Application Bulletin

Of interest to: Detergent industry; Environmental protection B 1, 2, 12

Polarographic determination of nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) according to DIN 38413 Part 5

Summary

According to the described method, NTA and EDTA can be determined in mass concentrations of 0.05 mg/L up to 25 mg/L in polluted water and waste water.

At first NTA and EDTA are converted to the corresponding Bi complexes by addition of Bi^{3+} ions at a pH value of 2.0. As these Bi complexes have significantly different peak potentials, they can be determined simultaneously by means of DP polarography. The interfering anions nitrite, sulfite and sulfide are removed from the sample by acidification and purging. Interfering cations are removed by cation exchange; any NTA or EDTA heavy metal complexes present in the sample are disintegrated during this procedure. To remove surfactants and other organic components interfering with the analysis, the sample solution is run through a column filled with non-polar resin adsorbent.

Instruments and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
- 757 VA Computrace

Reagents

All reagents used should be of the highest purity (p.a. or «suprapur»). Only ultrapure water should be used.

- Nitric acid, $w(HNO_3)$ = 65%, suprapur
- Basic bismuth(III) nitrate $Bi(OH)_2NO_3$, purum p.a., CAS 1304-85-4
- Potassium nitrate KNO_3, suprapur
- Methanol, puriss. p.a.
- Ascorbic acid (vitamin C), puriss. p.a., CAS 50-81-7
- Nitrilotriacetic acid NTA, ACS, for complexometry, puriss. p.a., CAS 139-13-9
- Ethylenediaminetetraacetic acid disodium salt dihydrate $Na_2EDTA \times 2\ H_2O$, ACS, puriss. p.a., CAS 6381-96-6
- Sodium hydroxide solution, $c(NaOH)$ = 0.1 mol/L
- Sodium hydroxide solution, $c(NaOH)$ = 2 mol/L
- Hydrochloric acid, $c(HCl)$ = 0.1 mol/L
- Nitric acid, $c(HNO_3)$ = 2 mol/L

- Highly acidic cation exchanger in Na^+ form:
  300 … 1000 µm (20 … 50 mesh), e.g. Amberlite IR 120
- Non-polar resin adsorbent based on polystyrene for analytical purposes:
  300 … 1000 µm (20 … 50 mesh), e.g. XAD 2
- Bismuth(III) nitrate solution, $\beta(Bi^{3+})$ = 2000 mg/L:
  Dissolve 2.8 g $Bi(OH)_2NO_3$ in 25 mL $w(HNO_3)$ = 65% and dilute to 1000 mL with dist. water.

  Instead of this solution a commercially available Bi standard solution [$\beta(Bi^{3+})$ = 1 g/L] can also be used. In this case the volumes added have to be doubled.
- Bi/NTA stock solution, $\beta(H_3NTA)$ = 1000 mg/L:
  a) Dissolve 4.5 g $Bi(OH)_2NO_3$ in 30 mL $w(HNO_3)$ = 65% and dilute to 400 mL with dist. water.
  b) Dissolve 1000 mg NTA in 20 mL c(NaOH) = 2 mol/L and dilute to 400 mL with dist. water.

  While stirring, combine the two solutions a) and b) and make up to 1 L with dist. water at 20 °C in a volumetric flask. The pH value should be about 0.7. The stock solution can be kept for four weeks.
- Bi/NTA standard solution, $\beta(H_3NTA)$ = 100 mg/L:
  Add 50 mL dist. water and 15 mL $c(HNO_3)$ = 2 mol/L to 10 mL Bi/NTA stock solution in a 100 mL volumetric flask. Fill to the mark with dist. water and mix. This standard solution is stable for approx. one week.
- Bi/EDTA stock solution, $\beta(H_4EDTA)$ = 1000 mg/L:
  a) Dissolve 3.1 g $Bi(OH)_2NO_3$ in 30 mL $w(HNO_3)$ = 65% and dilute to 400 mL with dist. water.
  b) Dissolve 1274 mg $Na_2EDTA \times 2\ H_2O$ in 20 mL c(NaOH) = 2 mol/L and dilute to 400 mL with dist. water.

