Application Bulletin 431/1 e

Determination of iron, copper and vanadium by adsorptive stripping voltammetry

Summary

This Application Bulletin describes the voltammetric determination of the elements iron, copper and vanadium. Fe as well as Cu and V can be determined as catechol complex at the HMDE by adsorptive stripping voltammetry (AdSV). Fe(II) and Fe(III) are determined as Fe(total) with the same sensitivity for both species in either phosphate buffer or PIPES electrolyte. Cu and V can be determined in PIPES buffer.

The methods are primarily suitable for the investigation of ground, drinking and surface waters, in which the concentration of these metals is important. But the methods can naturally also be used for trace analysis in other matrices.

The limit of detection for all three elements in PIPES buffer is 0.5 ... 1 µg/L, for iron in phosphate buffer it is approx. 5 µg/L.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting DP mode	
909 UV Digester	

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

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 1 h 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.
  - o High-pressure asher
  - o Microwave digestion

  Both techniques oxidize the sample in a closed digestion vessel by means of a mixture of concentrated mineral acids.
  - o Open wet digestion with H_2SO_4 and H_2O_2 according to Application Bulletin 113.

Method 1: Determination of Fe with phosphate buffer

Iron is determined as a complex with catechol. With adsorptive stripping voltammetry at the HMDE concentrations down to 5 µg/L can be determined. For concentrations >100 µg/L the polarographic determination at the SMDE is recommended.

Reagents

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

- Sodium dihydrogen phosphate, water free, NaH_2PO_4, for trace analysis*, CAS 7558-80-7
- Disodium hydrogen phosphate, water free, Na_2HPO_4, for trace analysis*, CAS 7558-79-4

- Catechol (Pyrocatechol, Brenzkatechin, 1,2-Dihydroxybenzene), for analysis, CAS 120-80-9
- Iron standard stock solution, $\beta(Fe^{3+})$ = 1 g/L, commercially available
- Hydrochloric acid, suprapur: w(HCl) = 30%, for trace analysis*, CAS 7647-01-0
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Solutions

Phosphate buffer pH 7.0	$c(NaH_2PO_4)$ = 0.2 mol/L $c(Na_2HPO_4)$ = 0.3 mol/L 23.996 g NaH_2PO_4 and 42.594 g Na_2HPO_4 are dissolved and filled up to 1 L with ultrapure water. The solution has pH 6.6 and is stable for approx. 1 month.
Catechol solution	c(catechol) = 1 mol/L 2.75 g catechol are dissolved in 25 mL oxygen-free 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.

Standard solutions

Fe standard solution	$\beta(Fe^{3+})$ = 10 mg/L Add 0.1 mL conc. HCl to 1.00 mL Fe standard stock solution and fill up to 100 mL with ultrapure water.

Analysis

Measuring solution

10 mL (diluted) sample or digestion solution

100 µL catechol solution or some catechol crystals

1 mL phosphate buffer pH 7.0

The measuring solution should have pH 7 ± 0.1.

The concentration is determined by standard addition.

Parameters for 5 to 100 µg/L Fe

Voltammetric	
Electrode operating mode	HMDE
Drop size	7
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.3 V
Waiting time 1	60 s
Equilibration time	5 s
Sweep	
Start potential	-0.2 V
End potential	-0.55 V
Potential step	0.004 V
Potential step time	0.4 s
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Substance	
Name	Fe
Characteristic potential	-0.38 V

