

METHOD STATEMENT



Determinand:

Determination of Ammoniacal Nitrogen, Total Oxidised Nitrogen, Nitrite Nitrogen, Chloride, Orthophosphate (including low range calibration), Silica and Alkalinity.

Matrix:

Sample Types: Raw, Potable, Surface and Ground waters. Low Level Phosphate (LLPO₄) is applicable to surface and ground waters only

Principle of Method:

This method uses the Aquakem 600 Discreet Analyser.

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 calibration curves produced for most analytes are not linear.

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

Specific details of colorimetric reactions are given below.

Spent reaction mixture and vials are removed to waste and collected in the machine

Nitrite

Nitrite ions react with sulphanilamide and N-1-naphthylethylene diamine in acidic media to form a pink azo dye, the intensity of which is proportional to the concentration of nitrite present and which is measured at 540 nm by automated discrete colorimetric analysis.

TON

Nitrate is reduced to nitrite using a copper/hydrazine reducing agent. The nitrite produced is then reacted as described above to give a value for the total oxidised nitrogen (nitrite plus nitrate) within the sample. Nitrate can then be calculated by difference.

To calculate nitrate from TON and nitrite, use the following equation.

$(NO_3 = TON - (NO_2 \times 1.3478))$.

Ammonia

In the presence of Sodium Nitroprusside catalyst, ammonia reacts with salicylate ions to produce a blue indophenol dye, whose intensity is proportional to the concentration of ammonia present and which is measured at 660 nm by automated discrete colorimetric analysis.

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 480nm.

Orthophosphate (including low range calibration)

In an acid medium, ammonium molybdate and antimony potassium tartrate react with orthophosphate to form an antimony-phosphor-molybdate complex. This is then reduced by ascorbic acid to form a blue complex, the intensity of which is proportional to the original concentration of orthophosphate ions present. The intensity of the colour formed is measured at a wavelength of 880 nm using automated discrete colorimetric analysis.

Alkalinity

In the Bromophenol Blue method, alkalinity is determined by measuring the absorbance of the complex formed when a sample is reacted with bromophenol blue in a phthalate buffer, spectrophotometrically at 600nm.

To convert alkalinity as CaCO₃ to alkalinity as HCO₃⁻, multiply by 1.22.

Silica

This method measures molybdate reactive silicon. These consist of mainly monomeric, dimeric and silicic acids. They react with ammonium molybdate under acidic conditions to form yellow molybosilicic acid that is reduced in situ with ascorbic acid to yield a silicomolybdenum blue complex. The intensity of

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the colour formed is measured at a wavelength of 700 nm using automated discrete colorimetric analysis.

To convert silica as Si to silica as SiO₂, multiply by 2.14.

Sampling and Sample Preparation:

Samples are normally collected in 500 ml PET bottles. Other size PET or HDPE bottles are also suitable. No special preservation is required

If analysis cannot be immediately undertaken, samples should be stored at a temperature of 3±2°C until the day of analysis.

Samples should be warmed up to room temperature prior to analysis. Analysis should be completed within stability stated below.

| Analyte | Maximum period of analyte stability prior to any extraction step (if relevant) | Maximum period of analyte stability after the extraction step (if relevant) | Source |
|---------------------|--|---|-----------------|
| Ammoniacal Nitrogen | 10 days | N/A | In-house data |
| TON | 10 days | N/A | In-house data |
| Nitrite Nitrogen | 10 days | N/A | In-house data |
| Chloride | 30 days | N/A | ISO 5667-3-2018 |
| Orthophosphate | 25 days | N/A | In-house data |
| Total Alkalinity | 10 days | N/A | In-house data |
| Silica | 30 days | N/A | ISO 5667-3-2018 |
| Low level phosphate | 10 days | N/A | In-house data |

Stability trials carried out at room temperature at Wakefield.

Interferences

Interference may be caused to any determinand depending on the colour and nature of the sample. Significant effects are not expected in potable waters.

Ammonia: - Interferences include aromatic amines, chloramines, ketones, aldehydes and alcohols.

Nitrate / Nitrite: - Amines, strong reducing agents and strong oxidising agents are the only substances known to interfere.

Chloride: - Interferences include thiocyanate, thiosulphate, cyanide, sulphide and sulphite. Iron in excess will mask the end point.

Phosphate: - Interferences include sulphide, arsenic and silicon.

Alkalinity: - There are no identified interferences for the Bromophenol Blue method.

Silicate: Phosphate, arsenate, germanate and nitrite are known to interfere with this test. The levels of the above needed for interference to occur are not typically found in potable water.

Performance of Method:

Range of Application:

| | |
|-------------------------|-------------------------------------|
| Ammoniacal Nitrogen | LOQ – 0.75 mg/l as NH ₄ |
| Total Oxidised Nitrogen | LOQ - 80 mg/l as NO ₃ |
| Nitrite Nitrogen | LOQ – 0.3 mg/l as NO ₂ |
| Chloride | LOQ - 300 mg/l as Cl |
| Orthophosphate | LOQ – 3.0 mg/l as P |
| LLPO4 | LOQ – 0.2 mg/l as P |
| Total Alkalinity | LOQ - 300 mg/l as CaCO ₃ |
| Silica | LOQ - 10 mg/l as Si |

The analytical range may be extended by sample dilution. Samples with a concentration higher than that of the top standard should be diluted with deionised water and re-analysed.

