

## Voltammetric determination of iron and manganese

Of interest to:

General analytical laboratories; Water analysis; Pharmaceutical industry; Food analysis

B 1, 2, 4, 7, 9

---

### Summary

Very sensitive methods to determine iron and manganese are described. They are primarily suitable for the investigation of ground, drinking and surface waters, in which the concentration of these metals is important. The methods can naturally also be used for trace analysis in other matrices.

Iron is determined in form of its catechol complex by AdSV. The limit of determination lies at  $\beta(\text{Fe}) = 5 \mu\text{g/L}$ .

Manganese is determined in an alkaline borate buffer by the ASV method. Interference by intermetallic compounds is prevented by the addition of zinc ions in the sample. The limit of determination lies at  $\beta(\text{Mn}) = 2 \mu\text{g/L}$ .

### 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 pretreatment.
- Low polluted waste waters can be digested with the 705 UV-Digester.  
Add 50  $\mu\text{L}$  hydrogen peroxide solution  $w(\text{H}_2\text{O}_2) = 30\%$  and 10  $\mu\text{L}$  hydrochloric acid  $w(\text{HCl}) = 30\%$  to 10 mL acidified sample ( $\text{pH} = 2$ ) and irradiate for 60 minutes at  $90^\circ\text{C}$ .
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
  - High-pressure asher
  - Microwave digestion  
Both techniques oxidise the sample in a closed digestion vessel by means of a mixture of concentrated mineral acids.

- Open wet digestion with  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  According to Application Bulletin 113.

### Literature

- 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 manganese 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 preceded 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
-

# 1. Determination of iron

## Principle

Iron is determined as catechol complex by adsorptive stripping voltammetry at the HMDE. The method is extremely sensitive. The standard additions are not linear any more in amounts of 200 ng in the measuring vessel. In these cases the sample has to be diluted or the analysis has to be done at the SMDE with DP polarography. Fe(II) and Fe(III) are analysed together. Especially with this method reagents of high purity have to be used. Even small concentrations of surfactants (detergents, organic complexing agents like humic acids etc.) interfere severely. They have to be digested before the analysis. Lower contaminated samples are treated with the 705 UV Digester. Samples with higher concentrations of organic substances have to be wet digested (refer to Application Bulletin 113).

## Reagents

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

- Hydrochloric acid, suprapur:  $w(\text{HCl}) = 30\%$
- Sodium dihydrogene phosphate, waterfree,  $\text{NaH}_2\text{PO}_4$ , suprapur, CAS 7558-80-7
- Disodium hydrogen phosphate, waterfree,  $\text{Na}_2\text{HPO}_4$ , suprapur, CAS 7558-79-4
- Catechol (Brenzkatechin, Pyrocatechol, 1,2-Dihydroxybenzol), CAS 120-80-9

Catechol can be purified by recrystallisation from toluene. It is also possible to make a sublimation of the catechol. Pyrocatechol Fluka No. 15890 can be used directly.

- Fe standard stock solution:  $\beta(\text{Fe}^{3+}) = 1 \text{ g/L}$ , commercially available

## Ready to use solutions

Phosphate buffer pH 7.0	$c(\text{NaH}_2\text{PO}_4) = 0.2 \text{ mol/L}$ $c(\text{Na}_2\text{HPO}_4) = 0.3 \text{ mol/L}$ <i>23.996 g/L <math>\text{NaH}_2\text{PO}_4</math> and 42.594 g/L <math>\text{Na}_2\text{HPO}_4</math> are dissolved in ultrapure water. The solution is stable for approx. 1 month.</i>
Catechol solution	$c(\text{catechol}) = 1 \text{ mol/L}$ <i>2.75 g catechol are dissolved in 25 mL deoxygenated ultrapure water under passage of nitrogen. The solution must be stored in the dark and allowed to stand for 1 h before use. The stability of the solution depends on the purity of the substance and ranges from one to several days.</i>

Fe standard solution	$\beta(\text{Fe}) = 10 \text{ mg/L}$  <i>Add 100 <math>\mu\text{L}</math> conc. HCl to 1.00 mL Fe stock solution and fill up to 100 mL with ultrapure water.</i>
----------------------	--

## Analysis

10 mL sample solution  
 + 100  $\mu\text{L}$  catechol solution or some catechol crystals  
 + 1 mL phosphate buffer pH 7.0

The voltammogram is recorded with the following parameters depending on the concentration:

### a) From 5 to 100 $\mu\text{g/L}$ Fe

working electrode	HMDE
drop size	7
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential	-300 mV
deposition time	60 s
equilibration time	5 s
pulse amplitude	50 mV
start potential	-200 mV
end potential	-550 mV
voltage step	4 mV
voltage step time	0.4 s
sweep rate	10 mV/s
peak potential	-380 mV

### b) From 100 $\mu\text{g/L}$ to 100 mg/L Fe

working electrode	SMDE
drop size	4
stirrer speed	2000 rpm
mode	DP
purge time	300 s
equilibration time	10 s
pulse amplitude	50 mV
start potential	-200 mV
end potential	-550 mV
voltage step	4 mV
voltage step time	0.4 s
sweep rate	10 mV/s
peak potential	-380 mV

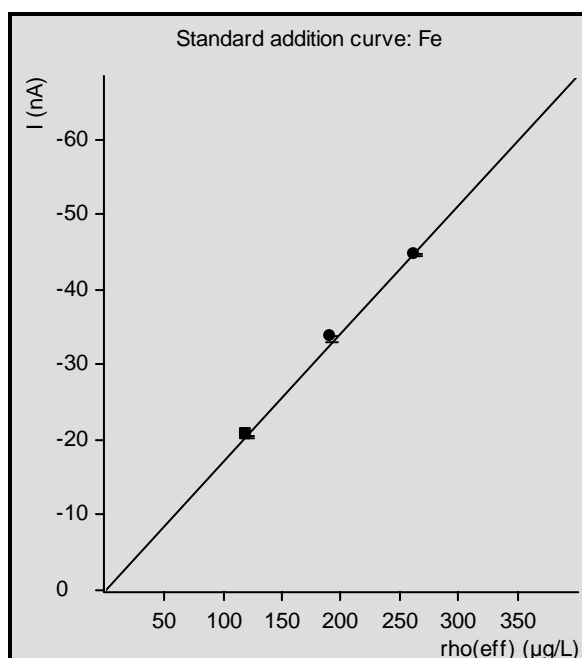
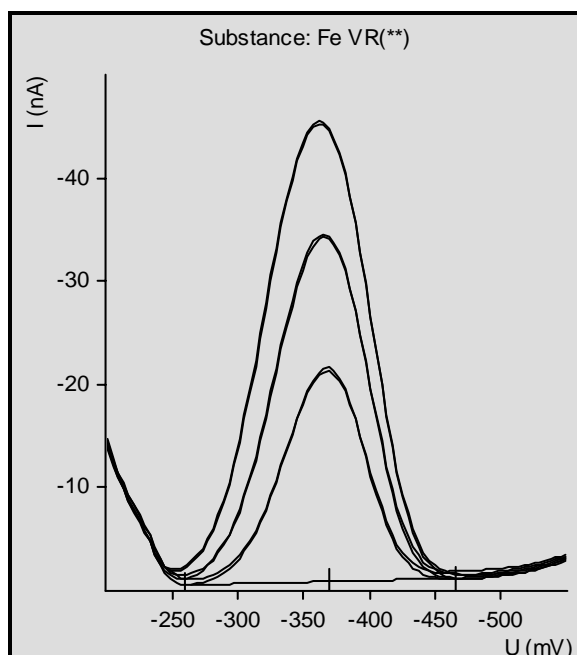
### c) Over 100 mg/L Fe

Samples with concentrations over 100 mg/L Fe have to be diluted.

The concentration is determined by standard addition.

**Example:**

**Determination of iron in tap water**



Sample volume 10 mL

Result 128  $\mu\text{g/L}$  Fe

**Remarks**

- The addition of catechol can be carried out using a solution as described above. This is recommended for automatic operation using a sample changer. In manual operation approx. 3 crystals of catechol can be dissolved directly in the acidic sample.
- Alternatively to the described phosphate buffer is PIPES buffer can be used instead. This method is described in Application Bulletin 74. Then copper and vanadium can be determined together with iron.
- Phosphate buffer has to be added after the addition of catechol. Otherwise insoluble iron phosphates can be formed, which cannot be determined voltammetrically.