Parameters for 0.1 to 100 mg/L Fe

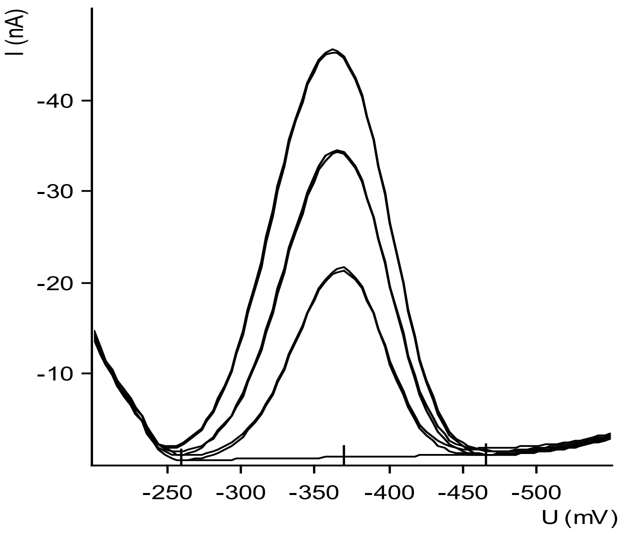
Voltammetric	
Electrode operating mode	SMDE
Drop size	4
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	10 s
Sweep	
Start potential	-0.2 V
End potential	-0.55 V
Potential step	0.004 V
Potential step time	0.4 s
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Substance	
Name	Fe
Characteristic potential	-0.38 V

Parameters for >100 mg/L Fe

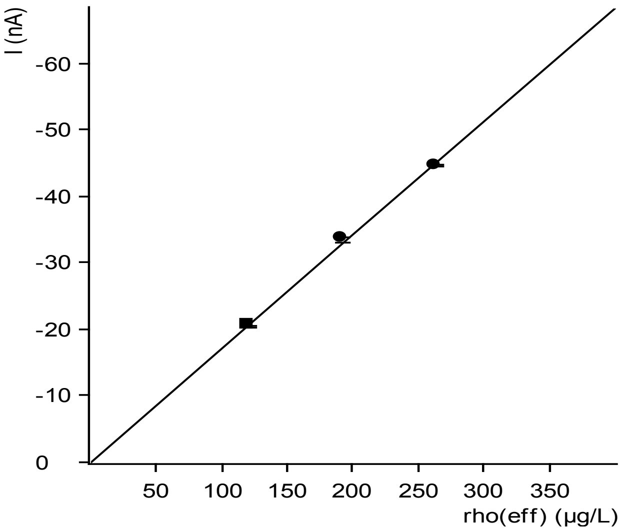
Samples with concentrations over 100 mg/L Fe have to be diluted.

Example

Substance: Fe VR(**)



Standard addition curve: Fe



Result

Sample	Water
Sample size	10.0 mL
β(Fe)	128 µg/L

Comments

- Phosphate buffer has to be added after the addition of catechol. Otherwise insoluble iron phosphates can be formed, which cannot be determined voltammetrically.
- Catechol can be purified by recrystallization from toluene. It is also possible to make a sublimation of the catechol. Catechol Sigma-Aldrich No. 15890 can be used directly.
- Using this method, purity of the applied reagents is of utmost importance. Small concentrations of surface-active substances (detergents, organic complexing agents such as humic acids etc.) are also interfering. These must be destroyed before beginning the analysis (see “Sample Preparation”).

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
- 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

Method 2: Determination of Fe with PIPES buffer

Iron is determined as a complex with catechol. With adsorptive stripping voltammetry at the HMDE concentrations down to 0.5 µg/L can be determined.

Reagents

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

- Sodium hydroxide solution, w(NaOH) = 30%, for trace analysis*, CAS 1310-73-2

- Ammonia solution, w(NH_3) = 25%, for trace analysis*, CAS 1336-21-6
- Catechol (Pyrocatechol, Brenzkatechin, 1,2-Dihydroxybenzene), for analysis, CAS 120-80-9
- PIPES, Piperazine-1,4-bis-2-ethane sulfonic acid, CAS 5625-37-6
- Iron standard stock solution, β(Fe^{3+}) = 1 g/L, commercially available
- Nitric acid, w(HNO_3) = 65%, for trace analysis*, CAS 7697-37-2
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Solutions

PIPES buffer	c(PIPES) = 1 mol/L Mix 6.05 g PIPES with 1 mL sodium hydroxide solution and a little high purity water. Adjust the pH value to 8.0 with ammonia solution and fill up to 20 mL with high purity water. The solution has to be prepared fresh daily. This buffer does not contain any Fe.
Catechol solution	c(Catechol) = 1 mol/L Dissolve 2.75 g catechol in 25 mL oxygen-free high purity water, which had been degassed by purging with nitrogen. Store the solution in a tightly closed dark bottle. Stability of the solution depends on the purity of the used catechol and can vary from 1 day to 1 month. The solution must rest for a few hours before use.
Ammonia solution diluted	w(NH_3) = 10%

Standard solutions

Iron standard solution	β(Fe^{3+}) = 1 mg/L The solution is diluted with c(HNO_3) = 0.015 mol/L. It is stable for max. 1 week.

