Application Bulletin

Of interest to:	Environmental protection; Electroplating	A 1, 2, 10

Potentiometric determination of cyanide

Summary

The determination of cyanide is very important not only in electroplating baths and when decontaminating waste water but, due to its high toxicity, also in water samples in general. Concentrations of 0.05 mg/L CN^- can already be lethal for fish.

This bulletin describes the determination of cyanide in samples of different concentrations by means of potentiometric titration.

Chemical reactions:

$$2\ CN^- + Ag^+ \rightarrow [Ag(CN)_2]^-$$

$$[Ag(CN)_2]^- + Ag^+ \rightarrow 2\ AgCN$$

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or
  726 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.223 and/or 6.3014.213 Exchange Units
- 6.0430.100 Ag Titrode with Ag_2S coating and 6.2104.020 electrode cable

Reagents

- Titrant c($AgNO_3$) = 0.1 mol/L ... 0.0002 mol/L
- Sodium hydroxide c(NaOH) = 1 mol/L
- Digestion chemicals: see under «3. Cyanide traces in water samples after sample preparation»

Analysis

1. Electroplating baths (high cyanide concentrations): alkaline baths for Ag, Cd, Cu, Pb, Zn, etc.

Pour ca. 50 mL dist. water as well as 5 mL c(NaOH) = 1 mol/L into a glass beaker. Add 2.0 mL of the plating bath sample and titrate with c($AgNO_3$) = 0.1 mol/L just past the first equivalence point.

Calculation

1 mL c($AgNO_3$) = 0.1 mol/L corresponds to 2.6018 mg CN^- or 6.5116 mg KCN or 4.9007 mg NaCN

g/L cyanide = EP1 * C01 / C00

EP1 = titrant consumption to reach the first EP in mL
C00 = 2.0 (sample volume in mL)
C01 = 2.6018 or 6.5116 or 4.9007 (equivalent weight of CN^- or KCN or NaCN in mg/mL)

2. Waste water for decontamination (1 ... 100 mg/L CN^-)

Pour 5 mL c(NaOH) = 1 mol/L into a glass beaker. Add 10 ... 100 mL sample solution (depending on the expected CN^- concentration) and titrate with c($AgNO_3$) = 0.01 mol/L just past the first equivalence point.

Calculation

1 mL c($AgNO_3$) = 0.01 mol/L corresponds to 0.2602 mg CN^-

mg/L CN^- = EP1 * C01 * C02 / C00

EP1 = titrant consumption to reach the first EP in mL
C00 = 10 ... 100 (sample volume in mL)
C02 = 0.2602 (equivalent weight of CN^- in mg/mL)
C03 = 1000 (conversion factor in mL/L)

3. Cyanide traces in water samples after sample preparation

The decomposition and separation of the cyanides are carried out according to DIN 38405 D13/D14).

One differentiates between the easily released cyanides and the total cyanide content.

Apparatus for decomposition and separation of the cyanides

The apparatus consists of a washing bottle, a three-necked round flask, a condenser and an absorption vessel (see Fig. 1).

3.1 Determination of the easily released cyanides

These are released from the sample as HCN at room temperature and a pH value of about 4 by means of an air stream and absorbed in sodium hydroxide solution.

Reagents

- Sodium hydroxide c(NaOH) = 1 mol/L (for the absorption vessel and washing bottle)
- Hydrochloric acid c(HCl) = 1 mol/L
- $ZnSO_4$/$CdSO_4$ solution:
  Dissolve 100 g $ZnSO_4$ * 7 H_2O as well as 100 g $CdSO_4$ * 8 H_2O in dist. water and make up to 1 L.

- EDTA solution:
  Dissolve 100 g $Na_2EDTA * 2 H_2O$ in 940 mL dist. water with heating.
- Buffer solution pH = 4.0:
  Dissolve 80 g potassium hydrogen phthalate in 920 mL dist. water with heating.
- Zinc powder, p.a.

