METHOD STATEMENT

Determinand:
pH, Electrical Conductivity at 20°C and 25°C

Matrix:
Surface water, Ground water, Land Leachates, Treated and Untreated Sewage Clean and Dirty process water, Recreational water and Trade Effluent.

Principle of Method:
The electrical conductivity of a solution depends upon the concentration of dissociated ions in solution and the temperature of that solution. The concentration of these ions will affect the current flow between two electrodes. The magnitude of this effect is directly proportional to the concentration of ions present, assuming a constant temperature. Consequently, after calibration with suitable standards and with the use of a temperature probe to correct for temperature differences between standards and samples, the EC of a solution may be measured.

The pH of a solution is equal to $Log_{10}\ ^{1}/_{[H+]}$ and is measured directly by a pH probe which has been previously calibrated using solutions of a known pH.

Sampling and Sample Preparation:
On receipt at the laboratory, samples are registered prior to analysis. No preservation is required for either pH or EC samples. Storage at room temperature is best as this reduces the possibility of changing either the pH or EC values due to altering chemical solubility with temperature. Samples should be kept in tightly sealed and preferably full containers with no air space in order to minimise the possibility of gas exchange with the atmosphere e.g. ammonia and carbon dioxide. Samples should be measured as soon as possible in order to minimise possible effects from the above problems.

Samples are stable for the times stated below, from sampling: -

pH	2 Days (In-House Data)
Electrical Conductivity	16 Days (In-House Data)

Interferences:
Gross suspended matter, oil or grease may cause interference by masking part of the electrode surface. As both pH and EC deal only with ions in solution, filtering of the samples to remove interferences is acceptable.
Above a pH of 12 the electrode response may not be linear for pH values. Also, if high sodium concentrations are present, the response for pH may not be perfectly linear above pH 10.
The EC measurement is temperature corrected by the instrument. However, large deviations between sample temperature and standard temperature (up to 5°C) may lead to inaccuracies during the compensation. Whenever possible, ensure that the samples and standards are at room temperature during measurement.
Conductivities above 100,000µS/cm or below 10µS/cm become difficult to measure accurately without specialist electronic equipment and cell capacities. Results outside this range must be considered indicative only.

Performance of Method:

pH

Instrument	Range	MCERTS Acc.	Low Standard			High Standard		
			pH Value	Tot. SD	Tot. Bias	pH Value	Tot. SD	Tot. Bias
Robot 4	1-13	✓	4	0.032	+0.010	10	0.018	-0.003
			1	0.057	-0.101	13	0.018	-0.083
Manual	1-13	✓	4	0.037	+0.066	10	0.038	+0.010
			1	0.036	+0.307	13	0.056	-0.171

Instrument	Treated Sewage		Trade Effluent		Untreated Sewage	
	pH Value	Total SD	pH Value	Total SD	pH Value	Total SD
Robot 4	7.751	0.201	9.265	0.217	7.086	0.211
Manual	7.506	0.231	x	x	7.324	0.253

Instrument	Land Leachate		Ground water		Surface water	
	pH Value	Total SD	pH Value	Total SD	pH Value	Total SD
Robot 4	7.479	0.220	7.318	0.267	8.374	0.142
Manual	8.001	0.097	7.521	0.266	7.548	0.132

Instrument	Trade to controlled		Trade to sewer		Recreational	
	pH Value	Total SD	pH Value	Total SD	pH value	Total SD
Robot 4	x	x	x	x	8.101	0.166
Manual	7.749	0.129	7.433	0.164	7.978	0.087

Instrument	Dirty Process		Clean Process	
	pH value	Total SD	pH value	Total SD
Robot 4 / 5	7.885	0.093	8.078	0.096
Manual	7.798	0.203	7.401	0.219

METHOD STATEMENT

EC

Instrument	Range µS/cm	LOD µS/cm	MRL µS/cm	Low Standard			High Standard		
				Conc µS/cm	%RSD	Bias %	Conc µS/cm	%RSD	Bias %
Robot 4	30-101000	16.0	30	650	1.00	0	101214	0.81	+0.3
Manual	30-101,000	27.009	30	650	1.58	-1.25	101214	1.14	+0.11

Instrument	Treated Sewage						Trade Effluent					
	Low Spike			High Spike			Low Spike			High Spike		
	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %
Robot 4	913	1.05	95.86	52800	0.77	100.63	913	1.01	96.24	52800	0.85	100.46
Manual	650	1.50	92.04	x	x	x	x	x	x	x	x	x

Instrument	Untreated Sewage						Land Leachate					
	Low Spike			High Spike			Low Spike			High Spike		
	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %
Robot 4	650	1.34	92.55	52800	1.12	100.46	650	0.76	94.21	52800	0.86	100.57
Manual	650	2.81	98.94	x	x	x	x	x	x	52800	1.32	95.62

Instrument	Surface Water						Groundwater					
	Low Spike			High Spike			Low Spike			High Spike		
	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %
Robot 4	650	1.15	96.82	52800	1.16	100.67	650	1.14	97.19	52800	0.82	101.20
Manual	650	3.24	95.99	x	x	x	913	1.23	92.33	x	x	x

Instrument	Dirty Process						Clean Process					
	Low spike			High spike			Low spike			High spike		
	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %
Robot 4 / 5	1277	2.27	90.65	52800	2.43	98.20	650	2.15	109.08	52800	2.75	103.86
Manual	x	x	x	52800	1.24	93.45	650	3.61	90.83	x	x	x

Instrument	Trade to controlled						Trade to sewer					
	Low spike			High spike			Low spike			High spike		
	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %
Robot 4 / 5	x	x	x	x	x	x	x	x	x	x	x	x
Manual	650	2.79	94.66	x	x	x	913	1.14	93.55	x	x	x

Instrument	Recreational Water					
	Low spike			High spike		
	Conc µS/cm	RSD %	Rec. %	Conc µS/cm	RSD %	Rec. %
Robot 4 / 5	650	2.26	96.93	52800	2.56	107.57
Manual	x	x	x	x	x	x

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 (%)
EC	20.28

The Uncertainty of measurement has been calculated using the following calculation.
UOM = Bias + (2 x SD)

Determinand	Uncertainty of Measurement pH Units
pH	0.427

References:

The Measurement of Electrical Conductivity and the Laboratory Determination of the pH Value of Natural, Treated and Waste Waters 1978 HMSO. Methods for the Examination of Waters and Associated Materials. ISBN: 011 7514284.
Standard Methods for the Examination of Water and Wastewater, 1989, 17th Edition, ISBN 0-87553-161-x.
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Conductivity Theory and Practice – Radiometer Analytical