Analysis

Measuring solution

10 mL acidified (diluted) sample

0.05 mL catechol solution

0.250 mL PIPES buffer

If necessary, adjust the pH value to 7.0 ± 0.1 with w(NH_3) = 10%.

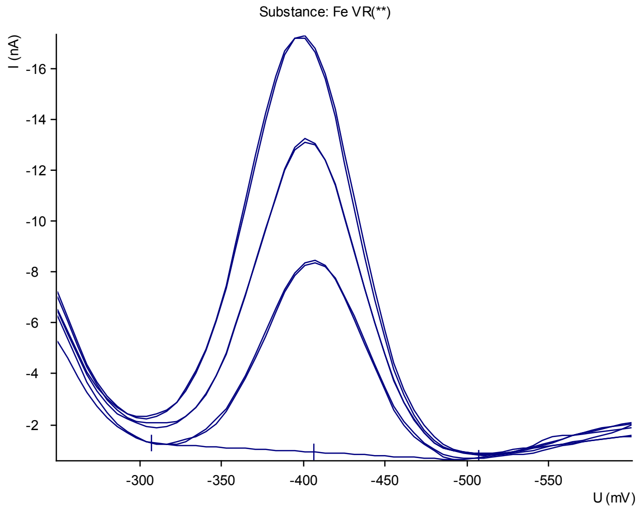
The measuring vessel should contain at least 10 ng but not more than 100 ng Fe.

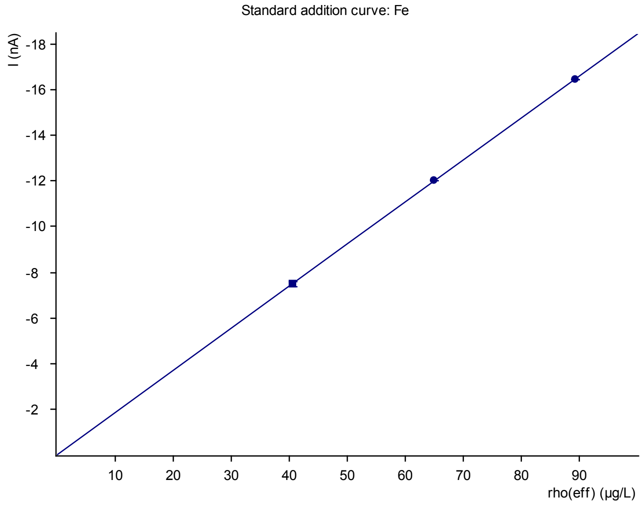
The concentration is determined by 2 standard additions.

Parameters

Voltammetric	
Electrode operating mode	HMDE
Drop size	7
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.25 V
Waiting time 1	60 s
Equilibration time	10 s
Sweep	
Start potential	-0.25 V
End potential	-0.6 V
Potential step	0.006 V
Potential step time	0.1 s
Sweep rate	0.06 V/s
Pulse amplitude	0.05 V
Substance	
Name	Fe
Characteristic potential	-0.4 V

Example


Substance: Fe VR(**)


Standard addition curve: Fe

Results

Sample	Sea water
Sample size	10 mL
β(Fe)	41.9 µg/L

Comments

- Catechol should be added to the acidic sample solution before the buffer is added. Otherwise iron may form hydroxo complexes, which cannot be determined any more. This results in low recovery rates.
- The peak potential of Fe is strongly dependent on the exact pH value and the sample matrix and may have to be adjusted.
- For amounts above 100 ng in the polarographic vessel, standard additions are no longer linear. Then, either the amount of the sample must be reduced or a DP polarographic analysis performed on the SMDE.
- If the total ion concentration is very high (e.g. sea water), the iron determination is much less sensitive and only relatively small peaks are achieved. Linear standard addition curves are achieved, however, with proportionally large standard additions and a reduction of the enrichment time.
- Catechol can be purified by recrystallization from toluene. It is also possible to make a sublimation of the catechol. Catechol Sigma-Aldrich No. 15890 can be used directly.

