

## 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 wave length 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.

### **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.

### **Performance of the Method:**

#### ***Range of Application:***

LOD –100 µg/l CN<sup>-</sup>

This range may be extended by sample dilution with a 0.01M sodium hydroxide solution.

Reporting Limit is 0.7 µg/l CN<sup>-</sup>

#### ***Limit of Detection:***

Statistically obtained limit of detection for free cyanide of 0.52 µg/l CN<sup>-</sup>

Statistically obtained limit of detection for total cyanide of 0.67 µg/l CN<sup>-</sup>



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## Recoveries of Compounds 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 (%)
Langsett	0.020	50.229	50	100.42	-
Wakefield Tap	-0.007	49.247	50	98.51	-
Bristol	0.115	49.092	50	97.95	-
Derwent	0.016	50.038	50	100.04	-
Le-Cowick	-0.059	49.878	50	99.87	-
Strathmore	-0.087	49.885	50	99.94	-
Std Total CN	20.317	-	-	-	1.58
Std Total CN	80.140	-	-	-	0.18

### Total CN:

Sample type	Mean sample result (µg/l)	Mean sample spike result (µg /l)	Conc. of spike (µg /l)	Spike recovery (%)	Bias (%)
Langsett	0.655	47.536	50	93.76	-
Wakefield Tap	0.527	47.580	50	94.11	-
Bristol	0.782	47.339	50	93.11	-
Derwent	0.770	48.248	50	94.96	-
Le-Cowick	0.557	46.042	50	90.97	-
Strathmore	0.514	47.236	50	93.45	-
Std Total CN	20.321	-	-	-	1.60
Std Total CN	80.684	-	-	-	0.86

### 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

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