Application Bulletin

Of interest to:	General analytical laboratories	B 1, 2, 7, 8, 11
	Water, environmental protection; Food; Fertilizers	

Polarographic determination of nitrite in water samples, meat and sausages

Summary

Nitrite can be determined by polarography after conversion to diphenylnitrosamine $(C_6H_5)_2NNO$. To ensure rapid and quantitative conversion, potassium thiocyanate is used as a catalyst. The reaction is carried out in an acidic solution at approx. pH = 1.5.

The determination limit is 5 µg/L NO_2^-.

Instruments and accessories

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

Electrodes

- Working electrode (WE):
  Multi-Mode Electrode MME 6.1246.020
- Reference electrode (RE):
  Ag/AgCl reference system 6.0728.020
  Electrolyte vessel 6.1245.010
  with intermediate electrolyte c($LiCH_3COO$) = 1 mol/L
- Auxiliary electrode (AE):
  Platinum rod 6.0343.000

Reagents

All reagents used should have the highest possible degree of purity (p.a. or suprapur). Only ultrapure water should be used.

- Potassium thiocyanate KSCN, puriss. p.a., CAS 333-20-0
- Perchloric acid, w($HClO_4$) = 70%, suprapur
- Diphenylamine $(C_6H_5)_2NH$, p.a., CAS 122-39-4
- Methanol, puriss. p.a., CAS 67-56-1
- Nitrite stock solution, β(NO_2^-) = 1 g/L (commercially available, e.g. Merck no. 119899)
- Lithium acetate dihydrate $LiCH_3COO \times 2\ H_2O$, MicroSelect, CAS 546-89-4

Ready-to-use solutions

- Supporting electrolyte: c(KSCN) = 0.05 mol/L, c($HClO_4$) = 0.2 mol/L:
  Dissolve 0.486 g KSCN in ultrapure water, add 1.72 mL w($HClO_4$) = 70% and make up to 100 mL with ultrapure water.
- Diphenylamine solution, c($(C_6H_5)_2NH$) = 2.6 * 10^{-3} mol/L:
  Dissolve 0.044 g diphenylamine in 40 mL methanol and make up to 100 mL with ultrapure water.
- Nitrite standard solution, β(NO_2^-) = 10 mg/L
  Diluted solutions have to be freshly prepared with ultrapure water every day.

Sample preparation for meat and sausages

Reagents

- Zinc acetate dihydrate $Zn(CH_3COO)_2$ x 2 H_2O, puriss. p.a., CAS 5970-45-6
- Potassium hexacyanoferrate(II) trihydrate $K_4[Fe(CN)_6]$ x 3 H_2O, puriss. p.a., CAS 14459-95-1

Ready-to-use solutions

- Zinc acetate solution: w($Zn(CH_3COO)_2$) = 30% in ultrapure water
- Potassium hexacyanoferrate(II) solution: w($K_4[Fe(CN)_6]$) = 15% in ultrapure water

10 g sample cut into small pieces is mixed with 100 mL ultrapure water for 5 min using a high-frequency mixer, then heated in the water bath for 1 h at 90 °C. Afterwards add 2 mL w($Zn(CH_3COO)_2$) = 30% and 2 mL w($K_4[Fe(CN)_6]$) = 15% and mix. Filter through a paper filter and – if the obtained filtrate is not completely clear – in addition through a microfilter 0.45 µm.

Apart from the nitrite determination, the sample solution can be also used for the determination of nitrate according to Application Bulletin No. 70.

Analysis

Measuring solution:

10 mL (diluted) sample solution
+ 3 mL supporting electrolyte
+ 1 mL diphenylamine solution

If necessary, adjust the pH value to 1.5 ± 0.5 with w($HClO_4$) = 70%.

The polarogram is recorded using the following parameters:

working electrode	DME
stirrer speed	2000 rpm
mode	DP
purge time	300 s
equilibration time	5 s
pulse amplitude	50 mV
start potential	–400 mV
end potential	–810 mV
voltage step	6 mV
voltage step time	0.6 s
sweep rate	10 mV/s
peak potential $(C_6H_5)_2NNO$	–660 mV

The concentration is determined by standard addition.

Remark

Using the 757 VA Computrace, the determination limit is approx. 20 µg/L NO_2^-.