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
- 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.,
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  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

Method 3: Determination of Fe, Cu and V

Iron, copper and vanadium are determined as a complex with catechol. With adsorptive stripping voltammetry at the HMDE concentrations down to 0.5 … 1 µg/L can be determined.

Reagents

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

- Sodium hydroxide solution, w(NaOH) = 30%, for trace analysis*, CAS 1310-73-2
- Ammonia solution, w(NH_3) = 25%, for trace analysis*, CAS 1336-21-6
- Catechol (Pyrocatechol, Brenzkatechin, 1,2-Dihydroxybenzene), for analysis, CAS 120-80-9
- PIPES, Piperazine-1,4-bis-2-ethane sulfonic acid, CAS 5625-37-6
- Iron standard stock solution, $\beta(Fe^{3+})$ = 1 g/L, commercially available
- Copper standard stock solution, $\beta(Cu^{2+})$ = 1 g/L, commercially available.
- Vanadium standard stock solution, $\beta(V^{5+})$ = 1 g/L, commercially available.
- Nitric acid, w(HNO_3) = 65%, for trace analysis*, CAS 7697-37-2
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Solutions

PIPES buffer	c(PIPES) = 1 mol/L Mix 6.05 g PIPES with 1 mL sodium hydroxide solution and a little high purity water. Adjust the pH value to 8.0 with ammonia solution and fill up to 20 mL with high purity water. The solution has to be prepared fresh daily. This buffer does not contain any Fe.
Catechol solution	c(Catechol) = 1 mol/L Dissolve 2.75 g catechol in 25 mL oxygen-free high purity water, which had been degassed by purging with nitrogen. Store the solution in a tightly closed dark bottle. Stability of the solution depends on the purity of the used catechol and can vary from 1 day to 1 month. The solution must rest for a few hours before use.
Ammonia solution diluted	w(NH_3) = 10%

Standard solutions

Iron standard solution	$\beta(Fe^{3+})$ = 1 mg/L
Copper standard solution	$\beta(Cu^{2+})$ = 1 mg/L
Vanadium standard solution	$\beta(V^{5+})$ = 1 mg/L
	The solution are diluted with c(HNO_3) = 0.015 mol/L. The are stable for max. 1 week.

Analysis

Measuring solution

10 mL acidified (diluted) sample

0.05 mL catechol solution

0.250 mL PIPES buffer

If necessary, adjust the pH value to 7.0 ± 0.1 with w(NH_3) = 10%.