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Limit of Quantification:

| Determinand | DAP_2 (asset 1967) | | DAP_3 (asset 2836) | | Units |
|----------------|--------------------|-----------------|--------------------|-----------------|---------------------------------------|
| | LOQ | Reporting Limit | LOQ | Reporting Limit | |
| Ammonia | 0.0071 | 0.010 | 0.0092 | 0.010 | mg/l as NH ₄ ⁺ |
| TON | 2.1251 | 2.13 | 1.1021 | 2.13 | mg/l as NO ₃ |
| Nitrate | 2.1053 | 2.13 | 1.1113 | 2.13 | mg/l as NO ₃ |
| Nitrite | 0.0015 | 0.003 | 0.0024 | 0.003 | mg/l as NO ₂ |
| Chloride | 4.3658 | 4.4 | 1.9227 | 4.4 | mg/l as Cl ⁻ |
| Orthophosphate | 0.0243 | 0.056 | 0.0559 | 0.056 | mg/l as PO ₄ ³⁻ |
| Alkalinity | 12.6821 | 18.6 | 18.5255 | 18.6 | mg/l as CaCO ₃ |
| Silica | 0.0302 | 0.10 | 0.0977 | 0.10 | mg/l as Si |
| LLP | 0.01336 | 0.014 | 0.00752 | 0.014 | mg/l as PO ₄ ³⁻ |

Recoveries of Compounds and Uncertainty of measurement:

DAP_2 (asset 1967)

Performance at PCV / 80% calibrated range

| | Concentration mg/l | % Bias | % RSD | % Uncertainty |
|------------|--------------------|----------------|---------------|----------------|
| Nitrite | 0.103 | 2.52 | 1.94 | 6.40 |
| TON | 50.659 | 1.32 | 1.13 | 3.58 |
| Ammonia | 0.502 | 0.48 | 1.82 | 4.12 |
| Chloride | 79.174 240.060* | -1.03 0.03* | 1.46 2.07* | 3.95 5.205* |
| Phosphate | 2.442 | 1.76 | 1.51 | 4.78 |
| Alkalinity | 245.227 | 2.18 | 0.82 | 6.4 |
| Silica | 8.067 | 0.83 | 1.76 | 4.36 |
| LLPO4 | 0.1704 | 6.52 | 4.00 | n/a |

Spike recoveries (%)

| | Soft | Medium | Hard | Borehole | Raw |
|------------|--------|----------------|--------|----------|--------|
| Nitrite | 98.23 | 98.04 | 98.21 | 98.13 | 90.69 |
| TON | 99.52 | 100.71 | 100.81 | 96.82 | 100.17 |
| Ammonia | 103.96 | 103.60 | 103.07 | 104.11 | 101.80 |
| Chloride | 98.34 | 96.22 99.94 | 93.24 | 96.54 | 94.02 |
| Phosphate | 95.08 | 99.11 | 94.10 | 102.69 | 100.59 |
| Alkalinity | N/A | 238.69 | N/A | N/A | N/A |
| Silica | 99.84 | 99.70 | 99.37 | 99.40 | 99.53 |
| LLPO4 | n/a | n/a | n/a | 99.36 | 100.24 |

DAP_3 (asset 2836)

Performance at PCV / 80% calibrated range

| | Concentration mg/l | % Bias | % RSD | % Uncertainty |
|----------------|---------------------|----------------|---------------|-----------------|
| Nitrite | 0.0991 | -0.87 | 2.17 | 6.476 |
| TON | 49.6578 | -0.68 | 1.56 | 6.567 |
| Ammonia | 0.4982 | -0.35 | 1.45 | 6.298 |
| Chloride | 79.1764 240.038* | -1.03 0.02* | 1.48 0.93* | 9.022 4.646* |
| Orthophosphate | 2.4870 | 3.63 | 1.66 | 8.806 |
| Alkalinity | 250.1273 | 4.22 | 2.71 | 12.525 |
| Silica | 2.16 | -1.12 | 2.16 | 9.138 |
| LLPO4 | 0.1573 | -1.66 | 2.89 | 23.191 |

Spike recoveries (%)

| | Soft | Medium | Hard | Borehole | Raw |
|----------|--------|--------|--------|----------|--------|
| Nitrite | 99.46 | 100.70 | 99.86 | 101.21 | 97.42 |
| TON | 100.35 | 100.34 | 102.16 | 100.78 | 98.77 |
| Ammonia | 101.77 | 102.27 | 101.62 | 101.93 | 102.68 |
| Chloride | 96.08 | 98.95 | 95.71 | 95.31 | 96.45 |

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| | Soft | Medium | Hard | Borehole | Raw |
|----------------|--------|--------|--------|----------|--------|
| | | 99.50 | | | |
| Orthophosphate | 98.52 | 94.80 | 96.67 | 98.15 | 98.46 |
| Alkalinity | 102.10 | 99.61 | 102.65 | 98.19 | 107.98 |
| Silica | 97.92 | 97.21 | 96.01 | 95.34 | 96.50 |
| LLPO4 | N/A | 0.1517 | N/A | N/A | N/A |

References:

Aquakem 600 user's guide

Chloride - Methods for the Examination of Waters and Associated Materials.1981, ISBN 0 11 751626 0

TON - Methods for the Examination of Waters and Associated Materials HMSO, 1981, ISBN 0 11 75193 0.

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Phosphorus- Methods for the Examination of Waters and Associated Materials 1980, ISBN 0 11 7515825