  While stirring vigorously, add solution b) to solution a) and, after cooling, make up to 1 L with dist. water. The stock solution can be kept for four weeks.
- Bi/EDTA standard solution, $\beta(H_4EDTA)$ = 100 mg/L:
  Add 50 mL dist. water and 15 mL $c(HNO_3)$ = 2 mol/L to 10 mL Bi/EDTA stock solution in a 100 mL volumetric flask. Fill to the mark with dist. water and mix. This standard solution is stable for approx. one week.

Preparation of the columns for solid phase extraction

Glass columns of 8 mm inner diameter and a one-way stopcock (bore 2.5 mm) are used, e.g. DIN Analyse-EHB 3 NS.

Cation exchanger

The cation exchange resin is stirred with the fivefold volume of c(HCl) = 0.1 mol/L for at least 2 h. It is washed with dist. water until free from acid, the excess water is decanted and the resin then converted to its Na^+ form by stirring it with the fivefold quantity of c(NaOH) = 0.1 mol/L for 2 h. The cation exchanger, thus treated, is then washed with dist. water until neutral.

- Equip the column with a glass wool plug.
- Suspend 5 mL cation exchange resin in dist. water, fill it into the column making sure there are no air bubbles and rinse with 20 mL dist. water. Filling height approx. 100 mm.
- Never let the water level sink below 2 ... 3 mm above the packing.
- Discard the cation exchange resin after use.

Non-polar resin adsorbent

- Equip the column with a glass wool plug.
- Fill 5 mL resin adsorbent suspended in methanol into the column making sure there are no air bubbles.
- Wash the resin with 10 mL methanol and 20 mL dist. water.
- Never let the water level sink below 2 ... 3 mm above the packing.
- Discard the resin adsorbent after use.

Sampling and sample preparation

The water sample is acidified to pH = 2.0 by addition of 1 mL/L concentrated nitric acid. If the sample contains undissolved substances that interfere with the subsequent analysis, these have to be removed by filtration through a membranous filter (pore width 0.45 µm). The sample, thus stabilized, can be kept in a refrigerator at 4 °C for one week.

10 g KNO_3 is dissolved in 100 mL of the prepared water sample. This solution is run through the resin adsorbent at a flow rate of 5 mL/min. The first 20 mL are discarded, the remaining 80 mL are run through the cation exchanger (flow rate 5 mL/min). The first 20 mL are also discarded here, so that 60 mL sample remain for the polarographic determination.

Analysis

Pipet 10 mL of the prepared sample solution into the polarographic vessel, add approx. 400 mg ascorbic acid and purge with nitrogen for 5 min. Afterwards record the DP polarogram between +0.1 V and –0.6 V. No peaks must appear at the peak potentials of the Bi-NTA and Bi-EDTA complexes.

25 µL bismuth(III) nitrate solution (with higher contents correspondingly more) is now added and the solution purged with nitrogen for 5 min under stirring, then the DP polarogram is recorded again (same conditions as above). The pure Bi peak should be about twice as high as the peaks of the corresponding Bi complexes (excess Bi). If this is not the case, more bismuth(III) nitrate must be added.

The peak potential of Bi is +20 mV.

The NTA and EDTA concentrations are determined by standard addition with the corresponding stock or standard solutions.

To rule out any mistakes during sample preparation, the recovery R has to be determined for each series of measurements. For this, 100 mL NTA standard solution or EDTA standard solution is subjected to the entire analysis procedure (including treatment with resin adsorbent and cation exchanger). The recovery must be >90% and be taken into account in the calculation. (With recoveries <90%, check the sample preparation, above all the quality of the cation exchanger.)

$$R \text{ in } \% = A * 100 / B$$

A = measured mass concentration of NTA or EDTA in mg/L

B = initial mass concentration of NTA or EDTA in mg/L

Calculation of the mass concentrations in the analyzed water sample with consideration of the recovery R:

D = C * 100 / R

C = mass concentration of NTA or EDTA measured in the sample solution in mg/L

D = actual mass concentration of NTA or EDTA in the sample solution in mg/L

The polarogram is recorded using the following parameters:

working electrode	DME
stirrer speed	2000 rpm
mode	DP
purge time	300 s
equilibration time	10 s
pulse amplitude	50 mV
start potential	+100 mV
end potential	–600 mV
voltage step	6 mV
voltage step time	0.6 s
sweep rate	10 mV/s
peak potential (Bi-NTA)	–220 mV
peak potential (Bi-EDTA)	–440 mV

