17. Januar 2007

Determination of Free Cyanide (CN_F) and Weak Acid Dissociable Cyanide (CN_{WAD}) in Waste Water and Sludge using classical Kjeldahl instrumentation for steam distillation.

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Introduction

Cyanide is one of nature's toxic substances. The fatal doses (KCN) for human adults are 50–100 mg if ingested, 120 mg/mL if inhaled (Swiss Toxicological Information Center). At normal pH and temperature, cyanide is toxic to most species in freshwater or marine environments at a level of 1–5 µg/L water. Cyanide toxicity is essentially based on an inhibition of the oxygen transport metabolism.

Depending on the cuvette used, the method is capable of measuring cyanide concentrations between 20 and 1000 µg/L in the aqueous phase using potassium cyanide as a standard. Complexed cyanide is not or not completely detected.

Official regulations

Distillation: EPA method 9010 C and method 335.2.
Photometric determination: Direct photometric method EPA method 9014.

Methodology

In this application the cyanide is released from cyanide complexes using a strong acid by means of steam distillation and absorbed in a receiver solution containing sodium hydroxide. The cyanide concentration in the absorbing solution is determined colorimetrically.
In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After completely final reaction a color change happens by the addition of pyridine-barbituric acid reagent. The absorbance is read at λ 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl.

Activated sludge from a waste water treatment plant in Switzerland was used to perform the spike recovery measurements. The activated sludge was spiked with intermediate standard cyanide (CN-) solution.

The analysis of the sludge samples have shown recovery rates of 96.6–103.1 % in a concentration range of 200 µg CN-/L–1000 µg CN-/L.

Spectrometric Determination and Calibration Procedure

Spectrometric Determination:
Pipet 50 mL of sample or 50 mL solution obtained from the distillation into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25 mol/L sodium hydroxide solution.

- Add 15 mL of 1 mol/L sodium phosphate solution and mix.
- Add 2 mL of chloramine-T and mix.
- After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix.
- Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at λ 578 nm within 15 minutes.

Calibration Procedure:
- Perform the following calibration for each batch of samples.
- Prepare a calibration curve by plotting the absorbance values of standards versus the corresponding phenol concentrations.
- Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 100 mL volumetric flasks. To each flask, add 20 mL of 1.25 N sodium hydroxide and dilute to 100 mL with water.
- Prepare a standard curve by plotting the absorbance values of standards versus the corresponding cyanide concentrations.

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Distillation

Settings:

Instrument	K-355
Sample size	100 mL
Steam power	90 %
Distillation time	3.5 min

Buchi Distillation Unit K-355

1. Prepare the Buchi Distillation Unit K-355 by preheating the unit.
2. Pipette 100 mL of sample into a 300 mL distillation tube.
3. Add 10 mL NaOH 1.25 mol/L to a 100 mL volumetric flask as receiving vessel.
4. Add 4 mL $MgCl_2$ solution to the distillation tube.
5. Attach the tube to the instrument and add 10 mL sulfuric acid 18 N by pumping the acid with the acid resistant pump.
6. Start the distillation.
   A distillation volume of approx. 80 ml will be achieved with distillation time of 3.5 minutes.

Verification

1. Recovery of cyanide (CN-) standard solutions:

Sample no	Recovery [%] **1000 µg CN-/L**	Recovery [%] **400 µg CN-/L**	Recovery [%] **200 µg CN-/L**
1	100.6	99.9	99.1
2	97.3	99.9	99.0
3	99.2	101.8	99.2
4	98.2	99.6	95.9
5	98.5	99.4	103.7
Mean value	**98.8**	**100.1**	**99.8**
RSD	**1.3**	**1.0**	**2.6**

2. Spike recovery rate of cyanide (CN-) in activated sludge:

Sample no	Recovery [%] **1000 µg CN-/L**	Recovery [%] **400 µg CN-/L**	Recovery [%] **200 µg CN-/L**
1	96.6	99.5	96.9
2	100.8	101.1	103.7
3	97.3	103.2	102.4
4	99.4	99.4	99.6
5	98.9	98.8	98.8
Mean value	**98.7**	**100.4**	**100.3**
RSD	**1.6**	**1.8**	**2.7**

Conclusion

EPA 9010 C Method vs Buchi Method:

	EPA 9010 C	**Buchi method**
Distillation type	reflux	steam
Distillation time	60 min	3.5 min
Sample size	500 mL	100 mL
Acid added/amount	sulfuric acid 18 N 50 mL	sulfuric acid 18 N 10 mL
$MgCl_2$ solution (2.5 M)	20 mL	4 mL
Receiver	1.25 N NaOH	1.25 N NaOH
Receiver volume	50 mL	10 mL
Recovery rate	97.4 %	98.8 / 98.7 %

The Buchi method shows the potential for WWTP to use their classical Kjeldahl instrumentation for more than classical TKN or ammonia determination. The Buchi method is based on a modification of EPA Method 9010 C, because of the standard capacity of the distillation tubes. It is faster and shows comparable method performance.

References

1. Method EPA 9014, 2. Method EPA 335.2 (Issued 1974, Technical Revision 1980), 3. Method EPA 9010 C (Revision 3, November 2004), 4. International Council on Metals and Environment, 5. Buchi Application Note K-355-007-B

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