Separation of the easily released cyanides

Fill the absorption vessel with 10 mL c(NaOH) = 1 mol/L, mount it directly onto the three-necked flask and connect it to the suction tubing. Add through the charging funnel 10 mL EDTA solution, 10 mL $ZnSO_4/CdSO_4$ solution, 50 mL buffer solution pH = 4 as well as 100 mL water sample, then mix well. If necessary, the pH value of the mixture is adjusted to 3.9 ± 0.1 by adding c(HCl) = 1 mol/L or c(NaOH) = 1 mol/L drop by drop through the funnel. Afterwards add 0.3 zinc powder through the side neck opening, then close this again. Connect the washing bottle containing ca. 100 mL c(NaOH) = 1 mol/L and switch on the suction pump. Set the air flow at 60 L/h and suck air through the apparatus for 4 h.

With water samples containing less than 0.1 mg/L CN^- a sample volume of 200 mL is used. In this case the additions of EDTA, $ZnSO_4/CdSO_4$ and buffer solution have to be doubled, too.

It is necessary to determine the blank of the chemicals used. Instead of the sample, take 100 mL dist. water for this analysis. The blank determination has to be repeated whenever new packages of chemicals are opened for use.

Analysis

The contents of the absorption vessel are rinsed into a glass beaker with ca. 20 mL dist. water.

For CN^- concentrations of 0.2 ... 10 mg/L, titrate with $c(AgNO_3)$ = 0.002 mol/L, for CN^- concentrations of 0.01 ... 0.5 mg/L titrate with $c(AgNO_3)$ = 0.0002 mol/L using the following parameter settings:

meas.pt.density	6
min.incr.	10.0 µL
titr.rate	max.
signal drift	20.0 mV/min
equilibr.time	20 s
pause	60 s
EPC	20

In order to condition the electrode, it is immersed before the first analysis for 20 min in sodium hydroxide solution with a concentration of c(NaOH) = 0.4 mol/L that additionally contains 0.3 mg/L CN^-.

Calculation

1 mL $c(AgNO_3)$ = 0.002 mol/L corresponds to 0.052 mg CN^-
1 mL $c(AgNO_3)$ = 0.0002 mol/L corresponds to 0.0052 mg CN^-

mg/L CN^- = (EP1 – C31) * C01 * C02 * C30 / C00

EP1 = titrant consumption in mL
C00 = 100 ... 200 (sample volume in mL)
C01 = 0.052 or 0.0052 (equivalent weight of CN^- in mg/mL)
C02 = 1000 (conversion factor in mL/L)

C30 = titer of the titrant
C31 = titrant consumption for the blank in mL

Remarks

- The titer of the titrant is determined with 0.1 mg [when using $c(AgNO_3)$ = 0.002 mol/L] or 0.05 mg CN^- standard [when using $c(AgNO_3)$ = 0.0002 mol/L] in 30 mL c(NaOH) = 0.4 mol/L:
  titer = 1.923 / EP1 or titer = 9.615 / EP1
- Low CN^- concentrations lead to a slow initial response of the electrode. Therefore a pause of 60 s is programmed on the titrator.

3.2 Determination of the total cyanide content

The cyanide compounds are decomposed by boiling with HCl in the presence of Cu(I) ions. The HCN formed is expelled with an air stream and absorbed in sodium hydroxide solution.

Reagents

- Sodium hydroxide c(NaOH) = 1 mol/L (for the absorption vessel and washing bottle)
- Concentrated hydrochloric acid w(HCl) = 35 ... 37%
- $CuSO_4$ solution:
  Dissolve 200 g $CuSO_4 * 5 H_2O$ in dist. water and make up to 1 L.
- Sn(II) solution:
  Dissolve 50 g $SnCl_2 * 2 H_2O$ as well as 40 mL c(HCl) = 1 mol/L in dist. water and make up to 100 mL. The solution is stable for about one week.

Decomposition and separation of the total cyanide

The absorption vessel is filled with 10 mL c(NaOH) = 1 mol/L, mounted onto the reflux cooler and connected to the suction tubing. Through the charging funnel add the following components one after the other: ca. 30 mL dist water, 10 mL $CuSO_4$ solution, 2 mL Sn(II) solution and finally 100 mL water sample. After addition of 10 mL conc. HCl, connect the washing bottle containing ca. 100 mL c(NaOH) = 1 mol/L to the funnel and heat up the contents of the flask to boiling point. Set the air flow at ca. 20 L/h; the reflux should be ca. 1 ... 2 drops/s. The decomposition is completed after 1 h.

