METHOD STATEMENT

Determinand:
Metals: -
(Aluminium, Cadmium, Chromium, Copper, Iron, Lead, Nickel, and Zinc).

Matrix:
Treated Sewage Effluents and Surface Waters

Principle of Method:
Metals are determined by ICP-MS after heated dissolution in the presence of nitric acid. The digestion pre-treatment ensures that any suspended or colloidal forms are converted to soluble forms.
For Filtered metals, the samples are filtered on site.

Sampling and Sample Preparation:
The samples should arrive in a 125ml Azlon bottle. Add 1.25ml of Nitric acid and return the samples to the fridge until extraction. At the same time, acidify a blank sample of 18MΩ/cm deionised water in a new Azlon bottle labelled with that day's date.

Samples prior to acidification are stable for the times stated below, from In-House data.

Fe	10 days (In-house Data)
Cr	10 days (In-house Data)
Al	10 days (In-house Data)
Ni	10 days (In-house Data)
Cu	10 days (In-house Data)
Zn	10 days (In-house Data)
Cd	10 days (In-house Data)
Pb	10 days (In-house Data)

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.

Performance of Method:

Total Metals CIP

Determinand	Range of Application (ug/l)	LOD (ug/l)	Routine Reporting Limit (ug/l)	Low Standard		High Standard	
				%RSD	%Bias	% RSD	% Bias
Aluminium	25 to 5000	2.7228	25	2.82	-7.13	1.45	-3.04
Cadmium	0.02 to 2	0.0038	0.02	4.35	-2.77	1.26	-2.04
Chromium	0.5 to 50	0.0974	0.5	4.03	-0.57	3.04	-2.32
Copper	0.3 to 30	0.2259	0.3	4.72	-2.60	2.03	-2.57
Iron	25 to 5000	2.3373	25	4.09	-0.63	1.21	-2.21
Lead	0.2 to 20	0.0412	0.1	4.14	0.17	1.49	2.20
Nickel	0.5 to 50	0.4576	0.5	3.73	-1.77	1.68	-3.17
Zinc	0.8 to 50	0.3571	0.5	5.07	-0.24	5.03	-2.87

Determinand	Final Effluent				Surface Water			
	20% & CLOI		80%		20% & CLOI		80%	
	% RSD	% Bias	% RSD	% Bias	% RSD	% Bias	% RSD	% Bias
Aluminium	2.77	-8.99	1.69	-4.46	N/A	N/A	1.65	-5.71
Cadmium	1.38	-5.45	1.13	-3.99	1.89	-3.30	1.07	-4.03
Chromium	2.33	-6.89	2.78	-6.09	N/A	N/A	2.93	-6.18
Copper	4.02	-6.85	3.59	-7.79	N/A	N/A	4.09	-5.30
Iron	0.95	-7.00	1.02	-6.38	1.44	-8.47	1.40	-7.38
Lead	1.47	-1.17	1.60	-0.16	1.26	-4.03	2.02	-1.45
Nickel	1.66	-9.37	1.26	-9.74	3.42	-6.81	2.06	-9.78
Zinc	3.99	-9.56	2.87	-8.45	N/A	N/A	3.70	-9.11

Filtered Metals CIP

Determinand	Range of Application (ug/l)	LOD (ug/l)	Routine Reporting Limit (ug/l)	Low Standard		High Standard	
				%RSD	%Bias	% RSD	% Bias
Aluminium	25 to 5000	3.9031	25	2.03	-6.86	1.25	-2.40
Cadmium	0.02 to 2	0.0073	0.02	1.92	-0.77	1.34	-1.85
Chromium	0.5 to 50	0.2328	0.5	2.97	-3.62	3.25	-2.62
Copper	0.3 to 30	0.1533	0.3	4.25	-4.04	3.12	-2.62
Iron	25 to 5000	19.0760	25	1.41	-0.48	1.48	-1.86
Lead	0.2 to 20	0.0807	0.1	1.43	-0.56	1.83	2.23
Nickel	0.5 to 50	0.3029	0.5	1.63	-1.67	1.63	-2.60
Zinc	0.8 to 50	0.4001	0.5	3.42	5.73	2.97	-1.43