Remarks

- EDTA may be adsorbed on the cation exchange resin, which decreases the recovery. NTA, by contrast, is not adsorbed on the cation exchanger. The used non-polar resin adsorbent showed no adsorption effects, neither for EDTA nor for NTA.
- Better recoveries are obtained if the addition of KNO_3 is increased to 20 g (instead of 10 g).
- According to DIN 38413 part 5, the differential pulse technique (DP technique) has to be used for the polarographic determination. However, with the 746 VA Trace Analyzer the sensitivity of the determination can be increased if the SQW technique (square wave) is used instead. The increase amounts to 35% for NTA and 45% for EDTA using the following parameters:

  U.ampl 20 mV
  t.step 0.6 s
  t.meas 2 ms
  Modul.freq. 150 Hz
  Prep.cycles 10
  Meas.cycles 10

Figures

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================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB076   .mth         OPERATION SEQUENCE
 Title : Determination of NTA and EDTA in water, AB76
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    DOS/M               V.added       0.050 mL
 2    SMPL/M              V.fraction          mL     V.total              L
 3    STIR                Rot.speed      2000 /min
 4    PURGE         300.0
 5    (ADD
 6      PURGE
 7      STIR        20.0   Rot.speed      2000 /min
 8      SEGMENT            Segm.name   pol
 9      ADD>M              Soln.name   NTA-Std        V.add         0.025 mL
10      ADD>M              Soln.name   EDTA-Std       V.add         0.100 mL
11    ADD)2
12    END