With water samples containing less than 0.1 mg/L CN^- a sample volume of 200 mL is used. In this case the additions of $CuSO_4$ solution, Sn(II) solution and conc. HCl have to be doubled, too.

It is necessary to determine the blank of the chemicals used. Instead of the sample, take 100 mL dist. water for this analysis. The blank determination has to be repeated whenever new packages of chemicals are opened for use.

Analysis

The contents of the absorption vessel are rinsed into a glass beaker with ca. 20 mL dist. water. The analysis is then carried out in the same way as described under «3.1 Determination of the easily released cyanides».

Figures

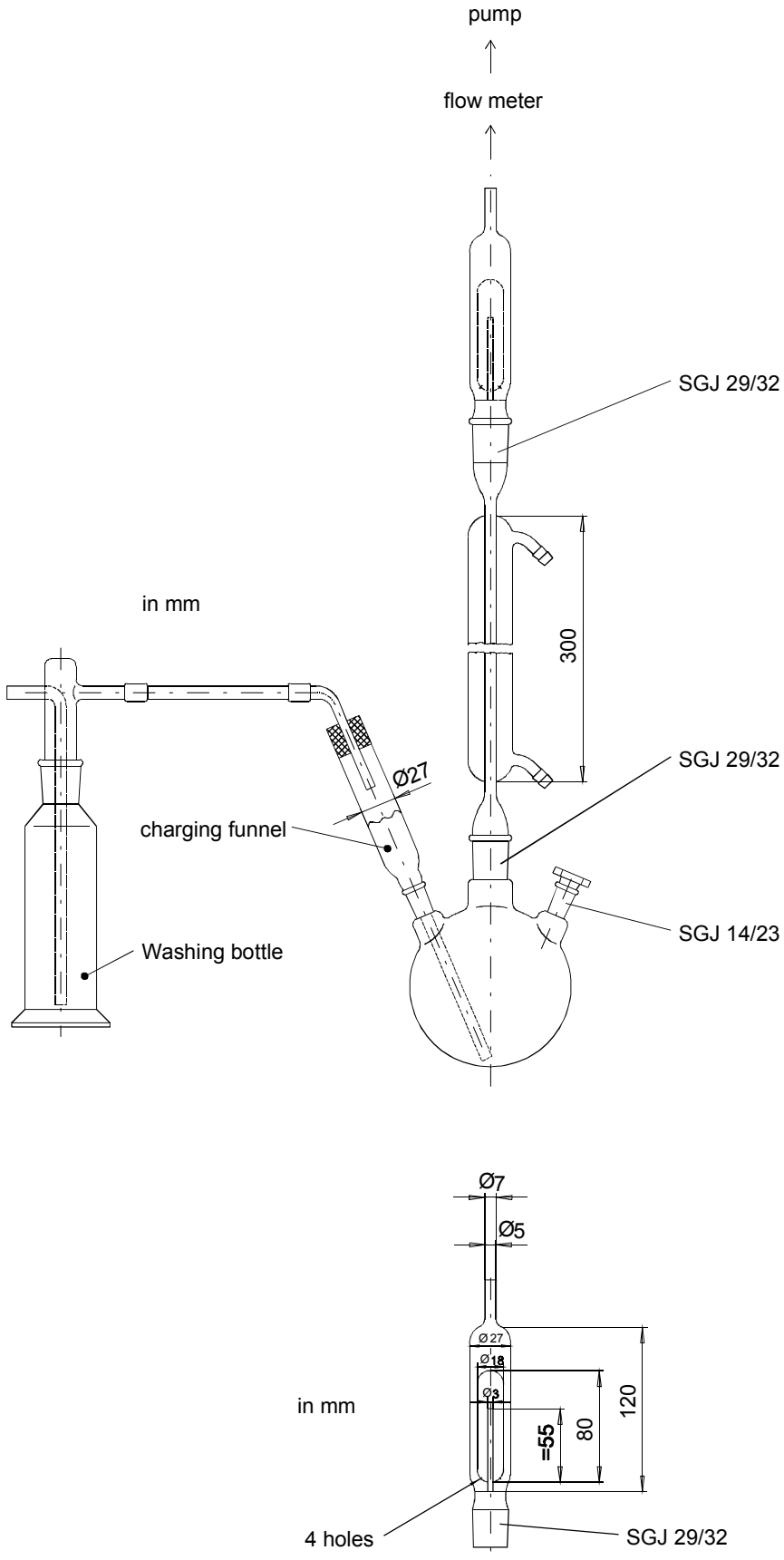

Fig. 1: *Apparatus for decomposition and separation of the cyanides.*

```
 'pa
785 DMP Titrino          02287   785.0010
date  1999-07-16    time  11:07         5
DET  U              ********
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  dos.rate               max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
>stop conditions
  stop V:                abs.
  stop V                   3 ml
  stop U                 OFF mV
  stop EP                  9
  filling rate           max. ml/min
>statistics
  status:                OFF
>evaluation
  EPC                      30
  EP recognition:        all
  fix EP1 at U           OFF mV
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  limit smpl size:       OFF
  activate pulse:        OFF
     -----------
```

Fig. 2: *Parameter settings on the 785 DMP Titrino for the determination of cyanide in waste water before decontamination.*

```
 'fr
785 DMP Titrino          02287   785.0010
date  1999-07-16    time  13:29         6
card label:Appl.751
U(init)          177 mV DET U    ********
smpl size         10 ml
EP1           1.906 ml            -182 mV
Cyanid        49.59 mg/L
stop V reached
          ============


 'cu
785 DMP Titrino          02287   785.0010
date  1999-07-16    time  13:29         6
