METHOD STATEMENT

Determinand:
Determination of Total and Dissolved (filtered) Aluminium, Manganese, Iron, Phosphorus, Boron, Calcium, Magnesium, Sulphate and Silica + Total Sodium and Total Potassium.

Matrix:
Sample Types: Raw, Potable, Surface, high purity, DI waters, Bottled and Ground waters.

Principle of Method:
This method uses the Agilent 5900 ICP-OES.
Samples are acidified and digested at elevated temperatures to ensure any particulate matter is brought into solution. The acidified samples are analysed on an ICP-OES instrument, where excitation of the sample within the 6,000oC plasma causes ionisation of atoms, which in turn causes the emission of electromagnetic radiation at specific wavelengths for each element. The intensity of the emission is measured and quantified by comparison against standards with known concentrations of elements.

Sampling and Sample Preparation:
Samples are normally collected in polyethylene (HDPE) bottles.
On receipt at the laboratory the samples are acidified with concentrated nitric acid such that the final concentration of acid is ~1% V/V (e.g. 1.00 ± 0.10 cm3 of acid to each 100 ± 10 cm3 of sample). If dissolved (filtered) metals analysis is required on a sample, the sample must be filtered through a 0.45 µm filter disc prior to acidification. Following acidification, the samples should be digested in the oven provided at 80°C ± 5 °C for a minimum of 6 hours and allowed to cool prior to analysis. See method No. WPC44 for the metals preparation and digestion procedure.
If samples require emergency analysis they may be acidified as above, microwaved for 1 minute each then run on the appropriate instrument. This has been shown in testing to be at least as effective as the oven digest. However, this should only be used for emergency samples and not routine analysis.
If analysis cannot be immediately undertaken, samples can be stored at room temperature until the day of analysis. Samples should be analysed within 30 days of the sampling date.

Interferences
Choice of analytical wavelength and placement of background correction points has been designed to eliminate possible interference from other elements within the sample.
This is further aided by the fact that the elements being measured are generally at significantly higher concentrations than any possible interfering species.

Performance of Method:

Range of Application:

Determinand	Calibration range
Fe	LOQ - 5000 µg/l
Mn	LOQ - 1000 µg/l
Al	LOQ - 5000 µg/l
P	LOQ - 5000 µg/l
B	LOQ - 1000 µg/l
Ca	LOQ - 250 mg/l
Mg	LOQ - 50mg/l
Na	LOQ - 200mg/l
K	LOQ - 20 mg/l
SO_4	LOQ - 250 mg/l
Si	LOQ - 20 mg/l

The analytical range may be extended by sample dilution. Samples with a concentration higher than that of the top standard should be diluted so that the final concentration of acid in the diluted solution should remain the same. This can be achieved by using the calibration blank solution or by using deionised (Milli-Q) water and concentrated nitric acid. The sample should then be reanalysed.

Limit of Quantification and Reporting limit:

Determinand	Units	3372 LOQ	3407 LOQ	Agilent 5900 and 720 Normal Reporting Limit
Al	µg/l	8.360	11.112	11.2
Fe	µg/l	11.665	12.512	12.6
Mn	µg/l	1.536	1.957	1.96
P	µg/l	29.673	48.918	49.0
Ca	mg/l	0.174	0.469	0.47
Mg	mg/l	0.0167	0.0863	0.09
Na	mg/l	0.131	0.644	0.65
K	mg/l	0.157	0.197	0.20
SO_4	mg/l	0.239	0.496	0.50
B	µg/l	1.829	3.184	6.30
Si	mg/l	0.0077	0.0344	0.04

Recoveries of Compounds:

3372

	Soft Water		Medium Water		Hard Water		Raw Surface	
	% Rec	% RSD	% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
Al	102.56	2.43	102.46	3.64	102.77	2.11	102.74	5.11
Fe	98.76	0.96	96.03	1.38	99.44	1.37	106.87	4.92
Mn	97.39	0.60	97.31	0.87	97.56	0.63	91.89	1.48
P	93.51	0.76	95.13	0.98	94.68	0.88	98.43	0.93
Ca	98.15	0.89	95.33	0.95	92.27	0.99	94.68	1.17
Mg	100.97	0.77	100.43	0.99	100.83	1.05	100.96	1.23
Na	100.99	1.09	100.69	1.19	100.74	1.22	101.26	1.33
K	101.77	1.01	101.67	1.11	102.02	1.48	101.69	1.44
SO4	96.85	0.87	94.92	1.25	91.23	1.23	98.76	1.19
B	99.40	1.14	99.09	1.22	99.88	1.30	99.58	0.99
Si	95.44	1.15	95.16	1.19	94.94	1.23	104.30	2.79

	Borehole Water		Filtered Hard Water	
	% Rec	% RSD	% Rec	% RSD
Al	102.04	2.41	101.42	2.18
Fe	96.12	2.59	99.53	1.29
Mn	101.91	6.60	97.19	0.81
P	98.35	1.26	92.89	0.94
Ca	95.82	1.02	91.32	1.01
Mg	92.34	0.89	100.71	0.98
Na	100.45	1.38	99.73	1.35
K	101.21	1.42	100.32	1.02
SO4	98.20	1.37	94.10	1.37
B	99.22	1.34	98.51	1.25
Si	92.89	1.25	95.19	1.16

3407

	Hard Water

	% Rec	% RSD
Al	111.27	2.63
Fe	100.49	3.39
Mn	101.63	2.93
P	100.00	1.37
Ca	100.00	2.34
Mg	99.99	2.30
Na	100.00	1.92
K	111.37	3.17
SO4	101.59	2.20
B	100.00	1.42
Si	100.01	1.18

References:

In house method based on SCA bluebook 263 The Determination of Metals in Raw and Potable Waters by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) 2018.
Agilent 5800 and 5900 ICP-OES User’s Guide.
Water Quality-Sampling-Part 3: Guidance on the Preservation and Handling of Water Samples. BS EN ISO 5667-3-2024.
In-house Method WPC44- Metals Digestion Procedure.