 Method: AB076                SEGMENT
                                   pol
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    0PURGE
 2    0STIR          5.0
 3    (REP
 4      DME
 5      DPMODE           U.ampl          -50 mV     t.meas         20.0 ms
                         t.step         0.60 s      t.pulse        30.0 ms
 6      SWEEP       72.0 U.start          100 mV     U.step            6 mV
                         U.end          -600 mV     Sweep rate       10 mV/s
 7    REP)1
 8    PURGE
 9    STIR           2.0   Rot.speed      2000 /min
10    0MEAS                U.standby           mV
11    END
```

Fig. 1: *Method for the determination of NTA and EDTA with the 746 VA Trace Analyzer*

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================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : A76_aw              User:                      Date: 1993-02-12
 Modified    : 1993-02-15 13:31:00  Run :  0                  Time: 15:59:50
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        Abwasser NTA                                                 10.0 mL
--------------------------------------------------------------------------------
 Method  :  A76
 Title   :  Bestimmung NTA und EDTA in Abwasser
 Remark1 :  10 ml Eluat + 400 mg Ascorbinsaeure + 50 ul Bi
 Remark2 :
--------------------------------------------------------------------------------

  Substance : NTA                                                  Comments
  Mass conc.:    2.302 mg/L            Mass     : 23.02 ug   ------------------
  MC.dev.   :    0.027 mg/L (1.17%)    Add.mass :    25 ug
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -229   -126.9  -126.6   0.3431
              01   -229   -126.4
              10   -230   -259.8  -260.6    1.084   -133.9   rear overlapping
              11   -229   -261.3
              20   -229   -390.2  -391.8    2.173   -131.2
              21   -229   -393.3

  Substance : EDTA                                                 Comments
  Mass conc.:    857.2 ug/L            Mass     : 8.572 ug   ------------------
  MC.dev.   :     47.3 ug/L (5.51%)    Add.mass :    10 ug
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -442   -21.88  -21.98   0.1452
              01   -442   -22.09
              10   -440   -49.56  -48.69    1.228   -26.70   front overlapping
              11   -441   -47.82
              20   -438   -71.65  -72.38    1.027   -23.69
              21   -438   -73.10

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 NTA          std.add.     -1.265e-07   -5.525e-05                 1.250e-09
 EDTA         std.add.     -2.238e-08   -2.624e-05                 1.073e-09

 Final results                        +/- Res.dev.   %      Comments
 ---------------------------------    -----------------     ------------------
        NTA =   2.3021 mg/L              0.027    1.17
       EDTA =   857.21 ug/L               47.3    5.51
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Fig. 2: *Results for the determination of NTA and EDTA in waste water using the 746 VA Trace Analyzer.*

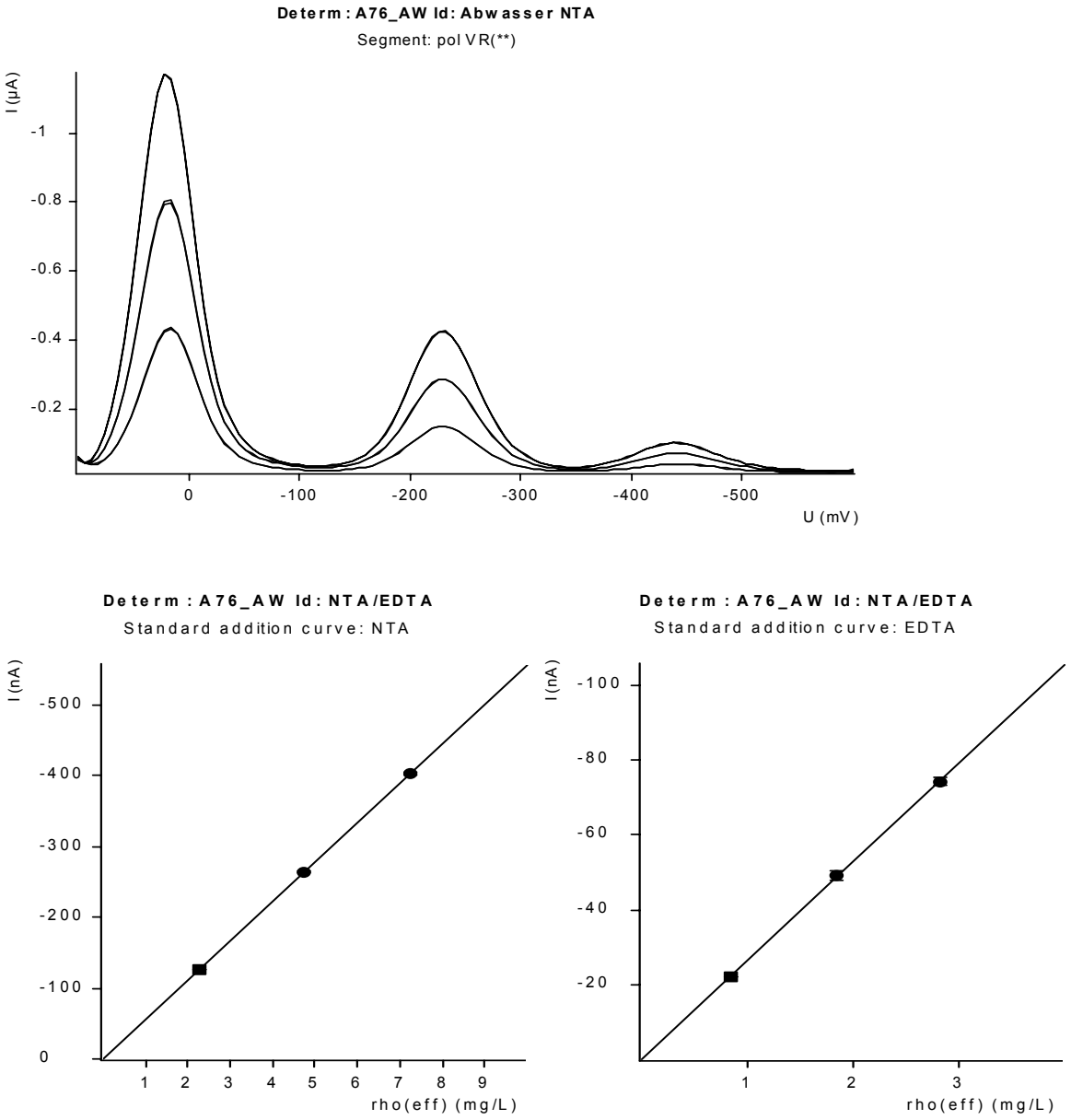

Fig. 3: *Polarograms and standard addition curves for the determination of NTA and EDTA in waste water using the 746 VA Trace Analyzer.*