

METHOD STATEMENT



Determinand:

Determination of Aluminium, Arsenic, Cadmium, Chromium, Cobalt, Copper, Iron, Manganese, Molybdenum, Nickel, Phosphorous, Lead, Selenium, Thallium, Vanadium and Zinc

Matrix:

Sample Type: Final Effluents, Trade Discharge, Crude Sewage and other similar waste water samples. Filtered samples may also be analysed using this method.

NOTE:

- For the Elan DRC-e ICPMS this method is not suitable for the analysis of Phosphorous in crude sewages or Selenium/Vanadium in any matrix.
- For the Agilent 7900 ICPMS this method is not suitable for the analysis of Selenium in crude sewages.

MCerts accreditation is provided for pre-filtered on-site samples. Dissolved metals analysis performed in the lab is not covered by MCerts accreditation.

Principle of Method:

The method describes a technique for multi - element determination of trace metals in solution. The basis of the method is the measurement of ions produced by an inductively coupled plasma and detected using a mass spectrometer.

The ELAN DRC-e analyses samples in standard mode while the Agilent 7900 uses helium and high energy helium collision mode to reduce any potential interferences.

Acidified samples are nebulised and the aerosol that is produced is transported to the plasma torch where excitation of the metal atoms occurs. Excitation is due to the high temperatures (up to 6,000-K) produced by the radio frequency inductively coupled plasma. The metal ions thus produced pass through an interface region into the mass spectrometer. There the ions are separated by a quadrupole where only ions having a specific mass to charge ratio are passed through at any moment in time. The dual mode detector then detects these ions and the resulting electrical signals are processed into digital information that is used to indicate ion intensity and subsequently elemental concentration.

Sampling and Sample Preparation:

Samples are normally taken in 1L PET bottles.

Samples should be prepared within 7 days of sampling (Coventry in-house data)

Prepared samples are stable for one month. Cd, Cr, Cu, Pb, Ni, Zn and As are stable for 6 months. (ISO 5667 - 3:2018)

If sample preparation cannot be immediately undertaken, samples should be refrigerated at $3 \pm 2^{\circ}\text{C}$. Once digested, samples are stored at room temperature.

Interferences

Careful choice of plasma conditions, interference equations and isotopes are all designed to minimise interference.

Performance of Method:

Range of Application:

Element	Elan DCR-e $\mu\text{g/L}$	Agilent 7900 $\mu\text{g/l}$
Al	LOD - 1000	LOD - 1000
P	LOD - 1000	LOD - 2500
Cr	LOD - 500	LOD - 250
Fe	LOD - 1000	LOD - 2500
Mn	LOD - 1000	LOD - 1000

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Element	Elan DCR-e µg/L	Agilent 7900 µg/l
Co	LOD - 100	LOD - 100
Ni	LOD - 500	LOD - 250
Cu	LOD - 500	LOD - 250
Zn	LOD - 500	LOD - 250
As	LOD - 100	LOD - 100
Se	LOD - 100	LOD - 100
Mo	LOD - 100	LOD - 100
Cd	LOD - 100	LOD - 100
Tl	LOD - 100	LOD - 100
Pb	LOD - 500	LOD - 250
V		LOD - 100

This range may be extended by sample dilution.

Limit of Detection, Recoveries of Compounds and Uncertainty of measurement:

Original Data of previous ELAN DRC-e used for comparison

Element	LOD µg/l	MRV µg/l		Final Effluent		Trade Discharge		Untreated Raw	
				Low Spike	High Spike	Low Spike	High Spike	Low Spike	High Spike
Al	24.8704	25	%recovery	95.89	97.95	97.91	99.03	99.34	102.53
			%rsd	4.83	4.90	4.51	3.20	3.81	3.02
P	72.0790	80	%recovery	101.64	104.43	99.43	103.48	-	-
			%rsd	2.75	3.60	2.15	3.53	-	-
Cr	0.8058	0.81	%recovery	95.93	95.27	96.52	95.41	97.52	96.17
			%rsd	2.89	3.47	3.60	3.09	2.99	3.25
Mn	0.3047	0.31	%recovery	100.02	98.09	98.35	98.52	102.55	97.91
			%rsd	3.44	3.65	2.76	5.77	4.33	2.06
Fe	27.3463	31	%recovery	100.71	95.99	95.21	93.39	92.05	94.83
			%rsd	3.18	3.69	4.88	2.57	4.86	3.75
Co	0.1752	0.18	%recovery	99.44	100.21	100.55	99.60	102.46	100.46
			%rsd	2.46	2.85	2.79	2.55	2.34	1.92
Ni	2.7421	2.8	%recovery	96.00	95.48	97.34	96.71	100.23	97.91
			%rsd	2.64	3.05	2.68	2.41	2.66	2.36
Cu	2.4795	2.5	%recovery	99.97	97.58	98.34	94.51	102.42	98.15
			%rsd	3.23	3.52	4.38	5.16	4.93	2.87
Zn	6.1950	7	%recovery	104.96	97.64	98.18	93.09	96.67	93.04
			%rsd	4.71	5.00	4.27	4.97	3.09	3.39
As	0.7137	0.8	%recovery	103.87	102.77	104.63	103.75	102.13	100.40
			%rsd	3.05	2.34	3.27	3.60	3.11	3.28
Mo	1.8571	1.9	%recovery	107.45	104.93	109.08	107.15	101.15	103.88
			%rsd	2.83	4.58	2.83	4.58	5.69	3.07
Cd	0.1152	0.12	%recovery	96.65	97.77	100.44	99.90	102.61	101.06
			%rsd	1.90	2.25	2.32	2.33	1.88	1.97
Tl	0.0277	0.03	%recovery	100.92	102.45	102.70	100.81	101.86	100.63
			%rsd	2.30	1.82	2.32	2.46	2.08	2.31
Pb	0.8074	0.81	%recovery	103.68	103.55	104.22	101.43	103.94	101.40
			%rsd	3.30	1.88	3.42	2.27	3.21	2.08

