Application Bulletin

Of interest to:	General analytical laboratories	B 1, 2
	Water, waste water, environmental protection	

Polarographic determination of free cyanide

Summary

This Bulletin describes a polarographic method for the determination of cyanide that allows to determine free cyanide fast and accurately. The determination also succeeds in solutions containing sulfides, where other methods fail. Cyanide concentrations in the range ß(CN^-) = 0.01...10 mg/L cause no problems. Interference caused by anions and complexed cyanides has been investigated.

Instruments and accessories

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

Reagents

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

- Potassium hydroxide KOH, puriss. p.a., purity ≥86%, CAS 1310-58-3
- Boric acid H_3BO_3, puriss. p.a., CAS 10043-35-3
- Potassium cyanide KCN, puriss. p.a., CAS 151-50-8

Ready-to-use solutions

- Supporting electrolyte: c(H_3BO_3) = 0.2 mol/L, c(KOH) = 0.17 mol/L, pH 10.2:
  Dissolve 11.2 g KOH in approx. 800 mL ultrapure water. Add 12.4 g boric acid, adjust the pH value to 10.2 if necessary and make up to 1 L with ultrapure water.
- Potassium hydroxide solution, c(KOH) = 0.01 mol/L:
  Dissolve 0.65 g KOH in ultrapure water and make up to 1 L.
- Cyanide standard solution, ß(CN^-) = 1 g/L:
  Dissolve 0.2503 g KCN in c(KOH) = 0.01 mol/L and make up to 100 mL.
  Additional standards can be prepared by dilution with KOH.

Analysis

Measuring solution:

10 mL (diluted) sample solution
+ 10 mL supporting electrolyte

If cyanide is present in concentrations above the linear working range, the sample solution has to be diluted accordingly with ultrapure water.

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	0 V
end potential	–500 mV
voltage step	8 mV
voltage step time	0.8 s
sweep rate	10 mV/s
peak potential CN^-	–240 mV

The concentration is determined by standard addition.

Remarks

- Cyanide can be determined in the presence of a 1000-fold excess of phosphate, nitrate and sulfate. A 50'000-fold excess of chloride does not interfere with the determination either.
- $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$ and $K_2[Ni(CN)_4]$ do not affect the height of the cyanide peak; $K[Zn(CN)_3]$ increases the peak height (decomposition of the complex); $K[Cu(CN)_2]$ somewhat distorts the shape of the peak when present in tenfold excess.
- If the CN^- concentration in the sample is greater than 10 mg/L, a smaller sample size has to be used. Concentrations as low as ß(CN^-) = 0.01 mg/L can still be determined with a precision of ±10%.
- It is also possible to determine cyanide in the presence of sulfide (e.g. in waste water distillates).
- The polarographic method for determining cyanide is quicker, sometimes more sensitive, and, above all, simpler than comparable methods.

Method	**Duration**
Titration ß(CN^-) = 1...100 mg/L	5...30 min
Direct potentiometry with the ion-selective electrode ß(CN^-) = 0.26...26 mg/L	up to 45 min (depending on conc.)
Colorimetry (benzidine/pyridine method) ß(CN^-) = 0.005...0.1 mg/L	approx. 15 min
Colorimetry (barbituric acid/pyridine method) ß(CN^-) = 0.005...0.5 mg/L	approx. 40 min
Polarography ß(CN^-) = 0.01...10 mg/L	approx. 5 min

The times listed for all the above methods refer to a single determination (without standard solution).

- With the method described only free cyanide can be determined. For the determination of the total cyanide content the cyanide has to be separated by distillation, e.g. according to DIN 38405 part 13.

Literature

- D. R. Canterford
Simultaneous determination of cyanide and sulfide with rapid direct current polarography
Anal. Chem. 47 (1975) 88–92

Figures

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================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB110   .mth         OPERATION SEQUENCE
 Title : Determination of cyanide. AB110
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    SMPL>M               V.fraction          mL     V.total               L
 2    DOS>M                Soln.name   electrol       V.add        10.000 mL
 3    PURGE
 4    STIR          300.0  Rot.speed      2000 /min
 5    (ADD
 6      PURGE
 7      STIR         10.0   Rot.speed      2000 /min
 8      0PURGE
 9      0STIR         5.0
10      (REP
11        SEGMENT           Segm.name   pol
12      REP)1
13      ADD>M               Soln.name   CN-std         V.add         0.050 mL
14    ADD)2
15    END