**Appendix**

**Full report of a determination of iron in tap water with the 746 VA Trace Analyzer**

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Determ.      : 06281559      User:      Date: 1999-06-28
Modified     : 1999-06-28 15:59:32  Run : 0      Time: 15:59:19
Sample table: -
-----
  Pos.  Ident.1/S1  Ident.2/S2  Ident.3/S3  Method.call  Sample size/S0
-----
         water
-----
Method   : AB123_1
Title    : Determination of Iron in Waters. AB123 Part 1
Remark1  : Determination of iron in water
Remark2  : 10mL sample + 50uL catechol (1 mol/L) + 0.5mL phosph buff
-----
Substance : Fe
Mass conc.: 128.1 ug/L      Mass      : 1.281 ug
MC.dev.   : 6.12 ug/L (4.78%)  Add.mass  : 750 ng
Cal.dev.  : -              V0.sample: 10 mL
-----
      VR   U/mV   I/nA   I.mean  Std.dev.  I.delta  Comments
-----
      00  -369  -20.48 -20.40   0.1208
      01  -369  -20.31
      10  -367  -33.59 -33.27   0.4580  -12.87
      11  -367  -32.94
      20  -364  -44.01 -44.02   0.0158  -10.75
      21  -364  -44.03
-----
Substance  Techn.      Y.reg/offset  Slope      Nonlin.      Mean deviat.
-----
Fe         std.add.      -2.072e-08   -1.706e-04
-----
Final results      +/- Res.dev.  %      Comments
-----
Fe = 128.13 ug/L      6.12  4.78
  
```

**Method print for the determination of iron with the 746 VA Trace Analyzer according to method 1a**

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB123_1.mth          OPERATION SEQUENCE
Title : Determination of Iron in Waters. AB123 Part 1
-----
Instructions  t/s  Main parameters  Auxiliary parameters
-----
1  DOS/M  V.added  0.550 mL
2  REM    PIPES buffer
3  SMPL/M  V.fraction  mL  V.total  L
4  PURGE
5  STIR    300.0  Rot.speed  2000 /min
6  (ADD
7  PURGE
8  STIR    60.0  Rot.speed  2000 /min
9  OPURGE
10 SEGMENT  Segm.name  DPAdSV
11 ADD>M  Soln.name  FeStd  V.add  0.050 mL
12 ADD)2
13 END

Method: AB123_1          SEGMENT
                        DPAdSV
-----
Instructions  t/s  Main parameters  Auxiliary parameters
-----
1  (REP
2  STIR    5.0  Rot.speed  2000 /min
3  HMDE    Drop size  7
4  DPMODE  U.ampl  -50 mV  Meas.cell  normal
                    t.meas  20.0 ms
5  MEAS    60.0  U.meas  -300 mV  t.pulse  40.0 ms
6  OSTIR   5.0
7  FSWEPT  31.2  U.start  -200 mV  U.step  4 mV
                    U.end  -500 mV  Sweep rate  10 mV/s
                    U.standby mV
8  OMEAS
9  REP)1
10 END

Method: AB123_1          SUBSTANCES
                        Fe  - DPAdSV
-----
Recognition  Display / Plot
-----
U.verify  -380 mV  I.scale  auto
U.tol (+/-)  50 mV  U.div  50.00 mV/cm
U.width min  10 mV  U.begin  -350 mV
U.width max  400 mV  U.end  -600 mV
I.threshold  100 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 18:25:14  Coefficients
-----
Technique  std.add.  Y.reg  -2.957e-09
Curve type  linear  Slope  -0.0001733
                    Nonlin.
                    Mean dev.  9.713e-11

Additions
-----
Soln.name  FeStd
-----
Mass conc.  10 mg/L  g/L  g/L  g/L
Range min  0 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_1          CALCULATION
                        max. 15 lines
-----
Quantity  Formula (R##, C##, A##)  Res.unit  Sig.dig.
-----
Fe  R1000=MC:Fe  #g/L  5
  
```

## 2. Determination of manganese

### Reagents

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

- Hydrochloric acid suprapur:  $w(\text{HCl}) = 30\%$
- Ammonia solution suprapur:  $w(\text{NH}_3) = 25\%$
- Sodium hydroxide solution, suprapur,  $w(\text{NaOH}) = 30\%$
- Di-sodium tetraborate decahydrate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ , puriss p.a., CAS 1303-96-4
- Mn standard stock solution,  $\beta(\text{Mn}^{2+}) = 1 \text{ g/L}$  commercially available
- Zn standard stock solution,  $\beta(\text{Zn}^{2+}) = 1 \text{ g/L}$  commercially available

