METHOD STATEMENT

Determinand:
Total cyanide, free cyanide and cyanide complexes excluding iron complexes

Matrix:
Treated sewage, trade effluent (to sewer and controlled waters), land leachate, process water, ground water, and surface water.

Principle of Method:
Automated on-line preparation followed by colorimetric determination using segmented flow analysis. Subsequent calculation of total complex cyanide and iron cyanides is possible.

Hydrogen cyanide reacts with chloramine-T, then isonicotinic acid and 1,3-dimethylbarbituric acid to give a red-blue colour measured at a wavelength of 600nm. Quantification is by comparison with standards.
Total cyanide determinations use a strong acid-UV digestion to break down the complex cyanide compounds present within the sample.
Total cyanide excluding iron-cyanide complexes is determined using a strong acid mixture, but without UV irradiation. Zinc sulphate minimises the break down of iron-cyanide complexes.
Free cyanide is determined under the mildest of the three digestion conditions, with a citric acid buffer and no UV irradiation.
Low-level free cyanide is determined as free cyanide above, but with the inclusion of a measurement cell with a longer path-length to increase sensitivity, combined with a lower calibrated range.
Samples must be preserved on site with sodium hydroxide.

Sampling and Sample Preparation:
Samples for cyanide analysis should be preserved on site with 2 pellets of sodium hydroxide per 60ml of sample prior to submission for analysis.
Samples are stable for 14 days (Standard Methods: -ISBN 0-87553-161-X) from sampling.

Interferences:
The distillation process will remove most analytical interferences. If the distillation reagents are too acidic, then interferences can occur, e.g. breakdown of thiocyanate to give cyanide or reaction of hydrogen sulphide with hydrogen cyanide to form thiocyanate.

Performance of Method:

Instrument CYN01:

Determinand:	Total Cyanide
Range of Application:	0.013 to 1mg/l as CN
Limit of Detection:	0.0081 mg/l as CN
Normal Reporting Limit:	0.013 mg/l as CN

Treated sewage has been validated to comply with the Mcerts standard, remaining matrices validated to ISO 17025.

Determinand	MCERTS Accreditation	Low Standard		High Standard	
		RSD %	Bias %	RSD %	Bias %
Total Cyanide	✓	4.06	1.73	2.92	2.21

Determinand		Finham treated sewage		Wolston treated sewage		Barston treated sewage	
		Low	High	Low	High	Low	High
Total Cyanide	% RSD	5.04	3.88	2.98	2.65	5.97	5.40
	% Rec.	92.95	98.19	92.70	98.86	97.14	98.95

Determinand		Land Leachate	Ground Water	Trade effluent to sewer	Surface Water	Process Water	Trade effluent to control
		High	High	High	High	High	High
Total Cyanide	% RSD	3.13	3.14	6.03	3.11	3.44	3.03
	% Rec.	97.55	100.27	87.99	98.58	95.37	100.64

Determinand: Cyanide Excluding Iron Complexes
Range of Application: 0.012 to 1mg/l as CN
Limit of Detection: 0.0083 mg/l as CN
Normal Reporting Limit: 0.012 mg/l as CN

Determinand	Low Standard		High Standard	
	Tot. RSD %	Bias %	Tot. RSD %	Bias %
Cyanide ex Ferri/Ferro	2.15	-0.52	1.77	1.45

Determinand		Finham treated sewage		Wolston treated sewage		Barston treated sewage	
		Low	High	Low	High	Low	High
Cyanide ex Ferri/Ferro	% RSD	2.09	1.28	2.10	1.51	6.41	5.14
	% Rec.	93.48	98.45	95.65	99.63	100.09	100.37

Determinand		Land Leachate	Ground Water	Trade effluent to sewer	Surface Water	Process Water	Trade effluent to control
		High	High	High	High	High	High
Cyanide ex Ferri/Ferro	% RSD	4.06	3.88	5.82	3.45	3.84	3.09
	% Rec.	97.48	100.32	92.18	99.57	97.08	99.47

Determinand: Free Cyanide
Range of Application: 0.014 to 1mg/l as CN
Limit of Detection: 0.0078 mg/l as CN
Normal Reporting Limit: 0.014 mg/l as CN

Treated sewage has been validated to comply with the Mcerts standard, remaining matrices validated to ISO 17025.

