Metrohm

Application Bulletin 131/3 e

Determination of aluminum by adsorptive stripping voltammetry

Summary

This Application Bulletin describes a voltammetric method for the determination of aluminum in water samples, dialysis solutions, sodium chloride solutions and digestion solutions (e.g. of lyophilisates). The method utilizes the complexation of the Al^{3+} ion by Calcon (Eriochrome blue black R). The formed complex can easily be reduced electrochemically at 60 °C. The limit of quantitation depends on the purity of the reagents used and is approx. 5 µg/L.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode	
Measuring vessel with thermostat jacket	6.1418.220
Recirculation thermostat	

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*).

- Sodium hydroxide solution, w(NaOH) = 30%, for trace analysis*, CAS 1310-73-2
- Acetic acid, w(CH_3COOH) = 100%, for trace analysis*, CAS 64-19-7
- Methanol, for analysis, CAS 67-56-1
- Al^{3+} stock solution, β(Al^{3+}) = 1 g/L (commercially available)
- Calcon (Eriochrome blue black R), Fluka no. 45550, C.I. no. 15705, CAS 2538-85-4
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Solutions

Sodium acetate buffer	c(NaOH) = 1.0 mol/L c(CH_3COOH) = 2.0 mol/L Place approx. 50 mL ultrapure water, 10 mL w(NaOH) = 30% and 11.4 mL w(CH_3COOH) = 100% in a 100 mL volumetric flask, fill to the mark with ultrapure water and mix.
Complexing agent	w(Calcon) = 0.05 % (0.5 g/L) in methanol This solution has to be freshly prepared every day.

Standard solutions

Al standard solution	β(Al^{3+}) = 1 mg/L This solution is prepared from the Al^{3+} stock solution by dilution with c(HCl) = 0.01 mol/L. The standard solution has to be stored in a plastic vessel and is stable for one week at most.

Sample preparation

Water samples contaminated by organic substances (surface water, waste water) have to be digested prior to the voltammetric determination. Depending on the content of organic substances (particularly surface-active substances), a UV digestion (909 UV Digester) or wet-chemical acid digestion (H_2SO_4/H_2O_2) is carried out.

Following we describe an acid digestion using an example of lyophilisates:

- 0.7 ... 0.9 g sample is mixed in a quartz Kjeldahl flask with 3 mL ultrapure water and 2 mL conc. sulfuric acid.
- Heat up the mixture carefully (formation of foam) and reduce through evaporation.

- Slowly add four portions each of 2 mL w(H_2O_2) = 30% and heat until the solution becomes clear and colorless.
- The sulfuric acid is evaporated down to a very small volume.
- After cooling down, rinse the sample solution with ultrapure water into a 100 mL volumetric flask and fill to the mark.

Analysis

The determination is to be carried out at 60 °C!

Measuring solution

20 mL sample solution at approx. pH = 2.0

2 mL buffer

If necessary, adjust the pH value to 4.5 ± 0.1 with sodium hydroxide solution or acetic acid.

Having purged the measuring solution for 180 s,

add 120 µL w(Calcon) = 0.05%,

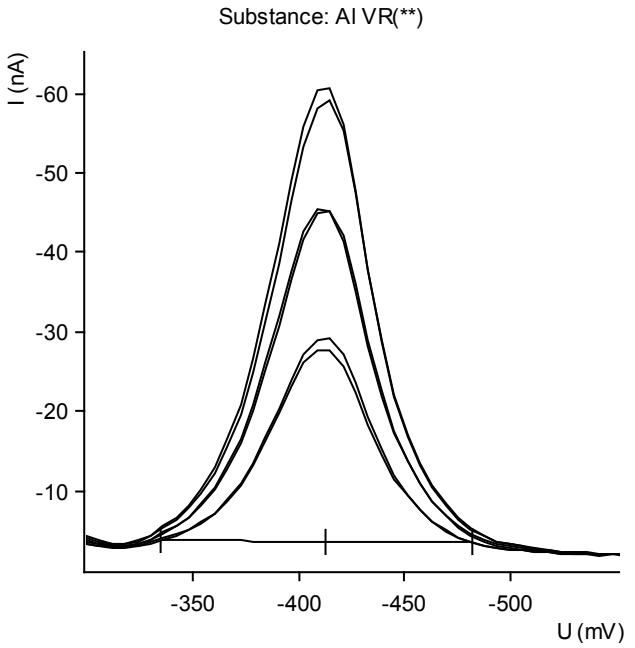
then record the voltammogram.