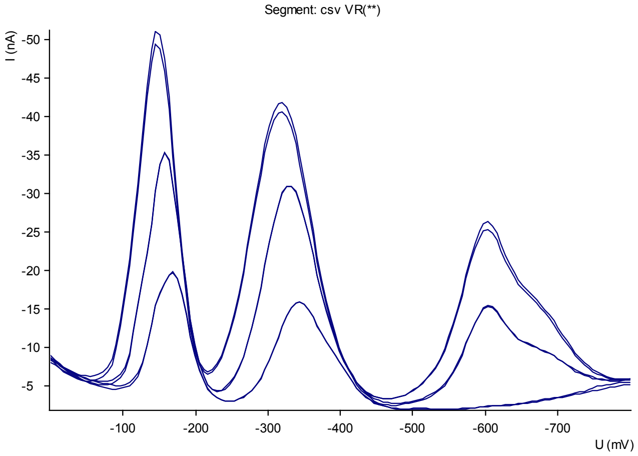
Parameters

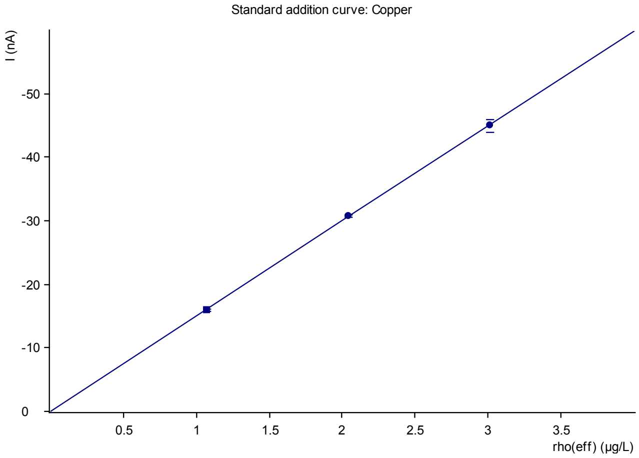
Voltammetric	
Electrode operating mode	HMDE
Drop size	7
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	0 V
Waiting time 1	60 s
Equilibration time	10 s
Sweep	
Start potential	0 V
End potential	-0.8 V
Potential step	0.006 V
Potential step time	0.1 s
Sweep rate	0.06 V/s

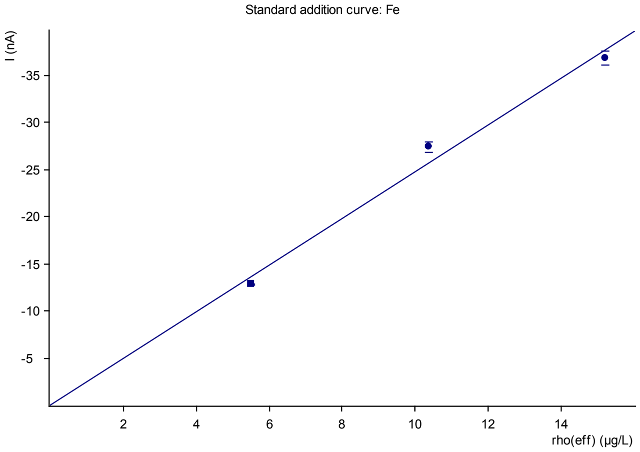
Pulse amplitude	0.05 V
Substance	
Name	Cu
Characteristic potential	-0.16 V
Name	Fe
Characteristic potential	-0.34 V
Name	V
Characteristic potential	-0.6 V

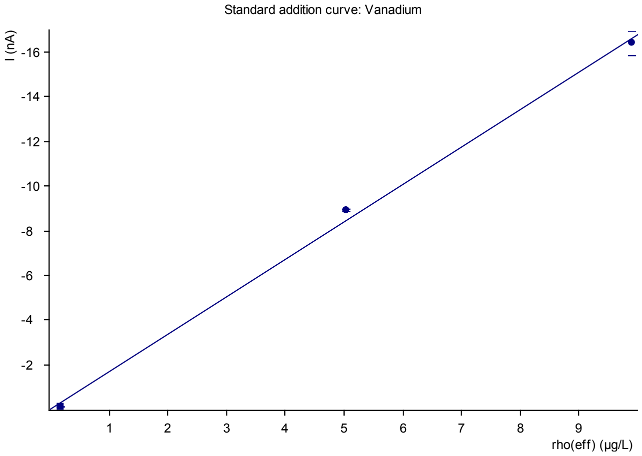
Example

Determination of Cu, Fe and V in salt solution









Results

Sample	1% salt solution
Sample size	10 mL
β(Cu)	1.1 µg/L
β(Fe)	5.7 µg/L
β(V)	< 1 µg/L

Comments

- Catechol should be added to the acidic sample solution before the buffer is added. Otherwise iron may form hydroxo complexes, which cannot be determined any more. This results in low recovery rates.
- Vanadium(IV) cannot be determined by voltammetry.
- If a large excess of Cu is present, it is recommended not to preconcentrate this, otherwise the Hg drop is overloaded and neither Fe, nor V can be determined accurately.
- The peak potentials are strongly dependent on the exact pH value and the sample matrix and may have to be adjusted.