start V      0.000 ml  DET U    ********
1.0 ml/div      dU=200.0 mV/div
```

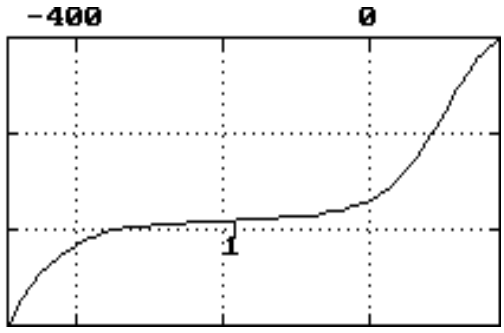

Fig. 3: *Result block and titration curve.*

```
 'pa
785 DMP Titrino          02287   785.0010
date  1999-07-19    time  15:03         9
DET  U              ********
parameters
>titration parameters
  meas.pt.density           6
  min.incr.              10.0 µl
  dos.rate               max. ml/min
  signal drift           20.0 mV/min
  equilibr.time            20 s
  start V:                OFF
  pause                    60 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                abs.
  stop V                    3 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      73
  EP recognition:         all
  fix EP1 at U            OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  limit smpl size:        OFF
  activate pulse:         OFF
          ------------
```

Fig. 4: *Parameter settings on the 785 DMP Titrino for the determination of cyanide traces in surface water after decomposition according to DIN 38405 part 14.*

```
 'fr
785 DMP Titrino          02287   785.0010
date  1999-07-19    time  14:30         9
card label:Appl.751
U(init)           48 mV DET U    ********
smpl size        100 ml
EP1            1.208 ml            -225 mV
CN-             0.63 mg/L
stop V reached
          ------------


 'cu
785 DMP Titrino          02287   785.0010
date  1999-07-19    time  14:30         9
start V      0.000 ml  DET U    ********
2.0 ml/div      dU=100.0 mV/div
```

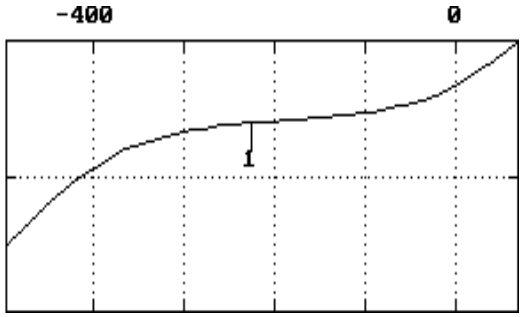

Fig. 5: *Result block and titration curve.*

Literature

- Metrohm Application Note T-22
  Cyanide in alkaline plating baths for cadmium, copper, lead or zinc
  Metrohm Ltd., Herisau.
- DIN 38405, part 13
  Anionen (Gruppe D). Bestimmung von Cyaniden.
- DIN 38405, part 14
  Anionen (Gruppe D). Bestimmung von Cyaniden in Trinkwasser, gering belastetem Grund- und Oberflächenwasser.