Application Bulletin

Of interest to: General analytical laboratories, Organic chemistry, Plastics, Food industry — B 1, 3, 6, 7

Polarographic determination of styrene in polystyrenes and copolymers

Summary

This Application Bulletin describes a simple polarographic method to determine monomeric styrene in polymers. The limit of determination lies by 5 mg/L. Before the determination styrene is converted into the electrochemically active pseudonitrosite using sodium nitrite.

Apparatus and accessories

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

Reagents

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

- Sodium acetate waterfree, puriss p.a., CAS 127-09-3
- Sodium nitrite, puriss p.a., CAS 7632-00-0
- Acetic acid, puriss p.a., w(CH_3COOH) = 96%
- Dioxane, puriss p.a., CAS 123-91-1
- Styrene (stabilised), for synthesis, CAS 100-42-5

Ready to use solutions

- Sodium acetate solution w($NaOOCH_3$) = 50% in water
  Dissolve 250 g sodium acetate in water in a 500 mL volumetric flask fill up to the mark with water.
- Sodium nitrite, w($NaNO_2$) = 30% in water
  Dissolve 30 g sodium nitrite in water in a 100 mL volumetric flask fill up to the mark with water.
- Styrene standard: β(styrene) = 1 g/L
  Dissolve 100 mg styrene in 3 mL dioxane in a 100 mL volumetric flask and add 22 mL acetic acid. After addition of 2 mL sodium nitrite solution, allow the solution to react for 20 min at room temperature. Add 20 mL sodium acetate solution and fill up to the mark with dist. water. The solution can be kept for about 1 month.

Sample preparation

Mix to a slurry approx. 1 g powdered sample and 15 mL dioxane in a beaker. Mix with 110 mL acetic acid and if the sample is not totally dissolved, filter the solution through a suitable filter paper (e.g. Schleicher&Schuell S&S 589/5).

Analysis

Pipette 5 mL filtrate into a polarographic vessel and mix with 0.75 mL sodium nitrite solution. After 20 min reaction time (room temperature), add 10 mL water and 5 mL sodium acetate solution.

The polarogram is registered with the following parameters:

Working electrode	DME
Stirrer speed	2000 rpm
Measurement mode	DP
Purge time	300 s
Pulse amplitude	50 mV
Equilibration time	5 s
Start potential	0 V
End potential	-0.4 V
Voltage step	6 mV
Voltage step time	0.60 s
Sweep rate	10 mV/s
Peak potential	-0.24 V

The determination of the concentration is done by standard addition.

Literature

- Alekseeva T.A., Usikova L.G., Bezuglyi V.D.
  Polarographic determination of 2,4- and 2,5-dimethyl styrene.
  Z. Anal. Khim. 18, (1963) 520-524
  Ref: Fresenius Z. Anal. Chem. 210, (1965) 461
- Kurenkov V.F., Kuznecov E.V., Mjagcenkov V.A.
  Differential determination of acrylamide and styrene in copolymers by using polarographic methods.
  Zh. Anal Khim. 28, (1973) 1236-1238
  Ref: Fresenius Z. Anal. Chem. 271, (1974) 395-396

Figures

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================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 08170915             User:                       Date: 1999-08-17
 Modified    : 1999-08-17 10:09:42  Run :  3                    Time: 09:15:32
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
                             1.0                                       1.006 g
--------------------------------------------------------------------------------
 Method  :  AB136
 Title   :  Polarographic method / Styrol in Polystyrol
 Remark1 :
 Remark2 :
--------------------------------------------------------------------------------

  Substance : Styrol                                          Comments
  Mass conc.:    46.33 mg/L           Mass     : 231.7 ug     ----------------
  MC.dev.   :     3.65 mg/L (7.89%)   Add.mass :   100 ug
  Cal.dev.  :    -                    V0.sample:     5 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ----------------
              00   -229   -33.76  -34.29   0.7575
              01   -226   -34.83
              10   -229   -46.84  -47.11   0.3783   -12.82
              11   -226   -47.38
              20   -227   -64.20  -62.86    1.885   -15.76
              21   -225   -61.53

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Styrol       std.add.     -3.378e-08   -3.026e-06                 1.369e-09


