METHOD STATEMENT

Determinand:
Ammonia, Chloride, Nitrate, Nitrite, Orthophosphate, Sulphate & TON

Matrix:
Treated Sewage, Untreated sewage, Trade effluent, Surface water, Land leachate, Clean Process water and recreational water.

Principle of Method:
Certain analytes, when reacted with specific reagents, will form coloured complexes. The intensity of the colour formed is proportional to the original concentration of the analyte.

The intensity of colour within samples can be evaluated by comparison with standards containing known concentrations of the analyte, thus allowing the concentration within the sample to be assessed.

The sample volumes, reagent volumes, mixing speeds, colour development time and development temperature are all controlled automatically using a discrete autoanalyser, which significantly improves method performance over manual colour assessment.

Specific details of colorimetric reactions are given below.

Ammonia
Ammonia in the sample reacts with hypochlorite ions generated from the sodium dichlorocyanurate reagent to form monochloramine. This reacts with salicylate at approximately pH 10.5 in the presence of sodium nitroprusside to form a blue iodophenol type compound. This is measured spectrophotometrically at 660nm.

Chloride
Chloride ions are mixed with acid-chloride colour reagent containing mercury II thiocyanate and iron III nitrate. The released thiocyanate ions react with the iron III nitrate to give a reddish-brown coloured iron III thiocyanate complex which is measured spectrophotometrically at 510nm.

Nitrite
Nitrite ions react with sulphanilamide and N-1-Naphthylethylenediamine dihydrochloride in a phosphoric acid matrix to form a characteristic azo-dye. The concentration of the dye is measured spectrophotometrically at 510nm.

Orthophosphate
Orthophosphate ions react with a solution containing molybdic acid, trivalent antimony ions and hydrogen ions to form a 12-Molybdophosphoric acid. This is reduced by ascorbic acid to give a phosphomolybdenum blue complex which is measured spectrophotometrically at 660nm.

TON
Nitrate ions are reduced to nitrite by hydrazine under alkaline conditions, using cupric ions as a catalyst. The total nitrite content of the sample is then reacted with sulphanilamide and N-1-Naphthylenediamine dihydrochloride under acidic conditions to form a characteristic pink dye which is read spectrophotomically at 540nm.

Sulphate
Sulphate reacts with an excess of acidified barium chloride to produce an insoluble precipitate of barium sulphate. The precipitate is held in suspension by gelatine and the concentration determined

turbidimetrically at 510nm. Sample blanking is carried out to overcome interferences caused by sample colour and turbidity.

Sampling and Sample Preparation:
There is no sample preservative used. There is likely be a loss of ammoniacal nitrogen and interconversion of the nitrogen species for samples left standing at room temperature. Samples should be analysed as soon after receipt as possible.

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

Ammonia	6 Days (In-House Data)
Chloride	28 Days (ISO 5667:3)
Nitrate	3 Days (In-House Data)
Nitrite	3 Days (In-House Data)
Orthophosphate	7 Days (In-House Data)
Total Oxidised Nitrogen (TON)	7 Days (In-House Data)
Sulphate	30 Days (In-House Data)

Interferences:
Ammonia - there has been shown to be a slight interference from sodium chloride, potassium cyanide, calcium chloride, copper sulphate, lead acetate, aniline, and ethanolamine. However, it is unlikely that these will be an issue for the types of samples analysed by this method. It has been found that samples with high levels of ammonia can lead to self-bleaching of the developing colour and give false low results. The ammoniacal nitrogen (high level) method overcomes these interferences by running samples on an initial 40-fold dilution, giving a calibrated range up to 3000mg/l as N. If the result is actually below 75mg/l, the sample is automatically rerun without dilution.

Nitrite, Nitrate and TON - no important interference problems are likely although there has been shown to be a slight interference from free chlorine and chloramines for nitrite.

Chloride - there has been shown to be a slight interference from high concentrations of cyanide, thiocyanate, sulphate, bromide, and non-ionic detergent. However, it is unlikely that these will be an issue for the types of samples analysed by this method.

Orthophosphate - no important interference problems are likely with unpolluted saline and fresh waters. The most likely interferences in heavily coloured samples and at very low phosphate levels are from high levels of arsenic, silicon, oxidising agents, hexavalent chromium, nitrite, nitrate, and sulphide. However, it is unlikely that these will be an issue for the types of samples analysed by this method.

Sulphate - Sample blanking is carried out to overcome interferences caused by sample colour and turbidity. High concentrations of calcium, nitrate, iron, phosphate, and chromate have been found to interfere. However, it is unlikely that these will be an issue for the types of samples analysed by this method.

