Metrohm

Application Bulletin 110/3 e

Determination of free cyanide by polarography

Summary

This Application 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 $\beta(CN^-)$ = 0.01...10 mg/L cause no problems. Interference caused by anions and complexed cyanides has been investigated.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode

Electrodes

WE	Multi-Mode Electrode pro Mercury drop capillary	6.1246.120 6.1226.030
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Pt rod electrode	6.0343.x00

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Potassium hydroxide, w(KOH) ≥ 85%, for analysis, CAS 1310-58-3
- Boric acid, H_3BO_3, for analysis, CAS 10043-35-3
- Potassium cyanide, KCN, for analysis, CAS 151-50-8
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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.

Standard solutions

Potassium hydroxide solution	c(KOH) = 0.01 mol/L Dissolve 0.65 g KOH in ultrapure water and make up to 1 L.
Cyanide stock standard solution	$\beta(CN^-)$ = 1 g/L Dissolve 0.2503 g KCN in c(KOH) = 0.01 mol/L and make up to 100 mL.
Cyanide standard solution	$\beta(CN^-)$ = 100 mg/L Additional standards can be prepared by dilution with c(KOH) = 0.01 mol/L.

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.

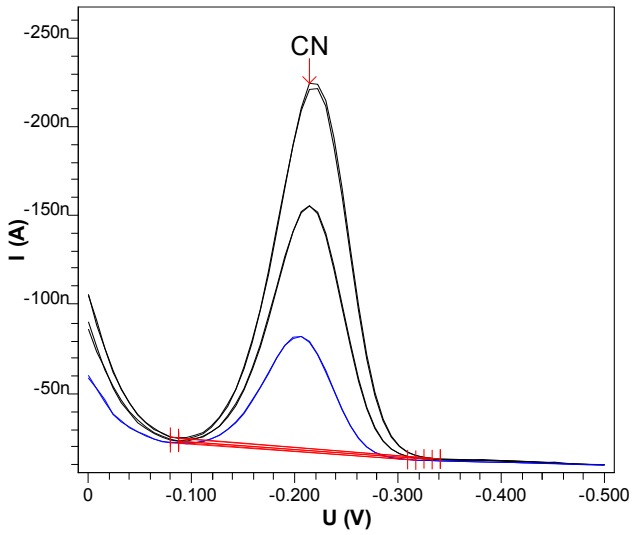
The concentration is determined by standard addition.

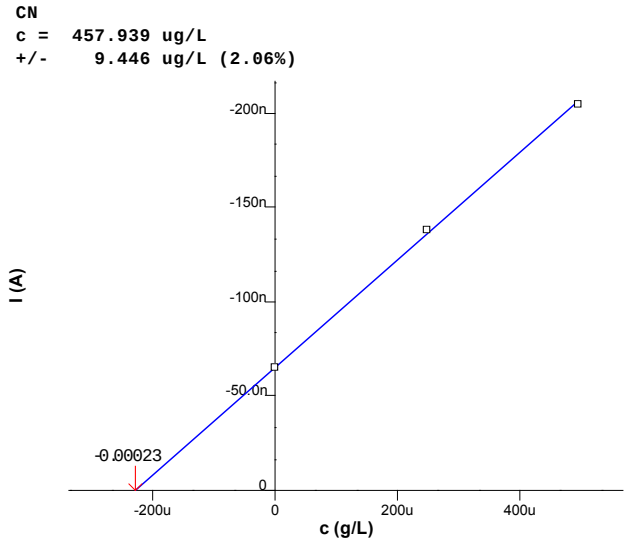
Parameters

Voltammetric	
Electrode operating mode	DME
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	5 s
Sweep	
Start potential	0.0 V
End potential	-0.5 V
Potential step	0.008 V
Potential step time	0.8 s

Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Substance	
Name	Cyanide
Characteristic potential	-0.24 V

Example





Result

Sample	Waste water
Sample size	10.0 mL
β(CN^-)	458 µg/L

Comments

- 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 β(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).
- 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 38405-13.
- The polarographic method for determining cyanide is quicker, sometimes more sensitive, and, above all, simpler than comparable methods. The times listed below for all the methods refer to a single determination (without standard solution).

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

References

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

Appendix

Report for the example determination of free cyanide in waste water

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========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 06261315_waste water.dth
 Sample ID      : waste water
 Creator method :                   Date :                      Time:
 Creator determ.:                   Date : 2001-06-26           Time:  13:15:36
 Modified by    :                   Date : 2001-06-26           Time:  16:08:59
--------------------------------------------------------------------------------
 Method         : AB110_Det of CN.mth
 Title          : Determination of free Cyanide
 Remark1        : 10 mL electrolyte + 10 mL sample
 Remark2        :
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  20.000 mL
--------------------------------------------------------------------------------
 Substance      : CN
 Conc.          : 228.970 ug/L
 Conc.dev.      :   4.723 ug/L     ( 2.06%)
 Amount         :   4.579 ug
 Add.amount     :   5.000 ug

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.206   -65.1   -65.1     0.119       0.0
 1 - 2  -0.206   -65.0
 2 - 1  -0.214  -138.0  -138.0     0.085     -73.0
 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 Mean deviat. Corr.Coeff.
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 CN           std.add.      -6.526e-008  -2.850e-004   1.802e-009      0.99960


 Final results                         +/- Res. dev.   %     Comments
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 CN:
 Cyanide           =  457.939  ug/L    9.446        2.063
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Method print for the determination of free cyanide

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--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method    : AB110_Det of CN.mth
Title     : Determination of free Cyanide
Remark1   : 10 mL electrolyte + 10 mL sample
Remark2   :

Calibration            : Standard addition
Technique              : Batch

Cell volume (mL)       : 20.000
Sample amount (mL)     : 10.000
Sample ID              : waste water

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                         : DP   - Differential Pulse

Highest current range        : 10  mA
Lowest current range         : 100 nA

Electrode                    : DME
Stirrer speed (rpm)          : 2000

No. of additions             : 2
No. of replications          : 2

Measure blank                : No
Addition purge time (s)      : 10


Initial purge time (s)       :      300
```

```
Sweep
Equilibration time (s)       :        5
Start potential (V)          :    0.000
End potential (V)            :   -0.500
Voltage step (V)             :    0.008
Voltage step time (s)        :    0.800
Sweep rate (V/s)             :    0.010
Pulse amplitude (V)          :    0.050
Pulse time (s)               :    0.040

Cell off after measurement   :      Yes

Peak evaluation
-------------------------------------------------------------------------------
Peak evaluation              : Height
Minimum peak width (V.steps) : 5
Minimum peak height (A)      : 1.000e-010
Smooth factor                : 4
Reverse peaks                : No
Reverse sweep                : No

Substances
-------------------------------------------------------------------------------
CN                           : -0.240 V   +/- 0.050 V
Standard solution            : 1   0.100 g/L
Addition volume (mL)         : 0.050

Cyanide                      : Final result (CN) = (1e+006 / 1) * Mass.conc + 0 - 0
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