TOTAL CYANIDE IN WATER, SOIL AND SLUDGE

1. Principle

Using hydrochloric acid the weaker acid HCN is expelled in the presence of Cu(I) ions at boiling temperature. The resulting hydrogen cyanide is received in a diluted sodium hydroxide solution and determined. Using this method, simple and complex bound cyanides up to 100 mg/l are identified.

2. Method

Based on DIN 38405 Part 13: Deutsche Einheitsverfahren zur Wasser, Abwasser und Schlammuntersuchung, Verfahren DIN 38405 Teil 13

3. Area of usage

Sample Type	Content	Recovery
Water	up to 100 mg/l	> 95 %
Sewage	up to 100 mg /l	> 95 %
Sludge, soil	up to 100 mg/kg	> 95 %

Should there be higher contents, the sample has to be diluted. When working with soil, lower initial sample weights have to be used.

4. Chemicals

4.1. Hydrochloric acid for the analysis d(HCl) = 1.125 g/ml
4.2. Hydrochloric acid c(HCl) = 1 mol/l
4.3. Sodium hydroxide solution c(NaOH) = 1 mol/l
4.4. Sodium hydroxide solution c(NaOH) = 5 mol/l
4.5. Tin(II)chloride solution:
Fill up 50 g $SnCl_2$ $2H_2O$ + 40 ml c(HCl) = 1 mol/l (4.2.) with distilled water to make 100 ml
(keeps for a week)
4.6. Chloroform solution:
0.03g phenolphthalein + 90 ml ethanol + 10 ml chloroform
4.7. Copper sulphate solution:
200 g $CuSO_4$ $5H_2O$ fill up with distilled water to make 1 l
4.8. Zinc-Cadmium sulphate solution:
100 g zinc sulphate $ZnSO_4$ $7H_2O$ and 100 g cadmium sulphate$3CdSO_4$ $8H_2O$ diluted and filled up with distilled water to make 1 l
4.9. Cadmium acetate-solution:
300 g Cadmium acetate, $Cd(CH_3COO)_2 \cdot 2H_2O$ diluted and filled up with distilled water to make 1 l
4.10. Buffer solution, pH value 5.4:
6 g NaOH pellets are diluted in 50 ml distilled water; then 11.8 g succinic acid $C_4H_6O_4$ are mixed into this solution and, after cooling to ambient temperature, filled up to make 100 ml.

5. Instruments

5.1. TURBOTHERMdecomposition and digestion instrument TT4CAR (automatic)- Cat. No. 705055 or TT4CMR (manual) - Cat. No. 715055
5.2. Measuring flask 100 ml
5.3. Measuring pipettes 5 ml, 10 ml

5. Sample Preparation

Homogenization of the sample.
Per liter sample, 5 ml NaOH c = 5 mol/l (4.4.), 10 ml chloroform solution (4.6.) and 5 ml of the tin(II)chloride solution(4.5.) are added.
a. Should the sample turn red, hydrochloric acid (4.2.) is added till the sample decolorizes.
b. Should the sample not turn red, caustic soda (4.3.) is added drop by drop till the solution turns red.
c. Should the sample be hazy or be strongly colored, the ph value at the electrode is set to 8.

10 ml Zinc-Cadmium sulphate solution(4.8.) is added per liter sample.

6. Distillation and Separation of the Cyanide Hydrogen

Preparation of the instrument:
Put the glasses into the instrument. Connect the air inlet tubing and mount the absorption recipients prepared and filled with 10 ml caustic soda (4.3.).
Add 30 ml distilled water, 10 ml copper sulphate solution, 2 ml tin(II)chloride solution and 100 ml of the pre-treated sample to the third connection of the digestion tubes.
Add 10 ml 4.1. hydrochloric acid (4.1.) into the drip funnel. Stopper it. Put the drip funnel on the third connection of the digestion tube.

Decomposition and Separation of the Hydrogen Cyanide

Set the air throughput at 20 l/h. Add the hydrochloric acid from the drop funnel by opening the tap and by slightly turning the screw cap. Upon complete addition, close tap and screw cap immediately.
Turn on cooling water and heat up the sample to a light boiling stage. The following program is suggested for the heating unit TURBOTHERM automatic:

Suggested program for non-problematic samples:

Heating step	Power [%]	Time [min]
1	100	10
2	35	50

Suggested program for heating up foaming samples:

Heating step	Power [%]	Time [min]
1	100	5
2	0	5
3	100	5
4	0	5
5	100	5
6	0	5
7	40	30

These programs can only serve as a guideline. With the help of interval heating, the problem of foaming at the beginning of the digestion can be almost entirely avoided.

After one hour, the boiling stage is aborted, the content of the absorption recipient is put quantitatively into a measuring flask and the content of cyanide is detected. Should the solution be hazed, the entire boiling process has to be done again after adding 10 ml cadmium acetate solution and 40 ml buffer solution.
After a cooling off period of the sample tubes the cooling water is turned off, the condensers are rinsed with distilled water and put into the condenser holder.

The air inlet tubings are taken off at the steckmatic connection. The insert rack with the sample tubes, drop funnel and air inlet tubing are taken out of the TURBOTHERM and have to be cleaned carefully.

Possible Results of Measurements

Sample type	Concentration in relation to 10 g soil sample:	Detected concentration[2]:
Standard solution from KCN received in 100 ml water	0.1 mg/kg easily released CN	0.092 - 0.105 mg/kg easily released CN
Standard solution from KCN received in 100 ml water	0.5 mg/kg easily released CN	0.42 - 0.55 mg/kg easily released CN
Standard solution from KCN received in 100 ml water	1 mg/kg easily released CN	0.93 - 1.05 mg/kg easily released CN
Ca. 50 mg ref.-material LGC 6138[3] (Batch 002) received in 100 ml water	108 mg/kg easily released CN 2340 mg/kg complex. CN	120 - 160 mg/kg easily released CN 3200 - 3700 mg/kg compl. CN

[2] The processing of the samples was done independently by 2 persons; each 'sample' was processed at least three times per person.

[3] The concentration given by the 'manufacturer' doesn't indicate how the sample preparation was done.

7. Quantitative Determination of Cyanide

a. Volumetrically with silver nitrate and Tyndall-effect, suitable for samples with cyanide content higher than 0.005 mg
b. Volumetrically with silver nitrate and indicator solution, suitable for samples with a cyanide content higher than 0.05 mg
c. Photometrically using barbituric acid and pyridine, suitable for samples with a cyanide content of 0.0025 mg to 0.025 mg cyanide

These methods for measuring are described in detail in the ‚Deutschen Einheitsverfahren DIN 38405 D13'.