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Performance of Method:

Determinand	Range of Application	Normal Reporting Level	LOD
Ammoniacal nitrogen	0.41 - 75.0 mg/l as N	0.41 mg/l as N.	0.4059 mg/l as N.
Nitrate / TON	0.7 - 50.0 mg/l as N.	0.7 mg/l as N.	0.6767 mg/l as N.
Nitrite	0.08 - 2.000 mg/l as N.	0.08 mg/l as N	0.0712 mg/l as N.
Chloride	3.7 - 500 mg/l as Cl.	3.7 mg/l as Cl.	3.6791 mg/l as Cl.
Phosphate	0.6 - 20.00 mg/l as P	0.6 mg/l as P	0.5006 mg/l as P
Sulphate	4.4 - 1000 mg/l as SO_4.	4.4 mg/l as SO_4	1.8598 mg/l as SO4

Standards - Precision and bias

Determinand	MCERTS Accreditation	Low standard		High Standard	
		Tot RSD %	Bias %	Tot RSD %	Bias %
Ammoniacal nitrogen	✓	2.25	2.58	1.60	1.87
Nitrate / TON	✓	3.40	1.72	1.60	3.08
Nitrite		2.64	0.73	3.04	1.97
Chloride		1.42	0.86	1.47	1.28
Phosphate	✓	2.01	0.96	1.30	0.47
Sulphate		1.22	1.32	1.97	1.40

Samples and Spiked Samples

Determinand		Treated Sewage Finham FE		Treated Sewage Hartshill FE		Treated Sewage Alton FE	
		20%	80%	20%	80%	20%	80%
Ammoniacal nitrogen	%RSD	1.82	1.18	2.99	1.95	x	x
	% Rec	101.07	95.14	99.09	96.01	x	x
Nitrate / TON	%RSD	4.26	1.81	2.43	1.45	x	x
	% Rec	97.63	92.38	95.58	95.20	x	x
Nitrite	%RSD	x	2.16	x	x	x	x
	% Rec	x	99.57	x	x	x	x
Chloride	%RSD	x	1.69	x	x	x	x
	% Rec	x	95.39	x	x	x	x
Phosphate	%RSD	2.68	1.38	4.16	1.12	2.53	1.20
	% Rec	98.27	95.66	100.20	95.49	97.42	101.66
Sulphate	%RSD	x	2.00	x	x	x	x
	%Rec	x	96.74	x	x	x	x

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Determinand		Crude		Trade Effluent	Surface Water
		20%	**80%**	**80%**	**80%**
Ammoniacal nitrogen	%RSD	2.02	3.20	0.97	2.03
	% Rec	91.94	98.34	95.33	94.79
Nitrate / TON	%RSD	3.62	2.18	5.30	2.37
	% Rec	107.58	91.15	95.50	100.08
Nitrite	%RSD	x	2.14	1.84	2.34
	% Rec	x	99.77	90.20	101.32
Chloride	%RSD	x	1.66	1.31	1.81
	% Rec	x	96.51	90.42	98.60
Phosphate	%RSD	x	2.58	5.22	1.42
	% Rec	x	90.48	90.24	96.35
Sulphate	%RSD	x	1.85	2.11	1.68
	% Rec	x	97.67	100.72	96.62

Determinand		Ground Water	Soil Leachate	Landfill Leachate
		80%	**80%**	**80%**
Ammoniacal nitrogen	%RSD	1.81	1.61	2.66
	%Rec	96.55	96.41	91.95
Nitrate / TON	%RSD	3.01	2.13	3.04
	%Rec	92.81	99.30	94.57
Nitrite	%RSD	2.24	2.20	4.82
	%Rec	101.39	100.76	95.10
Chloride	%RSD	1.88	2.09	2.16
	%Rec	101.30	100.96	90.01
Phosphate	%RSD	4.23	1.13	3.51
	%Rec	92.05	98.88	95.47
Sulphate	%RSD	2.06	1.85	1.46
	%Rec	99.83	100.64	99.87

Determinand		Recreational	Clean Process
		80%	**80%**
Ammoniacal nitrogen	%RSD	1.18	1.42
	%Rec	102.56	101.98
Nitrate / TON	%RSD	2.10	2.40
	%Rec	102.06	102.34
Nitrite	%RSD	3.56	2.24
	%Rec	95.76	97.58
Chloride	%RSD	1.72	1.91
	%Rec	98.72	99.08
Phosphate	%RSD	1.62	1.71
	%Rec	96.54	96.55
Sulphate	%RSD	1.15	1.70
	%Rec	99.41	100.57

X= where the determinand has not been validated for a particular matrix or concentration.

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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 (%)
Ammoniacal nitrogen	11.093
Nitrate / TON	12.963
Nitrite	10.15
Chloride	12.40
Phosphate	10.888
Sulphate	6.331

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