-110	-32.51	-32.53	0.1934		
01	-110	-32.35				
02	-110	-32.74				
10	-109	-51.53	-52.53	0.8722	-19.99	
11	-109	-52.93				
12	-109	-53.13				
20	-108	-70.72	-72.07	1.173	-19.54	
21	-109	-72.81				
22	-109	-72.68				

Substance	Techn.	Y.reg/offset	Slope	Nonlin.	Mean deviat.
Uranium	std.add.	-3.255e-08	-0.002078		7.961e-10

Final results	+/- Res.dev.	%	Comments
Uranium = 3.1788 mg/L	0.092	2.91	

Fig. 3 Uranium determination with the 746 VA Trace Analyzer