 Method: AB110                SEGMENT
                                   pol
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    DME
 2    DPMODE               U.ampl           -50 mV     t.meas         20.0 ms
                           t.step          0.80 s      t.pulse        40.0 ms
 3    SWEEP         53.6   U.start             0 mV     U.step            8 mV
                           U.end            -500 mV     Sweep rate       10 mV/s
 4    0MEAS                U.standby             mV
 5    END
```

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

```
==================== METROHM 757 VA COMPUTRACE (5.757.0020) ====================
 Determ.      : 06261315_waste water.dth
 Sample ID    : waste water
 Creator      :                    Date : 2001-06-26          Time:  13:15:36
 Modified by  :                    Date : 2001-06-26          Time:  16:08:59
 User         :                    Date : 2001-06-26          Time:  16:08:59
--------------------------------------------------------------------------------
 Cell volume:   20.000 mL
 Sample amount: 10.000 mL
--------------------------------------------------------------------------------
 Method  :  AB110_Det of CN.mth
 Title   :  Determination of free Cyanide
 Remark1 :  10 mL electrolyte + 10 mL sample
 Remark2 :
--------------------------------------------------------------------------------
  Substance : CN                                                  Comments
  Mass conc.:  232.297  ug/L                                      ----------
  MC.dev.   :    4.462  ug/L      (    1.92%)
  Mass      :    4.646  ug
  Add.mass  :    5.000  ug

              VR     V     nA      I.mean  Std.Dev. I.delta   Comments
             ----  -----  ------  ------  -------  -------   ----------
             1-1   -0.206  -65.9  -65.7   0.278
             1-2   -0.206  -65.5
             2-1   -0.214 -138.0  -138.0  0.085    -72.4
             2-2   -0.214 -138.1
             3-1   -0.214 -206.1  -204.7  1.966    -66.7
             3-2   -0.222 -203.3

 Substance    Calibr.    Y.reg/offset   Slope        Std.Dev.
 ---------    --------   ------------   -----------  ------------
       CN     std.add.   -6.584e-008    -2.834e-004   2.779e-010

 Final results                          +/- Res. dev.   %     Comments
 ----------------------------------     ----------------    ----------

 CN:
 Cyanide           =  464.593  µg/L    8.925        1.921
```

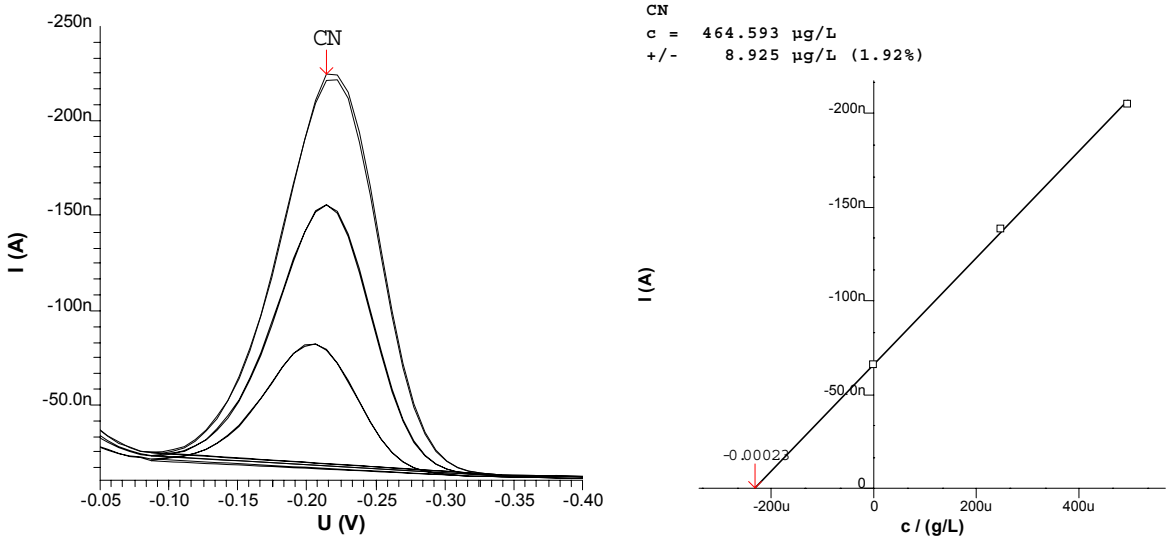

Fig. 2: *Determination of free cyanide in waste water with the 757 VA Computrace.*