METHOD STATEMENT

Determinand:
Low Level Metals:-
(Aluminium, Cadmium, Chromium, Copper, Iron, Lead, Mercury, Nickel, Silver, Zinc)

Matrix:
Potable waters, surface waters, groundwaters and lightly polluted effluents

Principle of Method:
Metals are determined by ICP-MS after dissolution via the action of microwaves in the presence of nitric acid. The digestion pre-treatment ensures that wherever possible, any suspended or colloidal forms are converted to soluble forms. Filtered (otherwise known as dissolved or soluble) metals may also be determined, by filtration through a 0.45µm membrane filter prior to acidification with nitric acid.
Some acid insoluble colloidal chemicals, such as mercury (I) chloride will also be determined unless the digested sample is filtered prior to analysis.
The sample digestion and subsequent analysis described within the method is suitable for any ICP-MS instrumentation

Sampling and Sample Preparation:
Total Metals.
The samples should arrive in a 125ml Azlon bottle. (If this is not the case, then the samples should be transferred to a 125ml Azlon bottle prior to starting the analysis. This should be noted as an analyst comment).
Shake the samples well and pour away part of each sample until the liquid level is approximately 2cm from the shoulder of the Azlon bottle.
Pipette into this 1ml ± 0.04ml Ultrapure Nitric acid.
Replace the caps and shake to mix.
Loosen the caps and place the samples in the microwave oven.
Microwave the samples in accordance with the guidance on the microwave oven being used (Currently, 1 minute for each Azlon bottle within the microwave at 650W).
Allow the samples to cool sufficiently to handle, screw the caps tight and shake to mix.
Allow any solids remaining within the sample to settle before pouring the supernatant digest into a sample tube.
Alternatively, if the solids within the sample do not settle sufficiently, rinse a 0.45µm filter and syringe with the 1% nitric acid blank. Draw the digested sample into the syringe and pass it through the filter and into a sample tube. This will also remove any acid insoluble colloidal chemicals such as mercury (I) chloride that might otherwise be detected by the method.

Filtered Metals
Rinse a series of 0.45µm syringe filters with the deionised water.
Draw approximately 8ml of sample into the rinsed syringe, attached the rinsed filter and pass the sample through the filter and into the sample tube.
Rinse the syringe between samples to avoid contamination.

Interferences:
The interferences for a number of elements are well documented and understood. Within the limitations of the method, these interferences are adequately compensated for by careful choice of elemental isotopes, interference equations and the use of reaction or collision gas technology. Appendix IV has details of the interference equations used.
If the sample falls outside these limitations, then this compensation may prove insufficient and results generated for certain elements should be viewed with caution.

Performance of Method:

Determinand	Range of Application (µg/l)	LOD & Source data (µg/ l)	Minimum Reporting Limit (µg/l)	Low Standard		High Standard	
				% RSD	% Bias	% RSD	% Bias
Aluminium	4 to 500	1.0103 (5x Blank)	4	4.66	-0.07	3.24	0.34
Cadmium	0.1 to 10	0.0649 (3 x Crude)	0.1	4.67	-0.61	2.85	0.63
Chromium	0.5 to 50	0.3308 (5 x Blank)	0.5	4.91	1.10	4.40	1.02
Copper	0.3 to 50	0.300 (5 x Blank)	0.3	4.73	1.43	5.03	2.06
Iron	5 to 500	1.093 (5 x Blank)	5	4.99	0.53	3.22	0.47
Lead	0.2 to 50	0.1167 (5 x Blank)	0.2	4.33	-2.55	2.18	-2.36
Mercury	0.03 to 10	0.0288 (3 x F E)	0.03	7.17	-3.39	3.17	-0.74
Nickel	0.5 to 50	0.2065 (5 x Blank)	0.5	5.30	1.99	3.64	2.10
Silver	0.5 to 10	0.4268 (5 x Blank)	0.5	6.55	-3.43	4.71	-1.03
Zinc	0.5 to 50	0.1827 (5 x Blank)	0.5	5.21	2.22	5.32	0.93

20% Low Spiked samples

Determinand	Final Effluent		Crude Sewage	
	% RSD	% Bias	% RSD	% Bias
Aluminium	4.51	1.00	4.22	-0.93
Cadmium	6.31	-3.03	4.99	-8.50
Chromium	6.36	-0.72	5.67	-2.37
Copper	4.29	0.23	4.99	4.13
Iron	5.49	1.19	5.04	-0.47
Lead	4.89	0.87	4.74	1.84
Mercury	7.35	-10.50	6.52	-5.95
Nickel	4.51	4.66	5.05	0.30
Silver	6.94	-8.87	8.58	-0.08
Zinc	2.97	6.43	3.89	5.25

80% High Spiked samples

Determinand	Final Effluent		Crude Sewage	
	% RSD	% Bias	% RSD	% Bias
Aluminium	3.76	-2.58	3.28	0.13
Cadmium	3.25	-2.51	3.16	-3.31
Chromium	3.96	0.34	2.85	-0.01
Copper	3.21	1.43	4.95	0.02
Iron	4.78	-1.41	3.10	-1.34
Lead	3.42	-1.69	3.36	1.83
Mercury	3.61	-2.05	4.06	-1.92
Nickel	2.90	-0.21	3.11	-1.03
Silver	4.17	-2.61	8.58	-0.06
Zinc	1.81	1.36	2.24	-0.51

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 %
Aluminium	8.91
Cadmium	10.76
Chromium	10.94
Copper	13.88
Iron	12.66
Lead	10.43
Mercury	13.54
Nickel	11.77
Silver	11.88
Zinc	13.91

References:

Real World Analysis of Trace Metals in Drinking Water using the Agilent 7500ce ICP-MS with Enhance ORS Technology, Agilent technologies Publication, 5989-0870EN

The Application of collision/reaction cell Inductively Coupled Plasma Mass Spectrometry to Multi-Element analysis in Variable Sample Matrices, using Helium as a non-reactive cell gas, E. McCurdy and G. Woods, (2004) *JAAS* 19, (3).

HP 4500 ICP-MS Training Course No. H4035A, Sheffield University Press, Dr. Cameron McLeod, March 1999.