Determinand	MCERTS Accreditation	Low Standard		High Standard	
		RSD %	Bias %	RSD %	Bias %
Free Cyanide	✓	3.72	0.43	3.46	0.10

Determinand		Finham treated sewage		Wolston treated sewage		Barston treated sewage	
		Low	High	Low	High	Low	High
Free Cyanide	% RSD	3.88	3.37	3.89	2.92	3.86	4.33
	% Rec.	93.80	98.15	95.77	98.99	100.80	100.03

Determinand		Land Leachate	Ground Water	Trade effluent to sewer	Surface Water	Process Water	Trade effluent to control
		High	High	High	High	High	High
Free Cyanide	% RSD	2.44	2.97	4.63	2.09	2.68	2.86
	% Rec.	97.83	99.98	91.94	99.13	96.80	100.35

Instrument CYN03:

Determinand: Total Cyanide
Range of Application: 0.013 to 1 mg/l as CN
Limit of Detection: 0.0126 mg/l as CN
Normal Reporting Limit: 0.013 mg/l as CN

Treated sewage, Untreated Sewage and Trade to Controlled have been validated to comply with the Mcerts standard, remaining matrices validated to ISO 17025.

Determinand	MCERTS Accreditation	Low Standard		High Standard	
		RSD %	Bias %	RSD %	Bias %
Total Cyanide	✓	2.54	1.14	1.23	0.33

Determinand		Finham Treated Sewage		Untreated Sewage		Trade to Controlled	
		Low	High	Low	High	Low	High
Total Cyanide	% RSD	3.13	1.50	7.34	4.46	3.20	1.25
	% Rec.	98.45	96.9	96.30	97.29	96.68	97.65

Determinand		Land leachate	Ground Water	Trade to sewer	Surface Water	Clean Process Water	Dirty Process Water
		High	High	High	High	High	High
Total Cyanide	% RSD	1.32	1.10	3.31	1.33	0.92	3.55
	% Rec.	99.10	97.57	94.64	98.38	98.87	99.77

Determinand: Free Cyanide
Range of Application: 0.014 to 1 mg/l as CN
Limit of Detection: 0.0131 mg/l as CN
Normal Reporting Limit: 0.014 mg/l as CN

Treated sewage, Untreated Sewage and Trade to Controlled have been validated to comply with the Mcerts standard, remaining matrices validated to ISO 17025.

Determinand	MCERTS Accreditation	Low Standard		High Standard	
		RSD %	Bias %	RSD %	Bias %
Free Cyanide	✓	2.71	1.23	3.11	0.62

Determinand		Treated Sewage		Untreated Sewage		Trade to Controlled	
		Low	High	Low	High	Low	High
Free Cyanide	% RSD	3.64	3.78	5.79	2.79	3.40	2.43
	% Rec.	100.11	98.02	98.14	98.82	98.11	98.27

Determinand		Land leachate	Ground Water	Trade to sewer	Surface Water	Clean Process Water	Dirty Process Water
		High	High	High	High	High	High
Free Cyanide	% RSD	3.19	3.67	3.83	2.31	2.76	2.57
	% Rec.	100.27	99.59	94.72	98.99	99.44	99.39

Determinand: Cyanide Excluding Iron Complexes
Range of Application: 0.012 to 1 mg/l as CN
Limit of Detection: 0.0111 mg/l as CN
Normal Reporting Limit: 0.012 mg/l as CN

Determinand	MCERTS Accreditation	Low Standard		High Standard	
		RSD %	Bias %	RSD %	Bias %
Cyanide ex ferri/ferro		4.34	-0.02	4.94	-1.19

Determinand		Treated Sewage		Untreated Sewage		Trade to Controlled	
		Low	High	Low	High	Low	High
Cyanide ex ferri/ferro	% RSD	5.26	3.05	5.77	5.58	3.65	2.74
	% Rec.	99.34	97.03	97.61	98.31	98.09	98.06

Determinand		Land leachate	Ground Water	Trade to sewer	Surface Water	Clean Process Water	Dirty Process Water
		High	High	High	High	High	High
Cyanide ex ferri/ferro	% RSD	2.85	4.86	5.75	3.16	4.48	2.85
	% Rec.	98.98	96.99	93.38	98.31	99.83	99.02

Uncertainty of Measurement:

The reported uncertainty is an expanded uncertainty calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.

Determinand	Uncertainty of Measurement %
Total Cyanide	29.70
Cyanide ex Ferri/Ferro	25.14
Free Cyanide	16.11

References:

Methods for the Examination of Waters and Associated Materials. ISBN 01175 22198
Water Quality – Determination of Total Cyanide and Free cyanide by Continuous Flow Analysis, ISO/ DIS 14403.

ISBN 0-87553-161-X, Standard Methods for the Examination of Water and Wastewater.