Appendix

Report of the example determination Fe in a water sample according to method 1

```
================== 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                                                          10.0 mL
--------------------------------------------------------------------------------
 Method  :  AB431_1
 Title   :  Determination of Iron in Waters. AB431 method 1
 Remark1 :  Determination of iron in water
 Remark2 :  10mL sample + 50uL catechol (1 mol/L) + 0.5mL phosph buff
--------------------------------------------------------------------------------

  Substance : Fe                                             Comments
  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                 6.153e-10

 Final results                         +/- Res.dev.   %      Comments
 ---------------------------------     -----------------     ------------------
         Fe =   128.13 ug/L                6.12    4.78
```

Method print for the determination of Fe according to method 1

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB431_1 .mth         OPERATION SEQUENCE
 Title : Determination of Iron in Waters. AB431 method 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      0PURGE
10      SEGMENT            Segm.name   DPAdSV
11      ADD>M              Soln.name   FeStd          V.add         0.050 mL
12    ADD)2
13    END

 Method: AB431_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        Meas.cell   normal
 4      DPMODE             U.ampl          -50 mV     t.meas         20.0 ms
                           t.step         0.40 s      t.pulse        40.0 ms
 5      MEAS        60.0   U.meas         -300 mV
 6      0STIR        5.0
 7      FSWEEP      31.2   U.start        -200 mV     U.step            4 mV
                           U.end          -500 mV     Sweep rate       10 mV/s
 8      0MEAS              U.standby           mV
 9    REP)1
10    END
```

Report of the example determination Fe in sea water according to method 2

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0100) ==================
 Determ.     :  09291112            User:                      Date:  99-09-29
 Modified    :  no                  Run :  1                    Time:  11:12:16
 Sample table:  -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        Sea Water                                                        10 mL
--------------------------------------------------------------------------------
 Method  :  AB431_1__
 Title   :  Determination of Iron
 Remark1 :  10 ml sample + 50 µl catechol + 250 µl buffer --> pH 7.0
 Remark2 :
--------------------------------------------------------------------------------

  Substance : Fe                                             Comments
  Mass conc.:    41.94 ug/L            Mass     : 419.4 ng    ------------------
  MC.dev.   :    0.573 ug/L (1.37%)    Add.mass :   250 ng
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -406   -7.561  -7.489   0.1006
              01   -407   -7.418
              10   -403   -11.76  -11.75   0.0127   -4.258
              11   -403   -11.74
              20   -398   -15.67  -15.68   0.0139   -3.934
              21   -400   -15.69

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Fe           std.add.     -7.511e-09   -1.845e-04                 6.494e-11


Final results                         +/- Res.dev.   %      Comments
 ---------------------------------    -----------------     ------------------
         Fe =   41.935 ug/L               0.573    1.37
```

Method print for the determination of Fe according to method 2

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB431_1 .mth         OPERATION SEQUENCE
 Title : Determination of Fe. AB 431 method 1
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    SMPL>M               V.fraction          mL     V.total              L
 2    DOS>M                Soln.name   Catechol       V.add         0.050 mL
 3    DOS>M                Soln.name   Buffer         V.add         0.250 mL
 4    PURGE
 5    STIR          300.0  Rot.speed      2000 /min
 6    (ADD
 7      PURGE
 8      STIR        60.0   Rot.speed      2000 /min
 9      0PURGE
10      (REP
11        SEGMENT          Segm.name   Fe_AdSV
12      REP)1
13      PURGE
14      ADD>M              Soln.name   Fe_Std         V.add         0.250 mL
15    ADD)2
16    END

