Metrohm

Application Bulletin 123/4 e

Determination of manganese in water samples by anodic stripping voltammetry

Summary

A sensitive methods to determine manganese is described. It is primarily suitable for the investigation of ground, drinking and surface waters, in which the concentration of manganese is important. The method can naturally also be used for trace analysis in other matrices.

Manganese is determined in an alkaline borate buffer by the anodic stripping voltammetry (ASV). Interference by intermetallic compounds is prevented by the addition of zinc ions in the sample. The limit of determination lies at β(Mn) = 2 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
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*).

- Hydrochloric acid, w(HCl) = 30 %, for trace analysis*, CAS 7647-01-0
- Ammonia solution, w(NH_3) = 25 %, for trace analysis*, CAS 1336-21-6
- Sodium hydroxide solution, w(NaOH) = 30%, for trace analysis*, CAS 1310-73-2
- Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10\ H_20$, for analysis*, CAS 1303-96-4
- Mn standard stock solution, $\beta(Mn^{2+})$ = 1 g/L commercially available
- Zn standard stock solution, $\beta(Zn^{2+})$ = 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

Electrolyte	c($Na_2B_4O_7$) = 0.1 mol/L c(NaOH) = 0.3 mol/L 3.81 g $Na_2B_4O_7$. 10 H_20 are dissolved in 50 mL water. Add 3 mL sodium hydroxide solution and fill up to 100 mL with ultrapure water.
Zinc solution	β(Zn) = 100 mg/L Add 100 µL conc. hydrochloric acid to 10 mL Zn stock solution and fill up to 100 mL with water.

Standard solution

Mn standard solution	β(Mn) = 10 mg/L Add 100 µL conc. hydrochloric acid to 1 mL Mn stock solution and fill up to 100 mL with water.

Sample preparation

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

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 µL hydrogen peroxide solution w(H_2O_2) = 30% and 10 µL hydrochloric acid w(HCl) = 30% to 10 mL acidified sample (pH = 2) and irradiate for 90 minutes at 90°C.

- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
  - High-pressure asher
  - Microwave digestion
  - Both techniques oxidize the sample in a closed digestion vessel by means of a mixture of concentrated mineral acids.
  - Open wet digestion with H_2SO_4 and H_2O_2 according to Application Bulletin 113.

Analysis

Measuring solution

10 mL (diluted) sample

50 µL ammonia solution

2.5 mL supporting electrolyte

10 µL Zn solution

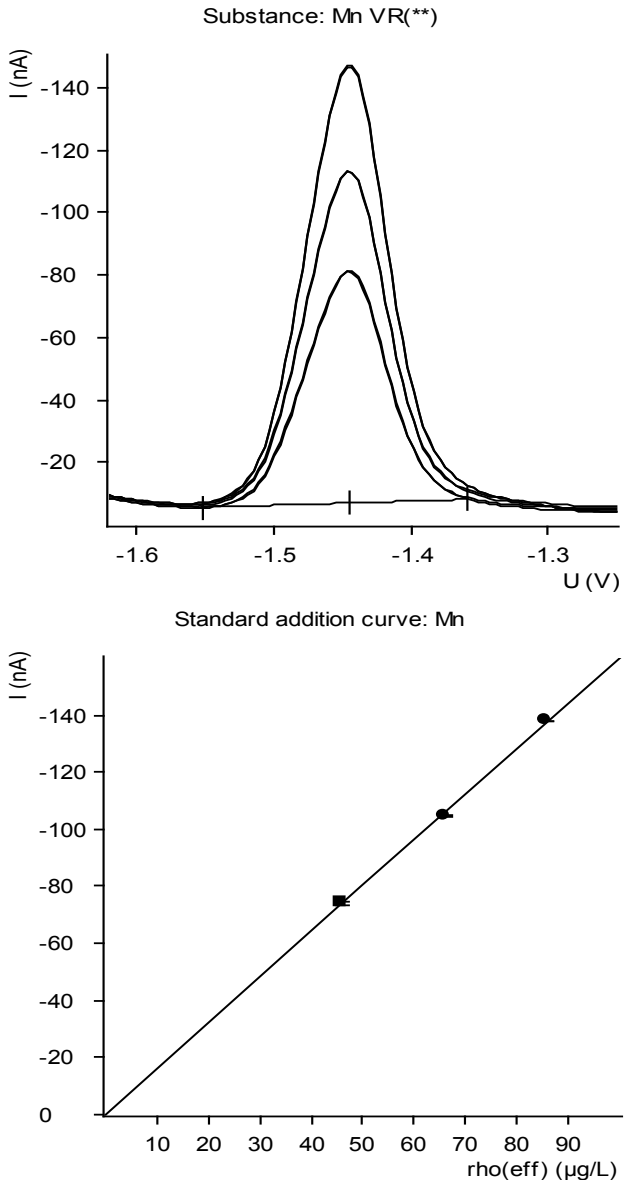
If necessary, the pH is adjusted to 9.5 ... 10 with ammonia solution.

The concentration is determined by the standard addition method.

Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-1.7 V
Waiting time 1	90 s
Equilibration time	5 s
Sweep	
Start potential	-1.62 V
End potential	-1.25 V
Potential step	0.004 V
Potential step time	0.5 s
Sweep rate	0.008 V/s
Pulse amplitude	**-0.075 V**
Substance	
Name	Mn
Characteristic potential	-1.44 V

Example



Results

Sample	Tap water
Sample size	10.0 mL
β(Mn)	57.8 µg/L

Comments

It is essential to use a negative pulse amplitude for this determination.