Literature

- Shaw-Kong Chang, R. Kozeniauskas, G. W. Harrington
  Determination of nitrite ion using differential pulse polarography
  Anal. Chem. 49 (1977) 2272–2275

Figures

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================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB127   .mth         OPERATION SEQUENCE
 Title : Determination of Nitrite. AB127
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    SMPL>M               V.fraction          mL     V.total               L
 2    DOS>M                Soln.name   electrol       V.add         3.000 mL
 3    DOS>M                Soln.name   diphenyl       V.add         1.000 mL
 4    PURGE
 5    STIR          300.0  Rot.speed      2000 /min
 6    (ADD
 7      PURGE
 8      STIR         10.0   Rot.speed      2000 /min
 9      0PURGE
10      0STIR         5.0
11      (REP
12        SEGMENT           Segm.name   NO2_SEG
13      REP)1
14      PURGE
15      ADD>M               Soln.name   NO2_Std        V.add         0.200 mL
16    ADD)2
17    END

 Method: AB127                SEGMENT
                               NO2_SEG
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    DME
 2    DPMODE               U.ampl           -50 mV     t.meas         20.0 ms
                           t.step         0.60 s       t.pulse        40.0 ms
 3    SWEEP         43.2   U.start        -400 mV      U.step            6 mV
                           U.end          -810 mV      Sweep rate       10 mV/s
 4    0MEAS                U.standby           mV
 5    END
```

Fig. 1: *Method for the determination of nitrite with the 746 VA Trace Analyzer.*

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==================== METROHM 757 VA COMPUTRACE (5.757.0020) ====================
 Determ.      : 11171007_NO2 in Salami.dth
 Sample ID    : NO2 in Salami
 Creator      : ---               Date : 1999-11-17          Time:  10:07:23
 Modified by  : zu                Date : 2001-06-28          Time:  15:13:35
 User         : zu                Date : 2001-06-28          Time:  15:13:35
--------------------------------------------------------------------------------
 Cell volume:   14.000 mL
 Sample amount: 10.000 mL
--------------------------------------------------------------------------------
 Method  :  AB127_2.mth
 Title   :  AB127_Nitrite
 Remark1 :  10 mL sample solution + 3 mL electrolyte + 1 mL diphenylamine
 Remark2 :
--------------------------------------------------------------------------------
  Substance : NO2                                                  Comments
  Mass conc.:  138.980  ug/L                                       ----------
  MC.dev.   :    8.458  ug/L      (    6.09%)
  Mass      :    1.946  ug
  Add.mass  :    2.000  ug

              VR     V     nA      I.mean  Std.Dev. I.delta   Comments
              ----  -----  ------  ------  -------  -------   ----------
              1-1   -0.664 -13.41  -13.27  0.203
              1-2   -0.664 -13.12
              2-1   -0.664 -25.43  -25.31  0.165    -12.05
              2-2   -0.664 -25.20
              3-1   -0.664 -40.06  -40.10  0.063    -14.79
              3-2   -0.664 -40.15

 Substance    Calibr.    Y.reg/offset   Slope         Std.Dev.
 ---------    --------   ------------   -----------   ------------
      NO2     std.add.   -1.311e-008    -9.434e-005   1.815e-010

 Final results                        +/- Res. dev.   %     Comments
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 NO2:
 Nitrite           =  194.572  µg/L    11.841       6.086
```

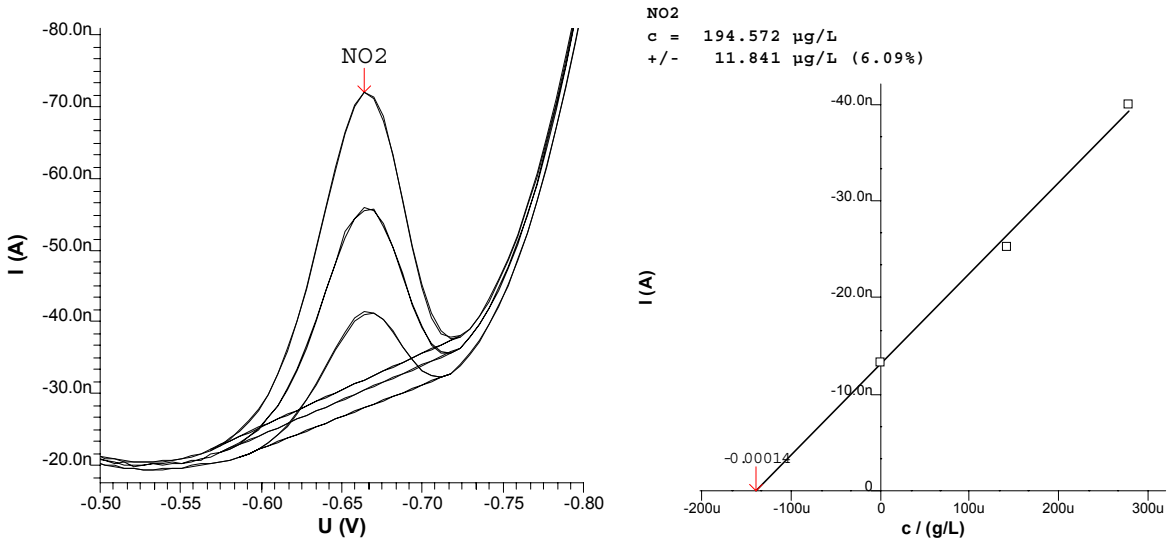

Fig. 2: *Determination of nitrite in salami with the 757 VA Computrace.*