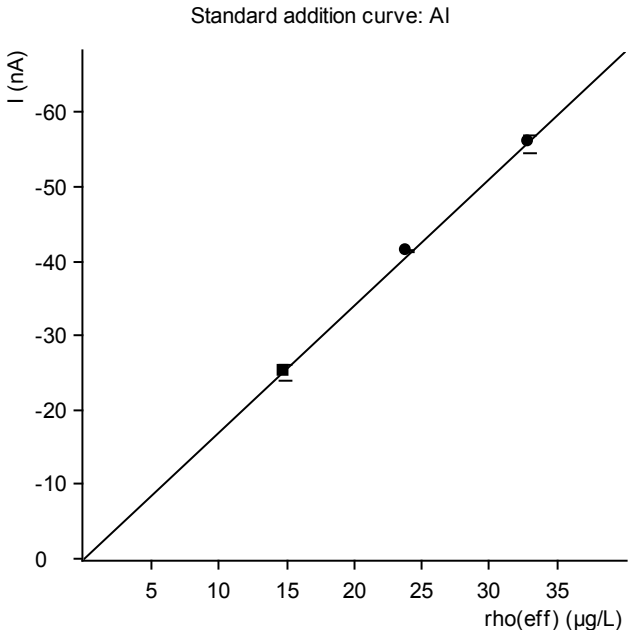
The concentration is determined by standard addition. It is important to observe a waiting time of 3 min after each addition to allow complexation.

Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.35 V
Waiting time 1	30 s
Equilibration time	10 s
Sweep	
Start potential	-0.3 V
End potential	-0.65 V
Potential step	0.006 V
Potential step time	0.4 s
Sweep rate	0.015 V/s
Pulse amplitude	0.05 V
Substance	
Name	Al
Characteristic potential	-0.42 V

Example





Result

Sample	Drinking water
Sample size	20.0 mL
β(Al)	16.4 µg/L

Comments

- As the voltammetric determination described is a highly sensitive method, it is necessary to determine the blank of the reagents used and take it into account when

calculating the results. The blank determination has to be carried out in exactly the same way as the analysis of the sample. The same quantity of Calcon has to be added as the blank also depends on the concentration of this complexing agent.

- Al^{3+} concentrations in the ppm range are determined at the dropping mercury electrode (DME or SMDE).
- After 45 min at the most the determination should be finished, as the dyestuff may alter.
- A tenfold excess of Fe^{3+} does not yet interfere with the determination in the ppb range. However, for determinations in the ppm range the Fe^{3+} concentration should not exceed the Al^{3+} concentration. If more iron is present, it can be removed from the sample by electrolysis.
- An alternative voltammetric method for the determination of aluminum is described in Application Bulletin 186. With this method the interference caused by Fe^{3+} ions is far lower; however, high salt concentrations do interfere.
- If great amounts of Cu^{2+} ions (over 50-fold excess) are present, the solution turns a bright violet and the aluminum peak is suppressed.
- At pH 4 lead is reduced at approximately the same potential as the aluminum complex. However, the lead peak is less sensitive than the aluminum peak. Interferences will only occur if Pb^{2+} is present in great excess.

