METHOD STATEMENT

Determinand:
Ammonia, Chloride, Nitrite, Orthophosphate, Total Oxidised Nitrogen (TON), Silica, Sulphate

Matrix:
Treated Effluent, Surface and Groundwaters

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 540nm.

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.

Total Oxidised Nitrogen (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.

Silica: - Silica reacts with ammonium molybdate under acid conditions to form yellow molybdosilicic acid. This is reduced in situ with ascorbic acid to yield a silicomolybdenum blue complex. This is measured spectrophotometrically at 700nm.

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 5667-3:2024)
Nitrate	3 Days (In-House Data)
Nitrite	3 Days (In-House Data)
Orthophosphate	7 Days (In-House Data)
Total Oxidised Nitrogen (TON)	4 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.

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 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.

Silica - phosphate may interfere slightly.

Performance of Method:

Determinand	Range of Application	Normal Reporting Level	LOD
Ammoniacal nitrogen	0.06 - 2 mg/l as N	0.06 mg/1 as N	0.0503 mg/l as N
Nitrate / TON	0.2 - 20 mg/l as N	0.2 mg/l as N	0.1019 mg/l as N
Nitrite	0.006 - 0.1mg/l as N	0.006 mg/l as N	0.0053 mg/l as N
Chloride	2 - 250 mg/l as Cl	2 mg/l as Cl	1.222 mg/l as Cl
Phosphate	0.02 - 2 mg/l as P	0.02 mg/l as P	0.0091 mg/l as P
Sulphate	5 - 250 mg/l as SO_4	5 mg/l as SO_4	2.971 mg/l as SO_4
Reactive silica	0.024 - 20 mg/l as SiO_2	0.3 mg/l as SiO_2	0.0240 mg/l as SiO_2

Determinand	Low standard		High Standard	
	Tot RSD %	Bias %	Tot RSD %	Bias %
Ammoniacal nitrogen	3.95	1.33	1.17	-0.74
Nitrate / TON	4.86	-1.26	1.72	-1.26
Nitrite	4.03	2.16	1.96	-0.73
Chloride	1.17	6.29	2.29	-0.49
Phosphate	2.59	-3.59	2.13	-3.28
Sulphate	2.45	-6.14	1.71	2.94
Reactive silica	1.83	2.21	1.53	1.39

Determinand		Final Effluent		Surface water		Groundwater	
		20%	80%	20%	80%	20%	80%
Ammoniacal nitrogen	%RSD	8.36	3.48	4.14	2.49	5.26	2.33
	%Bias	-5.69	-2.06	-2.38	-0.54	-1.28	0.52
Nitrate / TON	%RSD	4.51	3.24	2.76	2.03	3.75	2.48
	%Bias	-5.01	-4.73	-5.67	0.11	-7.40	-4.45
Nitrite	%RSD	8.29	7.45	8.08	3.65	7.17	1.43
	%Bias	-1.42	-6.46	-3.54	-4.17	-2.04	-2.97
Chloride	%RSD	2.97	2.28	1.49	2.53	2.09	5.15
	%Bias	-1.02	-5.44	-1.10	-5.38	2.39	-0.08
Phosphate	%RSD	2.12	1.85	2.12	1.88	7.60	1.60
	%Bias	-0.71	-1.09	-3.57	-3.17	-6.78	-3.81
Sulphate	%RSD	-	1.74	-	1.85	-	1.49
	%Bias	-	-4.22	-	-6.85	-	-4.00
Reactive silica	%RSD	1.82	1.38	7.59	2.40	5.45	5.80
	%Bias	1.17	0.80	1.66	-0.43	2.69	6.60

Standards - Precision and bias

Determinand	MCERTS Accreditation	Low standard		High Standard	
		RSD %	Bias %	RSD %	Bias %
Ammoniacal nitrogen	✓	3.81	-0.61	1.42	3.42

Samples and Spiked Samples

Determinand		Finham FE		Nuneaton FE		Albrighton FE	
		20%	80%	20%	80%	20%	80%
Ammoniacal nitrogen	%RSD	3.12	1.22	3.12	1.05	3.78	1.37
	%Bias	3.91	-0.09	0.72	-0.92	3.22	0.05

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	8.28
Nitrate / TON	16.93
Nitrite	18.89
Chloride	16.35
Phosphate	11.62
Sulphate	39.38
Reactive silica	13.35

References:

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ISO 5667-3:2024 - Water quality Sampling Part 3: Guidance on the preservation and handling of water samples

EPA-600/4-79-020 -Methods for Chemical Analysis of Water and Wastes.