### Ready to use solutions

Supporting electrolyte	$c(\text{Na}_2\text{B}_4\text{O}_7) = 0.1 \text{ mol/L}$ $c(\text{NaOH}) = 0.3 \text{ mol/L}$ <i>3.81 g <math>\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}</math> are dissolved in 50 mL water. Add 3 mL sodium hydroxide solution and fill up to 100 mL with dist. water.</i>
Zinc solution	$\beta(\text{Zn}) = 100 \text{ mg/L}$ <i>Add 100 <math>\mu\text{L}</math> conc. hydrochloric acid to 10 mL Zn stock solution and fill up to 100 mL with water.</i>
Mn standard solution	$\beta(\text{Mn}) = 10 \text{ mg/L}$ <i>Add 100 <math>\mu\text{L}</math> conc. hydrochloric acid to 1 mL Mn stock solution and fill up to 100 mL with water.</i>

### Analysis

- 10 mL (diluted) sample
- + 50  $\mu\text{L}$  ammonia solution
- + 2.5 mL supporting electrolyte
- + 10  $\mu\text{L}$  Zn solution

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

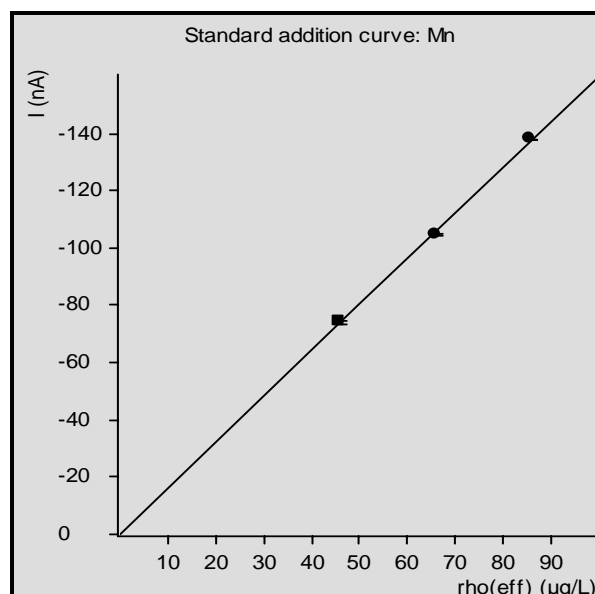
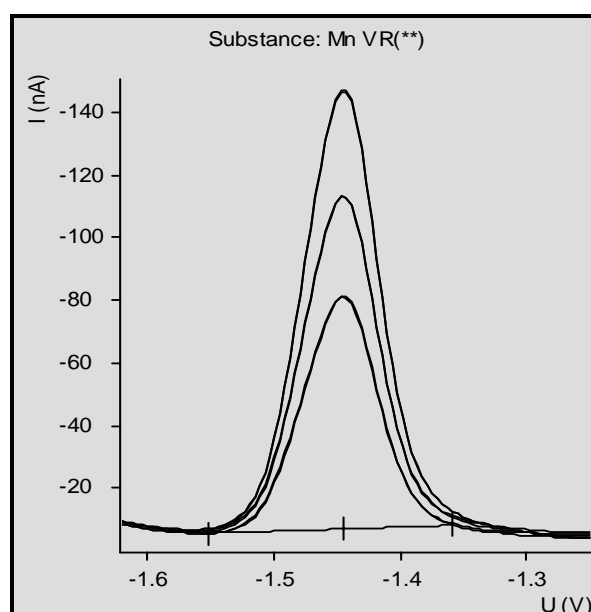
working electrode	HMDE
drop size	4
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential	-1700 mV
deposition time	90 s
equilibration time	5 s
pulse amplitude	<b>-75 mV</b>
start potential	-1620 mV
end potential	-1250 mV

voltage step	4 mV
voltage step time	0.5 s
sweep rate	8 mV/s
peak potential	-1440 mV

The content is determined by the standard addition method.

### Example:

#### Determination of manganese in tap water



Sample volume 10 mL

Result 57.8  $\mu\text{g/L}$  Mn

### Remarks

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

### Appendix

#### Full report of a determination of manganese in tap water with the 746 VA Trace Analyzer

```

===== 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_2
Title  : Determination of Manganese in Waters. AB123 Part 2
Remark1 : Determination of manganese in water
Remark2 : 10 ml sample + NH3 buffer + borate buffer + Zn standard
-----
Substance : Mn
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 with the 746 VA Trace Analyzer**

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB123_2.mth OPERATION SEQUENCE
Title : Determination of Manganese in Waters. AB123 Part 2
-----

```

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 OPURGE			
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 OSTIR	5.0		
11 SWEEP	48.0	U.start -1620 mV	U.step 4 mV
		U.end -1250 mV	Sweep rate 8 mV/s
12 OMEAS		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	Coefficients
2000-11-30 18:31:53	
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
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: AB123_2 CALCULATION max. 15 lines
-----

```

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