Metrohm

Application Bulletin 266/2 e

Determination of titanium by adsorptive stripping voltammetry

Summary

This Application Bulletin describes the determination of titanium by adsorptive stripping voltammetry (AdSV) using mandelic acid as complexing agent. The method is suitable for the analysis of ground, drinking, sea, surface and cooling waters, in which the concentration of titanium is of importance. The methods can, of course, also be used for the trace analysis in other matrices.

The limit of detection is approx. 0.5 µg/L.

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

Reagents

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

- DL-mandelic acid, for analysis, CAS 611-72-3
- Ammonia solution, $w(NH_3)$ = 25 %, for trace analysis*, CAS 1336-21-6
- Ti standard stock solution, $\beta(Ti)$ = 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

Mandelic acid solution	c(mandelic acid) = 0.4 mol/L 6.1 g mandelic acid are dissolved in 100 mL ultrapure water. The solution is stable for 1 week.
Diluted ammonia solution	$w(NH_3)$ = 10%

Standard solutions

Ti standard solution	$\beta(Ti)$ = 1 mg/L The standard stock solution is diluted with c(HCl) = 0.1 mol/L. The standard has to be prepared fresh daily.

Sample preparation

- Ground water, surface waters, mineral waters and drinking waters can usually be analyzed without pre-treatment.

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

- Low polluted waste waters can be digested with the 909 UV Digester.
  - Add 50 - 100 µL $w(H_2O_2)$ = 30% and 10 µL w(HCl) = 30% to 10 mL acidified sample (pH = 2) and irradiate for 90 min 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 digestion

  Both techniques oxidize the samples in a closed digestion vessel by means of a mixture of concentrated mineral acids.

Analysis

Measuring solution

10 mL (diluted) sample

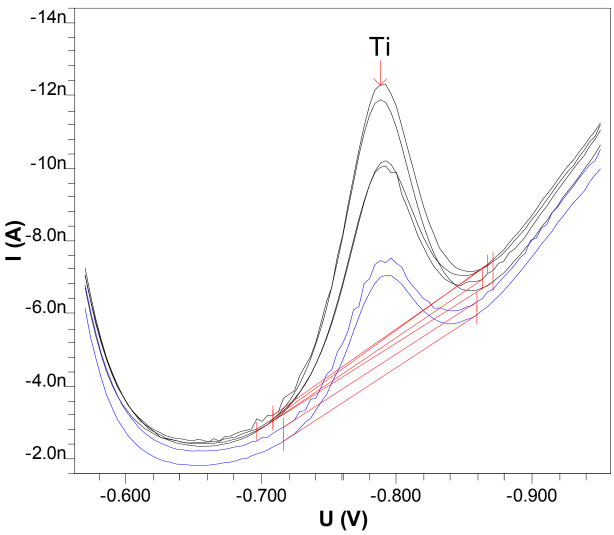
1 mL mandelic acid solution

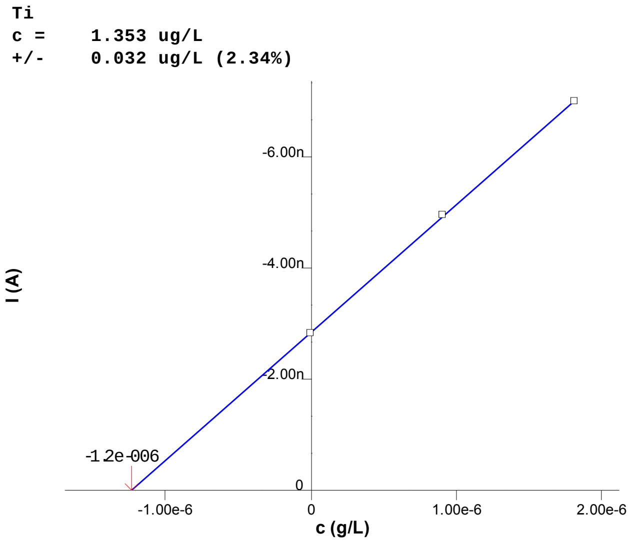
Adjust the pH value to 3.0 with $w(NH_3) = 10\%$.

Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.57 V
Waiting time 1	30 s
Equilibration time	10 s
Sweep	
Start potential	-0.57 V
End potential	-0.95 V
Potential step	0.004 V
Potential step time	0.2 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V
Substance	
Name	Ti
Characteristic potential	-0.79 V

Example





```
Ti
c =     1.353 ug/L
+/-     0.032 ug/L (2.34%)
```

Result

Sample	Sea water
Sample size	10.0 mL
β(Ti)	1.4 µg/L

References

- 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

Appendix

Report for the example determination titanium in seawater

```
==================== 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
--------------------------------------------------------------------------------
 Cell volume:   11.000 mL
 Sample amount: 10.000 mL
--------------------------------------------------------------------------------
 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
--------------------------------------------------------------------------------
  Substance : Ti                                             Comments
  Mass conc.:    1.230  ug/L                                 ------------------
  MC.dev.   :    0.031  ug/L      (    2.55%)
  Mass      :   13.534  ng
  Add.mass  :   10.000  ng

              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


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

 Ti:
 Titanium          =    1.353  µg/L    0.035        2.554
```

Method print for the determination of titanium

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB266 Det of Ti.mth
Title           : Determination of Titanium. AB266 method 1
Remark1         : 10 mL sample + 1 mL mandelic acid --> pH 3
Remark2         :

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : sample
Sample amount (mL): 10.000
Cell volume (mL): 11.000

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)                :   -1.200
End potential (V)                  :   -0.100
No. of cycles                      :        0

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :   -0.100
Cleaning time (s)                  :    0.000
Deposition potential (V)           :   -0.570
Deposition time (s)                :   30.000

Sweep
Equilibration time (s)             :    5.000
Start potential (V)                :   -0.570
End potential (V)                  :   -0.950
Voltage step (V)                   :    0.004
Voltage step time (s)              :    0.200
Sweep rate (V/s)                   :    0.020
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
--------------------------------------------------------------------------------
Ti                         : -0.790 V   +/- 0.050 V

Standard solution          : 1   1.000 mg/L
Addition volume (mL)       : 0.010

Titanium                   : Final result (Ti) =
                             Conc * (11 / 10) * (1e+006 / 1) + 0 - 0

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