Determinand	Final Effluent				Surface Water			
	20% & CLOI		80%		20% & CLOI		80%	
	% RSD	% Bias	% RSD	% Bias	% RSD	% Bias	% RSD	% Bias
Aluminium	1.40	-8.76	1.45	-3.38	N/A	N/A	1.42	-4.58
Cadmium	1.51	-4.98	1.03	-3.94	1.41	-3.53	1.45	-4.37
Chromium	2.98	-6.60	3.94	-5.9	N/A	N/A	4.12	-6.26
Copper	3.64	-2.98	2.51	-7.51	N/A	N/A	2.56	-6.79
Iron	1.01	-5.72	1.17	-5.70	1.02	-6.77	1.19	-6.42
Lead	1.38	-0.79	1.75	-0.22	1.15	-4.31	1.48	-1.87
Nickel	1.88	-8.12	1.24	-8.91	3.59	-5.67	1.23	-9.57
Zinc	3.61	4.92	3.51	-0.31	N/A	N/A	3.0	-8.40

Filtered Metals - MCERTS

Determinand	MCERTS Accreditation	Range of Application (ug/l)	LOD (ug/l)	Routine Reporting Limit (ug/l)
Cadmium	Y	0.02 to 2	0.0102	0.02
Copper	Y	0.95 to 30	0.2914	0.95
Lead	Y	0.021 to 20	0.0150	0.021
Nickel	Y	0.5 to 50	0.1072	0.5
Zinc	Y	2.1 to 50	0.8210	2.1

Standards Precision & Bias and Limits of Detection

Determinand	Low Standard		High Standard	
	%RSD	%Bias	% RSD	% Bias
Cadmium	1.98	2.31	1.43	2.01
Copper	1.41	0.55	1.77	-0.62
Lead	2.20	0.74	1.93	-0.20
Nickel	1.37	1.04	1.89	0.08
Zinc	2.30	-0.62	1.69	-1.95

Spiked samples

Determinand	Spike Level	Treated Sewage - Finham		Treated Sewage - Whitwell		Treated Sewage - Bubbenhall	
		RSD %	Rec. %	RSD %	Rec. %	RSD %	Rec. %
Cadmium	20%	2.74	97.20	1.79	98.19	2.11	99.76
	80%	1.37	97.87	1.48	98.04	2.09	99.64
Copper	20%	2.41	95.36	2.10	92.30	2.02	94.33
	80%	1.89	92.86	1.92	90.33	2.11	93.38
Lead	20%	2.05	97.52	1.96	96.12	1.75	98.49
	80%	1.84	97.11	1.77	96.31	2.36	98.78
Nickel	20%	1.76	95.94	1.85	93.98	2.16	96.21
	80%	1.88	95.48	1.84	93.32	2.13	96.01
Zinc	20%	3.01	93.60	3.96	92.63	4.00	96.52
	80%	2.08	93.76	2.39	93.51	2.22	97.05

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 % - CIP	
	Total Metals	Filtered Metals
Aluminium	14.39	12.62
Cadmium	9.37	9.25
Chromium	15.15	3.84
Copper	15.56	14.49
Iron	14.42	12.23
Lead	6.88	6.54
Nickel	18.33	16.74
Zinc	20.70	13.64

Determinand	Uncertainty of Measurement % - MCERTS
	Filtered Metals
Cadmium	6.75
Copper	15.929
Lead	9.112
Nickel	11.671
Zinc	13.563

References:

Handbook of Inductively Coupled Plasma Mass Spectrometry. K.E Jarvis, A.L. Gray, R.S.Houk. ISBN 0-216-912-1

Principles of Instrumental Analysis 6th Edition. Holler, Sloog, Crouch. ISBN 0-495-12570-9

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