Application Bulletin 186/2 e

Determination of aluminum in water samples by adsorptive stripping voltammetry

Of interest to:
General analytical laboratories; Water analysis; Pharmaceutical industry; Food analysis
B 1, 2, 4, 7, 9

Summary

This Bulletin describes the voltammetric determination of aluminium in water samples down to a concentration of 1 µg/L. An aluminium complex is formed with alizarin red S (DASA) and enriched at the HMDE. The following determination employs differential pulse adsorptive stripping voltammetry (DP-AdSV). Disturbing Zn ions are eliminated by addition of CaEDTA.

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 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 60 minutes at 90°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 H_2SO_4 and H_2O_2 According to Application Bulletin 113.

Reagents

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

- Hydrochloric acid, suprapur, w(HCl) = 30 %
- Sodium hydroxide solution, suprapur, w(NaOH) = 30 %
- BES (N,N-bis-(2-hydroxyethyl)-2-aminoethansulfonic acid), CAS 10191-18-1
- DASA (alizarin red S; 3,4-dihydroxy-2-anthraquinonsulfonic acid Na-salt), C.I. No. 58005, CAS 130-22-3
- CaEDTA dihydrate, CAS 6766-87-6
- Aluminium standard stock solution, ß(Al^{3+}) = 1 g/L

Ready to use solutions

Hydrochloric acid	w(HCl) = 10 % *10 mL hydrochloric acid w(HCl) = 30% are mixed with 20 mL ultrapure water.*
BES buffer	c(BES) = 0.5 mol/L pH 7.1 *5.3 g BES are mixed with ultrapure water in a 50 mL calibrated flask. The pH value is adjusted to pH 7.1 ± 0.1 with sodium hydroxide solution. The solution is made up to the mark with ultrapure water.*
DASA solution	c(DASA) = 1 mmol/L in ultrapure water *34 mg DASA are dissolved in ultrapure water in a 100 mL calibrated flask. The solution is made up to the mark with ultrapure water.*
Ca-EDTA solution	c(CaEDTA) = 0.02 mol/L *0.82 g CaEDTA are dissolved in ultrapure water in a 100 mL calibrated flask. The solution is made up to the mark with ultrapure water.*
standard solution	ß(Al) = 1 mg/L *1 mL DASA solution and 100 µL Al standard stock solution are pipetted into a 100 mL calibrated flask. The solution is made up to the mark with ultrapure water.*

Analysis

10 mL (diluted) sample
+ 100 µL hydrochlorid acid
+ 200 µL DASA solution
+ 100 µL Ca-EDTA solution
+ 100 µL BES buffer

The solution is then set to pH = 7.1 ± 0.1 with NaOH.

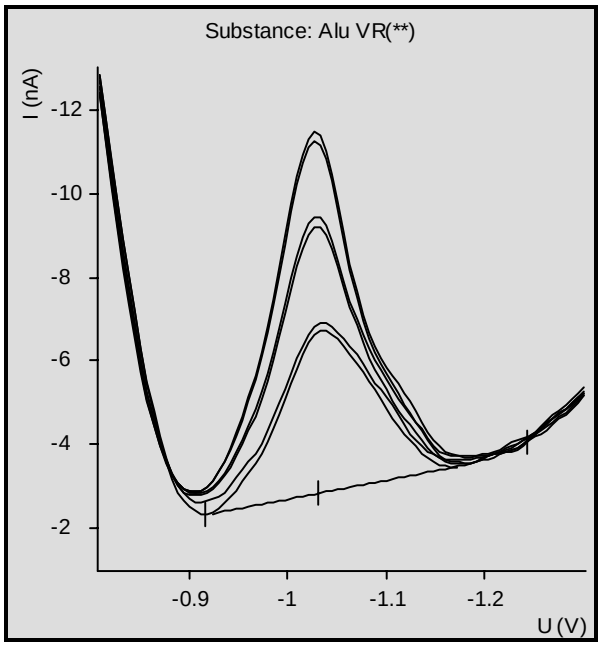
The voltammogram is recorded with the following parameters:

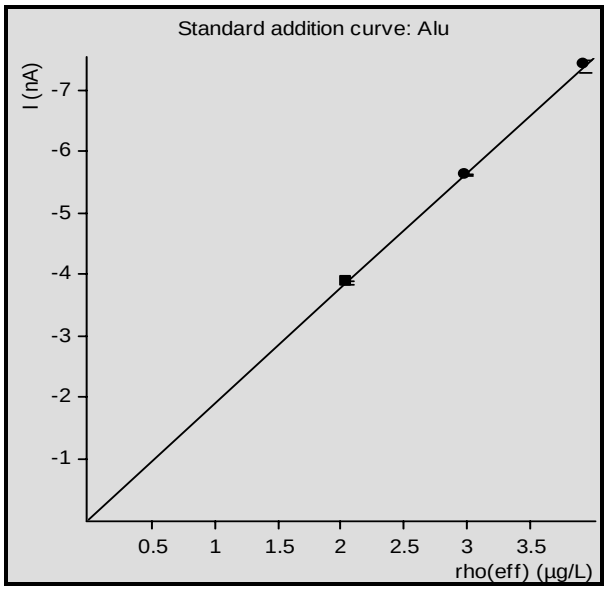
Working electrode	HMDE
Stirrer speed	2000 rpm
Mode	DP
drop size	7
Purge time	300 s
Deposition potential	-875 mV
Deposition time	30 s
Equilibration time	10 s
Pulse amplitude	50 mV
Start potential	-810 mV
End potential	-1300 mV
Voltage step	6 mV
Voltage step time	0.1 s
Sweep rate	60 mV/s
Peak potential	-1000 mV

The concentration is determined by standard addition.