References

- G. S. P. Ritchie, A. M. Posner, J. M. Ritchie
  The determination of trace levels of aluminum by differential pulse polarography
  Anal. Chim. Acta 117 (1980) 233–239.
- C. M. G. van den Berg, K. Murphy, J. P. Riley
  The determination of aluminum in sea water and fresh water by cathodic stripping voltammetry
  Anal. Chim. Acta 188 (1986) 177–185.
- E. Stryjewska, S. Rubel, K. Kusmierczyk
  Trace electrochemical determination of aluminum in environmental samples
  Fresenius Z. Anal. Chem. 334 (1989) 627.
- L. Chiang, B. D. James, R. J. Magree
  Adsorptive stripping voltammetry of some trace elements in biological samples. Nickel, arsenic, aluminum and selenium
  Mikrochim. Acta (1989) 149–152.

Appendix

Report for the example determination of aluminum in drinking water

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 06040939             User:                      Date: 1999-06-04
 Modified    : 1999-06-04 09:40:38  Run :  0                   Time: 09:39:28
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        tap water                                                      20 mL
--------------------------------------------------------------------------------
 Method  :  AB131
 Title   :  Determination of aluminum. AB131
 Remark1 :  Determination of Al at 60 °C
 Remark2 :  20mL sample + 2mL buffer --> pH 4.5 + 120µL Erio R (0.5 g/L)
--------------------------------------------------------------------------------

  Substance : Al                                              Comments
  Mass conc.:    16.44 ug/L            Mass     : 328.8 ng   ------------------
  MC.dev.   :        1 ug/L (6.08%)    Add.mass :   200 ng
  Cal.dev.  :    -                     V0.sample:    20 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -412   -25.69  -24.98   0.9975
              01   -412   -24.27
              10   -411   -41.00  -40.94   0.0863   -15.96
              11   -413   -40.87
              20   -413   -53.86  -54.75    1.258   -13.81
              21   -413   -55.64

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Al           std.add.     -2.529e-08    -0.001702                 9.781e-10

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

  Soln.name    Pos.    Std.subst.   Mass conc.       Remark
  ---------    ----    ----------   -------------    -------------------------


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


Final results                        +/- Res.dev.   %      Comments
 ---------------------------------     -----------------     ------------------
         Al =   16.439 ug/L               1.00    6.08
```

Method print for the determination of aluminum

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB131   .mth         OPERATION SEQUENCE
 Title : Determination of aluminum. AB131
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  -------------------------
 1    DOS/M                V.added       2.000 mL
 2    SMPL/M               V.fraction          mL     V.total              L
 3    PURGE
 4    STIR          180.0  Rot.speed      2000 /min
 5    DOS>M                Soln.name   ErioR          V.add         0.120 mL
 6    PURGE         300.0
 7    (ADD
 8      PURGE
 9      STIR        180.0  Rot.speed      2000 /min
10      0PURGE
11      SEGMENT            Segm.name   csv
12      PURGE
13      ADD>M              Soln.name   Al-std         V.add         0.200 mL
14    ADD)2
15    END

 Method: AB131                SEGMENT
                                   csv
--------------------------------------------------------------------------------
```

```
      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        30.0   U.meas         -350 mV
 6      0STIR       10.0
 7      SWEEP       24.8   U.start        -300 mV    U.step            6 mV
                           U.end          -650 mV    Sweep rate       15 mV/s
 8      0MEAS              U.standby           mV
 9    REP)1
10    STIR                Rot.speed      2000 /min
11    END

  Method: AB131                    SUBSTANCES
                                Al       - csv
-------------------------------------------------------------------------------

      Recognition                              Display / Plot
      -------------------------                ---------------------------
      U.verify          -420 mV                I.scale       auto
      U.tol (+/-)         50 mV                U.div          50.00 mV/cm
      U.width min         10 mV                U.begin         -300 mV
      U.width max        400 mV                U.end           -550 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   2000-11-28 17:11:34            Coefficients
  ---------------------------------            -------------------------
  Technique     std.add.                       Y.reg        -2.529e-08
  Curve type    linear                         Slope         -0.001702
                                               Nonlin.
                                               Mean dev.     9.781e-10

               Additions
               ------------------------------------------------------------
  Soln.name       Al-std
  ----------
  Mass conc.          1 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: AB131                 CALCULATION
                              max. 15 lines
-------------------------------------------------------------------------------

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