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

 Final results                        +/- Res.dev.   %      Comments
 ---------------------------------    -----------------    ----------------
     Styrol =   5.8489 mg/g              0.461    7.89
```

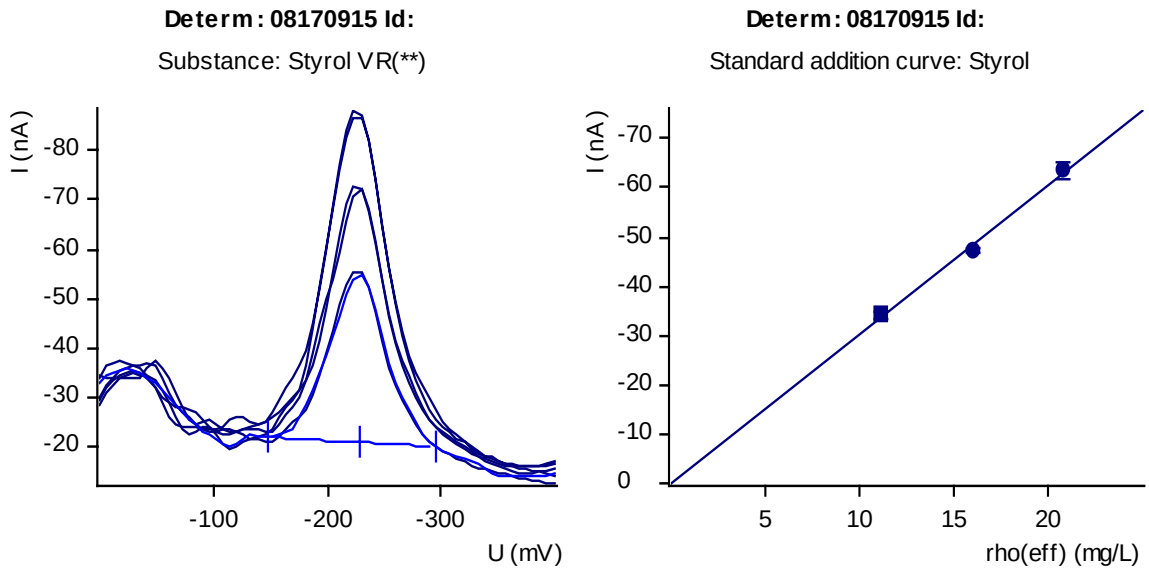

Fig. 1 Example of a styrene determination in PS beakers with the 746 VA Trace Analyzer

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB136   .mth          OPERATION SEQUENCE
 Title : Determination of Styrene. AB136
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    SMPL/M               V.fraction    5.000 mL    V.total        0.125 L
 2    DOS>M                Soln.name   NaNO2         V.add          0.750 mL
 3    DOS>M                Soln.name   water         V.add         10.000 mL
 4    DOS>M                Soln.name   NaAcetat      V.add          5.000 mL
 5    PURGE
 6    STIR          300.0  Rot.speed      2000 /min
 7    (ADD
 8      PURGE
 9      STIR         20.0   Rot.speed      2000 /min
10      0PURGE
11      0STIR        10.0
12      (REP
13        SEGMENT            Segm.name   pol
14      REP)1
15      PURGE
16      STIR                 Rot.speed      2000 /min
17      ADD>M                Soln.name   StyrStd       V.add          0.100 mL
18    ADD)2
19    END

 Method: AB136                SEGMENT
                                pol
--------------------------------------------------------------------------------

      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         42.0   U.start          0 mV     U.step            6 mV
                           U.end         -400 mV     Sweep rate       10 mV/s
 4    0MEAS                U.standby        mV
 5    END

  Method: AB136                SUBSTANCES
                              Styrene  - pol
--------------------------------------------------------------------------------

      Recognition                              Display / Plot
      -------------------------                -------------------------
      U.verify          -230 mV                I.scale       auto
      U.tol (+/-)         50 mV                U.div          50.00 mV/cm
      U.width min         10 mV                U.begin            0 mV
      U.width max        200 mV                U.end            200 mV
      I.threshold        200 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   2000-12-18 11:46:33            Coefficients
  ---------------------------------            -------------------------
  Technique     std.add.                       Y.reg         3.137e-07
  Curve type    linear                         Slope         2.824e-05
                                               Nonlin.
                                               Mean dev.     5.371e-09

                Additions
                ------------------------------------------------------------
  Soln.name      StyrStd
  ----------
  Mass conc.           1 g/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: AB136                CALCULATION
                             max. 15 lines
--------------------------------------------------------------------------------

 Quantity        Formula (R##, C##, A##)                  Res.unit   Sig.dig.
 ------------    ---------------------------------------  --------   --------
 Styrene         R1000=MC:Styrene * Vtot / S0             #g/g          5
```

Fig. 2 Method for the determination of styrene in PS beakers with the 746 VA Trace Analyzer