References

- Monien H., Jacob P.
  Voltammetrische Bestimmung kleiner Eisenmengen ohne Abtrennung der Matrix.
  Fresenius Z. Anal. Chem. 260, (1972) 195-202
- Davidson W.
  Comparison of differential pulse and D.C. sampled polarography for the determination of ferrous and manganeous ions in lake water.
  J. Electroanal. Chem. 72, (1976) 229-237
- Colombini M.P., Fluoco R.
  Determination of manganese in ng/ml levels in natural waters by differential pulse polarography.
  Talanta 30, (1983) 901-905; Ref: Metrohm Info 3/84, 14
- Huang Z.Q., Van den Berg C.M.G.
  Determination of iron in seawater using cathodic stripping voltammetry preceeded by adsorptive collection with the hanging mercury drop electrode.
  J. Electroanal. Chem. 177, (1984) 269-280; Ref: Metrohm-Info 1/85, 19
- Weidenauer M., Lieser K.H.
  Bestimmung von Spurenelementen in Flusswasser mit Hilfe der Voltammetrie.
  Fresenius, Z. Anal. Chem. 320, (1985) 550-555
- Wang J., Mahmoud J.
  Chelate adsorption of trace voltammetric measurements of iron(III).
  Fresenius, Z. Anal., Chem. 327, (1987) 789-793
- Labuda J., Vanickova M., Beinrohr E.
  Determination of dissolved manganese in natural waters by differential pulse cathodic stripping voltammetry.
  Mikrochim. Acta 1989/I, 113-120; Ref: Fresenius, Z. Anal. Chem. 335, (1989) 433

Appendix

Report for the example determination of manganese in tap water

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 05180901             User:                     Date: 1999-05-18
 Modified    : 2000-11-30 18:27:52  Run :  0                  Time: 09:01:26
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        water                                                        10 mL
--------------------------------------------------------------------------------
 Method  :  AB123
 Title   :  Determination of Manganese in Waters. AB123
 Remark1 :  Determination of manganese in water
 Remark2 :  10 ml sample + NH3 buffer + borate buffer + Zn standard
--------------------------------------------------------------------------------

  Substance : Mn                                          Comments
  Mass conc.:    57.83 ug/L            Mass     : 578.3 ng   ------------------
  MC.dev.   :     1.28 ug/L (2.22%)    Add.mass :   250 ng
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -1444  -74.42  -74.10   0.4504
              01   -1445  -73.78
              10   -1445  -104.7  -104.4   0.4077   -30.29
              11   -1445  -104.1
              20   -1445  -137.2  -137.2   0.1228   -32.86
              21   -1445  -137.3

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Mn           std.add.     -7.365e-08    -0.001600                 8.389e-10

                                SOLUTIONS
                                 max. 40
--------------------------------------------------------------------------------

  Soln.name    Pos.    Std.subst.   Mass conc.       Remark
  ---------    ----    ----------   -------------    -------------------------
  PbStd          -     Pb                 1 g/L     from: Pb


 C#  Workg.com.var  Remark
 --  -------------  ----------------

 Final results                       +/- Res.dev.   %      Comments
 ---------------------------------   -----------------     ------------------
        Mn =   57.825 ug/L               1.28    2.22
```

Method print for the determination of manganese

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB123 .mth         OPERATION SEQUENCE
 Title : Determination of Manganese in Waters. AB123
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    SMPL>M               V.fraction          mL     V.total              L
 2    DOS>M                Soln.name   ammonia        V.add         0.050 mL
 3    DOS>M                Soln.name   borate         V.add         2.500 mL
 4    DOS>M                Soln.name   Zn-std         V.add         0.010 mL
 5    PURGE
 6    STIR          300.0  Rot.speed      2000 /min
 7    (ADD
 8      PURGE
 9      STIR        20.0   Rot.speed      2000 /min
10      0PURGE
11      SEGMENT            Segm.name   DPAdSV
12      ADD>M              Soln.name   MnStd          V.add         0.025 mL
13    ADD)2
14    END

 Method: AB123_2              SEGMENT
                                DPAdSV
--------------------------------------------------------------------------------
```

	Instructions	t/s	Main parameters		Auxiliary parameters	
1	(REP					
2	STIR		Rot.speed	2000 /min		
3	DME	10.0				
4	HMDE		Drop size	7	Meas.cell	normal
5	HMDE		Drop size	7	Meas.cell	normal
6	HMDE		Drop size	7	Meas.cell	normal
7	HMDE		Drop size	4	Meas.cell	normal
8	DPMODE		U.ampl	-75 mV	t.meas	20.0 ms
			t.step	0.50 s	t.pulse	40.0 ms
9	MEAS	90.0	U.meas	-1700 mV		
10	0STIR	5.0				
11	SWEEP	48.0	U.start	-1620 mV	U.step	4 mV
			U.end	-1250 mV	Sweep rate	8 mV/s
12	0MEAS		U.standby	mV		
13	REP)1					
14	END					

Method: AB123_2 SUBSTANCES

Mn - DPAdSV

Recognition		Display / Plot	
U.verify	-1440 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	2000-11-30 18:31:53	Coefficients	
Technique	std.add.	Y.reg	-7.365e-08
Curve type	linear	Slope	-0.0016
		Nonlin.	
		Mean dev.	8.389e-10

Additions

Soln.name	MnStd			
Mass conc.	10 mg/L	g/L	g/L	g/L
Range min	g/L	g/L	g/L	g/L
Range max	g/L	g/L	g/L	g/L
M.conc./cm	g/L	g/L	g/L	g/L

Method: AB123_2 CALCULATION

max. 15 lines

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