

METHOD STATEMENT



Determinand:

Determination of Total and Free Cyanide

Matrix:

Sample Types: drinking waters, groundwaters, surface waters and bottled waters.

Principle of Method:

This method uses Skalar Sans ++ cyanide system.

Cyanides may be present in groundwaters as ionic cyanide such as some of the group one simple metal cyanides but also as complex transition metal cyanides. Complex cyanides can be quite stable compounds in which cyanide acts as a ligand around a central metal ion, usually a transition series metal of which Iron maybe the most common but could also be zinc, copper, nickel etc. Before the cyanide can be liberated as HCN the ligands must first be dissociated from the central metal ion, something that happens to little or no extent with simple steam distillation. The stability of complex cyanides will vary greatly depending on the central metal ion and on the configuration of the cyanide ligands. Lesser stable complex cyanides may even breakdown under relatively mild conditions such as those used when determining the easily liberated ionic cyanides.

In practice, 'total cyanides' are defined by the analytical conditions under which they are liberated. Total Cyanide is the sum of organically bound cyanides, free cyanide ions, complex compounds and the cyanide bound in simple metal cyanides, with the exception of cyanide bound in cobalt complexes. Thiocyanate is not included. The sample is decomposed at a pH of 3.8 by UV-B light. A UV-B lamp (312nm) and a borosilicate glass coil are used to eliminate UV light with a wavelength less than 290nm, thus preventing the conversion of thiocyanate to cyanide. The hydrogen cyanide present at pH 3.8 is separated by on line distillation at 125°C. The hydrogen cyanide is then determined photometrically by the reaction of cyanide with chloramine-T to form cyanogen chloride, which reacts with pyridine-4-carboxylic and 1,3-dimethylbarbituric acid to give a blue dye whose absorbance is measured at 600nm.

Free cyanide is the sum of cyanide ions and the cyanide bound in simple metal cyanides, which is determined according to this standard. Organic cyanides are not included. The UV lamp is switched off when determining free cyanide content. Before distillation a zinc sulphate solution is added to the sample in order to precipitate any iron cyanides present as the zinc-cyanoferrate complex. The hydrogen cyanide present at pH 3.8 is separated by on line distillation at 125°C. The hydrogen cyanide is then determined photometrically by the reaction of cyanide with chloramine-T to form cyanogen chloride, which reacts with pyridine-4-carboxylic and 1,3-dimethylbarbituric acid to give a blue dye whose absorbance is measured at 600nm.

Sampling and Sample Preparation:

Samples are normally collected in a dark bottle. Any size dark bottle is suitable as long as the final strength of NaOH is 0.1M.

Samples are preserved with sodium hydroxide such that the final concentration is 0.1M NaOH. If analysis cannot be immediately undertaken, samples should be stored at a temperature of $3\pm 2^{\circ}\text{C}$ until the day of analysis. Samples should be warmed up to room temperature prior to analysis and analysed for free cyanide within 7 days and for total cyanide within 14 days of the sampling date.

Interferences

The distillation process whereby hydrogen cyanide is liberated from the test portion of sample and then "fixed" in a sodium hydroxide solution essentially removes many of the potential interferences.

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Performance of Method:

Range of Application:

LOQ - 60µg/l CN

This range may be extended by sample dilution with 0.1M sodium hydroxide solution.

Limit of Quantification:

Statistically obtained limit of quantification for free cyanide of 1.18 µg/l CN-

Statistically obtained limit of quantification for total cyanide of 1.11 µg/l CN-

Recoveries of Compounds, Bias and Uncertainty of measurement:

Free CN:

| Sample type | Mean sample result (µg/L) | Mean sample spike result (µg/L) | Conc. of spike (µg/L) | Spike recovery (%) | Bias (%) |
|------------------------|---------------------------|---------------------------------|-----------------------|--------------------|----------|
| Soft- Langsett | 0.463 | 49.176 | 50 | 97.43 | - |
| Medium- Wakefield Tap | 0.538 | 48.477 | 50 | 95.88 | - |
| Hard- Bristol (Purton) | 0.303 | 48.870 | 50 | 97.14 | - |
| Surface- Derwent | 0.172 | 49.352 | 50 | 98.36 | - |
| Borehole- Ainderby | 0.164 | 46.675 | 50 | 93.02 | - |
| Pure- MilliQ | 0.091 | 48.754 | 50 | 97.33 | - |
| 12 µg/L Std CN | 12.111 | - | - | - | 0.92 |
| 48 µg/L Std CN | 48.057 | - | - | - | 0.12 |

Total CN:

| Sample type | Mean sample result (µg/L) | Mean sample spike result (µg/L) | Conc. of spike (µg/L) | Spike recovery (%) | Bias (%) |
|------------------------|---------------------------|---------------------------------|-----------------------|--------------------|----------|
| Soft- Langsett | 0.509 | 47.977 | 50 | 94.94 | - |
| Medium- Wakefield Tap | 0.485 | 47.530 | 50 | 94.09 | - |
| Hard- Bristol (Purton) | 0.400 | 46.591 | 50 | 92.38 | - |
| Surface- Derwent | 0.292 | 46.675 | 50 | 92.77 | - |
| Borehole- Ainderby | 0.418 | 46.890 | 50 | 92.94 | - |
| Pure- MilliQ | 0.265 | 46.973 | 50 | 93.41 | - |
| 12 µg/l Std CN | 12.101 | - | - | - | 0.84 |
| 48 µg/l Std CN | 48.020 | - | - | - | 0.04 |

References:

Standard Methods for the Examination of Water and Wastewater. 19th edition. Method 4500 CN - D. APHA. Washington. USA. ISBN 0 87553 223 3.

Spectrophotometric Determination of Cyanide with Isonicotinic Acid and Barbituric Acid. Intern. J. Environ. Anal. Chem., 1981, Vol. 10, pp. 99-106 Anal. Chem., 1981, Vol. 10, pp. 99-106

Auto Analyser Method no. G-259-01 Rev. 15

Water Quality-Sampling-Part 3: Guidance on the Preservation and Handling of Water Samples. BS EN ISO 5667-3-2012.

15.5 Water quality — Determination of total cyanide and free cyanide using flow analysis (FIA and CFA) - Part 2: Method using continuous flow analysis (CFA) ISO 14403-2:2012