METHOD STATEMENT

Determinand:
Total Nitrogen, Total Oxidised Nitrogen, Kjeldahl Nitrogen and Total Organic Nitrogen, Total Soluble Nitrogen

Matrix:
Crude Sewage, Treated Effluent, Trade Effluent and Surface water

Principle of Method:
The total UV digestible nitrogen and total oxidised nitrogen (TON) are determined by automated segmented flow analysis. The Kjeldahl nitrogen and total organic nitrogen content of the sample can subsequently be calculated from the data. Total soluble nitrogen (filtered Kjeldahl nitrogen) may also be determined by filtering the sample prior to analysis.

Under appropriate conditions, nitrite reacts with sulphanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride to form a pink coloured complex (the Griess Reaction). The intensity of the pink coloration is directly proportional to the concentration nitrite present and can be measured at a wavelength of 540nm. Quantification is by comparison with standard solutions.

On the first instrument channel, the sample undergoes dialysis and is then buffered at pH 8.2 and passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite prior to colour formation via the Griess reaction. This measures TON.

On the second channel, a powerful UV-catalysed oxidation converts nitrogen compounds to nitrate, and then nitrates are reduced to nitrite. This is followed by dialysis and is then buffered at pH 8.2 and then passed through a copper-cadmium column prior to colour formation via the Griess reaction. This measures total nitrogen.

Kjeldahl nitrogen may be calculated by subtracting the TON result from the total nitrogen result. Total organic nitrogen may be calculated by subtracting the ammonia result (determined separately) from the Kjeldahl nitrogen result. Total soluble nitrogen (filtered nitrogen) and filtered Kjeldahl nitrogen may be determined by this method, provided the sample is filtered prior to analysis

Sampling and Sample Preparation:
There is no recommended sample preservative. Samples should be analysed as soon after receipt as possible. Samples that require filtration prior to analysis should list the type of filtration process used as results will vary depending upon the degree of filtration used.

Samples are stable for times stated below, from sampling.

Total Nitrogen 10 Days (In-House Data)
Kjeldahl Nitrogen 7 Days (In-House Data)

Interferences:
Nitrogen species undergo chemical and bacterial interconversion. Samples should be analysed as quickly as possible after receipt to minimise these effects.

The main potential interference effects arise from dissolved or suspended organic matter present in the samples, which compete for the oxidation capacity of the peroxodisulfate reagent. Samples with a COD value that exceeds 120 mg/l, expressed as O_2, or TOC value that exceeds 40 mg/l, expressed as C, may not guarantee a sufficient excess of the oxidation reagent.

Very acidic or alkaline samples may not be sufficiently buffered by the reagent to attain the correct pH. This will result in incomplete reaction and a low estimation of concentration. High levels of bleaching agents may decolourise the pink complex, leading to low results. High levels of reducing agents may react with the potassium persulphate leading to low results.

Performance of Method:

Determinand	Range of Application mg/l as N	Limit of Detection mg/l as N	Normal Reporting Limit mg/l as N
Total Nitrogen	0.50 to 100	0.477	0.50
Total Oxidised Nitrogen (TON)	0.3 to 100	0.246	0.30
Kjeldahl Nitrogen	0.50 to 100	0.429	0.50

Determinand	MCERTS Accreditation	Low Standard		High Standard	
		RSD %	Bias %	RSD %	Bias %
Total Nitrogen	✓	2.76	0.7	2.03	0.62
TON		1.61	-0.06	1.66	0.37
Kjeldahl Nitrogen	✓	4.49	1.92	3.23	0.56

Determinand		Treated Sewage (West Malvern)		Trade Effluent (To Sewer)		Trade Effluent (To Controlled)	
		Low	High	Low	High	Low	High
Total Nitrogen	% RSD	2.64	1.62	2.38	1.72	1.99	1.58
	% Rec.	93.89	100.08	98.48	99.38	98.56	99.60
TON	% RSD	5.89	1.68	1.80	1.93	2.82	1.59
	% Rec.	89.02	98.20	97.91	99.15	98.29	98.48
Kjeldahl Nitrogen	% RSD	4.55	2.99	3.85	2.30	3.58	2.90
	% Rec.	98.78	101.97	99.05	99.60	99.28	100.72

Determinand		Untreated Effluent		Surface Water	
		Low	High	Low	High
Total Nitrogen	% RSD	2.50	1.41	1.84	1.71
	% Rec.	101.57	97.31	99.96	99.64
TON	% RSD	1.51	1.70	2.45	1.57
	% Rec.	98.28	97.75	100.98	99.99
Kjeldahl Nitrogen	% RSD	3.74	2.64	4.44	2.97
	% Rec.	104.86	96.88	98.94	99.28

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 Nitrogen	7.53
TON	9.53
Kjedahl Nitrogen	9.33

References:

Kroon H, 'Determination of Nitrogen in Water; Comparison of Continuous Flow Method with on-line UV Digestion with the Original Kjeldahl Method', Analytica Chimica Acta, 276 (1993) pages 287-293

Houba V J G, Novozamsky I, Uittenbogaard J and van der Lee J J, 'Automatic Determination of Total Soluble Nitrogen in Soil Extracts', Landwirth. Forschung 40 (4), 295-302 (1987)

ISO 5667-3 2018 - Water quality Sampling Part 3: Guidance on the preservation and handling of water samples

Skalar User Manual - Issue 101920/99366038