 Method: AB431_1               SEGMENT
                                Fe_AdSV
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    STIR           5.0   Rot.speed      2000 /min
 2    HMDE                 Drop size         7        Meas.cell   normal
 3    DPMODE               U.ampl          -50 mV     t.meas         20.0 ms
                           t.step         0.10 s      t.pulse        40.0 ms
 4    MEAS          60.0   U.meas         -250 mV
 5    0STIR          5.0
 6    FSWEEP         6.2   U.start        -250 mV     U.step            6 mV
                           U.end          -600 mV     Sweep rate       60 mV/s
 7    0MEAS                U.standby           mV
 8    END
```

Report of the example determination Cu, Fe, V in a salt solution according to method 3

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 02021647             User:                      Date: 1998-02-02
 Modified    : 1998-02-03 07:48:39  Run :  0                   Time: 16:47:28
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        FeCuVrecal                                                       10 mL
--------------------------------------------------------------------------------
 Method  :  AB431_3
 Title   :  Determination of Iron and Vanadium AB431 method 3
 Remark1 :  1% salt solution
 Remark2 :
--------------------------------------------------------------------------------

  Substance : Fe                                             Comments
  Mass conc.:    5.669 ug/L            Mass     : 56.69 ng   ------------------
  MC.dev.   :    0.847 ug/L (14.9%)    Add.mass :    50 ng
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -341   -12.79  -12.79   0.0041
              01   -341   -12.78
              10   -329   -26.73  -27.11   0.5436   -14.33   front overlapping
              11   -328   -27.50                             front overlapping
              20   -318   -35.53  -36.04   0.7203   -8.924   front overlapping
              21   -318   -36.55                             front overlapping
  Substance : Vanadium                                       Comments
  Mass conc.:    192.9 ng/L            Mass     : 1.929 ng   ------------------
  MC.dev.   :      216 ng/L (112%)     Add.mass :    50 ng
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -607   -0.0845 -0.0966  0.0170
              01   -609   -0.1086
              10   -602   -8.838  -8.819   0.0270   -8.722
              11   -601   -8.800
              20   -599   -15.67  -16.05   0.5327   -7.232
              21   -600   -16.43

  Substance : Copper                                         Comments
  Mass conc.:    1.103 ug/L            Mass     : 11.03 ng   ------------------
  MC.dev.   :    0.047 ug/L (4.23%)    Add.mass :    10 ng
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -167   -16.00  -15.89   0.1642
              01   -168   -15.77
              10   -159   -30.57  -30.45   0.1661   -14.57   rear overlapping
              11   -159   -30.34                             rear overlapping
              20   -148   -43.32  -43.97   0.9232   -13.51   rear overlapping
              21   -148   -44.62                             rear overlapping

 Substance    Techn.      Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Fe           std.add.     -1.364e-08    -0.002478                 1.572e-09
 Vanadium     std.add.     -3.145e-10    -0.001680                 4.705e-10
 Copper       std.add.     -1.601e-08     -0.01495                 5.295e-10

 Final results                         +/- Res.dev.   %     Comments
 ---------------------------------     -----------------     ------------------
         Fe =   5.6686 ug/L               0.847    14.9
   Vanadium =   192.87 ng/L                216.    112.
     Copper =   1.1031 ug/L               0.047    4.23
```

Method print for the determination of Cu, Fe, V according to method 3

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB431_3 .mth         OPERATION SEQUENCE
 Title : Determination of Cu, Fe and V. AB 431 method 3
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    SMPL>M               V.fraction          mL     V.total               L
 2    DOS>M                Soln.name   Catechol       V.add         0.050 mL
 3    DOS>M                Soln.name   Buffer         V.add         0.250 mL
 4    PURGE
 5    STIR          300.0  Rot.speed      2000 /min
```

```
 6    (ADD
 7      PURGE
 8      STIR        60.0   Rot.speed      2000 /min
 9      0PURGE
10      (REP
11        SEGMENT          Segm.name   AdSV
12      REP)1
13      PURGE
14      ADD>M              Soln.name   Cu_Std         V.add         0.010 mL
15      ADD>M              Soln.name   Fe_Std         V.add         0.050 mL
16      ADD>M              Soln.name   V_Std          V.add         0.050 mL
17    ADD)2
18    END

 Method: AB431_3               SEGMENT
                                   AdSV
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  -------------------------  -------------------------
 1    STIR           5.0   Rot.speed      2000 /min
 2    HMDE                 Drop size         7        Meas.cell   normal
 3    DPMODE               U.ampl          -50 mV     t.meas         20.0 ms
                           t.step         0.10 s      t.pulse        40.0 ms
 4    MEAS          60.0   U.meas            0 mV
 5    0STIR          5.0
 6    FSWEEP        13.6   U.start           0 mV     U.step            6 mV
                           U.end          -800 mV     Sweep rate       60 mV/s
 7    0MEAS                U.standby           mV
 8    END
```