Example:

Determination of aluminium in tap water





Sample volume 1 mL

Result 21.7 µg/L Al

Remarks

- It is important that the reagents are added to the sample in the correct order.
- BES and DASA additions as well as the addition of standard solution depend on the Al contents expected.
- The sample has to be acidified before the complexing agent DASA is added to prevent hydrolysis of the aluminium.
- The pH value of the final solution must be checked for exact adherence to the correct value in each case, it may have to be adjusted after addition of the buffer (pH = 7.1 ± 0.1).
- Aluminium contents of 1...100 µg/L are determined by the voltammetric method, higher contents by the polarographic method (SMDE, DME).
- The determination limit in drinking water lies at approx. 1 µg/L.
- The standard solution is added as DASA-Al complex. Otherwise, a 5 min waiting time would be needed for formation of the complex.
- With high salt concentrations, e.g. in dialysis concentrations the aluminium determination can be disturbed. In such samples, aluminium is determined according to Application Bulletin 131.

Literature

Van den Berg, C.M.G., Murphy, K., Riley, J.P. The determination of aluminium in seawater and freshwater by cathodic stripping voltammetry Anal. Chim. Acta 188, (1986) 177-185

Appendix

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

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 08041654             User:                      Date: 1998-08-04
 Modified    : 2000-11-29 11:17:19  Run :  0                   Time: 16:54:51
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        water                                                          1 mL
--------------------------------------------------------------------------------
 Method  :  AB186
 Title   :  Determination of Al-Traces (samples containing Fe)
 Remark1 :  10ml sample + 100ul HCl + 200ul DASA + 100ul CaEDTA
 Remark2 :  +100ul BES buffer --> pH 7.1 with NaOH
--------------------------------------------------------------------------------

  Substance : Alu                                                 Comments
  Mass conc.:    21.72 ug/L            Mass     : 21.72 ng   ------------------
  MC.dev.   :    0.591 ug/L (2.72%)    Add.mass :    10 ng
  Cal.dev.  :    -                     V0.sample:  1000 uL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -1032  -3.883  -3.858   0.0363            crit.basept.interp
              01   -1033  -3.832
              10   -1028  -5.592  -5.601   0.0130   -1.743
              11   -1028  -5.610
              20   -1028  -7.317  -7.389   0.1014   -1.788
              21   -1028  -7.460

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Alu          std.add.     -3.850e-09    -0.001880                 5.602e-11

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

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



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

 Final results                        +/- Res.dev.   %      Comments
 ---------------------------------    -----------------     ------------------
       Alu =   21.718 ug/L               0.591    2.72
```

Method print for the determination of aluminium with the 746 VA Trace Analyzer

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB186   .mth         OPERATION SEQUENCE
 Title : Determination of Al-Traces (samples containing Fe)
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    SMPL>M               V.fraction          mL     V.total              L
 2    DOS/M                V.added       9.605 mL
 3    REM                  sample + 9mL water + 100uL HCl + 200 µL DASA
 4    REM                  + 100 µL CaEDTA + 100 µL BES + NaOH --> pH 7.1
 5    PURGE
 6    STIR          300.0  Rot.speed      2000 /min
 7    (ADD
 8      PURGE
 9      STIR         60.0   Rot.speed      2000 /min
10      0PURGE
11      SEGMENT             Segm.name   Al_DASA
12      PURGE
13      ADD>M               Soln.name   std-al         V.add         0.010 mL
14    ADD)2
15    END

 Method: AB186                 SEGMENT
                                Al_DASA
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    (REP
 2      STIR          3.0   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         0.10 s     t.pulse        40.0 ms
 5      MEAS         30.0   U.meas         -875 mV
 6      0STIR        10.0
 7      SWEEP         8.5   U.start        -810 mV    U.step            6 mV
                            U.end         -1300 mV    Sweep rate       60 mV/s
 8      0MEAS               U.standby           mV
 9    REP)1
10    STIR                  Rot.speed      2000 /min
11    END

  Method: AB186                    SUBSTANCES
                                Alu      - Al_DASA
--------------------------------------------------------------------------------

      Recognition                              Display / Plot
      -------------------------                ---------------------------
      U.verify         -1021 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       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   2000-11-29 11:21:01            Coefficients
  ---------------------------------            -------------------------
  Technique     std.add.                       Y.reg         -3.85e-09
  Curve type    linear                         Slope          -0.00188
                                               Nonlin.
                                               Mean dev.     5.602e-11

                Additions
                ------------------------------------------------------------
  Soln.name       std-al
  ----------
  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: AB186                  CALCULATION
                               max. 15 lines
--------------------------------------------------------------------------------

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