Elan DRC-e Asset 0082 Comparison Data)

Element	LOD µg/l	MRV µg/l		Final Effluent		Dissolved Det
				Low Spike	High Spike	
Al	28.8767	29	%recovery	98.36	96.36	x
			%rsd	3.12	3.43	
P	17.4963	80	%recovery	103.43	98.25	x

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Element	LOD µg/l	MRV µg/l	Final Effluent			Dissolved Det
			%rsd	Low Spike	High Spike	
Cr	0.3242	0.81	%recovery	3.11	3.84	x
			%rsd	99.41	97.15	
Mn	5.2357	5.30	%recovery	3.40	5.72	x
			%rsd	96.91	95.16	
Fe	12.5782	31	%recovery	3.71	4.97	x
			%rsd	96.46	93.91	
Co	0.1209	0.18	%recovery	2.91	3.30	-
			%rsd	95.54	93.43	
Ni	0.6644	2.8	%recovery	2.61	3.47	x
			%rsd	95.62	93.30	
Cu	3.5987	3.6	%recovery	1.53	3.55	x
			%rsd	92.92	92.06	
Zn	7.3428	8	%recovery	2.52	3.53	x
			%rsd	89.44	89.95	
As	1.5386	1.6	%recovery	1.89	3.50	x
			%rsd	99.76	92.14	
Mo	0.6410	1.9	%recovery	2.74	4.83	-
			%rsd	103.37	101.43	
Cd	0.0517	0.12	%recovery	2.37	4.34	x
			%rsd	98.43	97.02	
Tl	0.1221	0.13	%recovery	2.68	5.24	-
			%rsd	96.49	94.51	
Pb	0.2524	0.81	%recovery	2.11	4.02	x
			%rsd	97.72	95.98	
			%rsd	2.71	4.20	

Agilent 7900 data

Element	LOD (µg/l)	MRV (µg/l)	Final Effluent (Sutton)		Trade Discharge		Untreated Raw		Dissolved Det	
			Low Spike	High Spike	Low Spike	High Spike	Low Spike	High Spike		
Al	9.10	25	%recovery	100.80	100.51	103.63	102.55	101.96	103.05	x
			%rsd	2.03	1.63	2.10	1.67	2.67	1.32	
P	35.3	36	%recovery	103.79	104.84	107.35	106.55	103.45	104.72	x
			%rsd	2.03	2.01	1.44	1.41	2.00	1.72	
V	2.56	2.6	%recovery	101.22	101.32	103.64	102.87	102.58	101.85	-
			%rsd	2.41	1.90	2.77	1.43	2.60	1.86	
Cr	0.227	0.81	%recovery	98.85	99.08	93.18	99.59	100.07	100.86	x
			%rsd	1.66	1.88	1.78	1.85	1.53	1.68	
Mn	0.646	0.81	%recovery	98.94	99.06	100.18	100.54	99.07	100.00	x
			%rsd	1.59	1.63	1.75	1.31	1.46	1.21	
Fe	9.61	31	%recovery	96.73	98.11	97.36	99.72	98.09	89.43	x
			%rsd	1.66	1.93	1.63	1.57	1.99	2.16	
Co	0.114	0.18	%recovery	99.89	99.57	101.89	101.61	100.86	100.64	-
			%rsd	2.03	2.11	1.51	1.79	1.57	1.40	
Ni	0.539	2.5	%recovery	96.44	96.81	100.35	99.94	96.07	96.78	x
			%rsd	2.08	2.03	1.79	1.67	1.64	1.58	
Cu	1.18	2.5	%recovery	98.30	98.73	102.22	100.94	93.71	98.64	x
			%rsd	1.91	1.85	2.46	1.58	2.82	2.32	
Zn	7.46	7.5	%recovery	100.66	104.64	99.64	108.18	104.23	97.25	x
			%rsd	2.77	1.92	2.98	4.61	5.56	1.45	
As	0.201	0.80	%recovery	100.53	100.86	101.60	100.91	97.71	97.34	x
			%rsd	1.66	1.72	1.41	1.57	1.47	1.05	
Se	0.272	0.80	%recovery	99.45	99.40	98.79	99.65	-	-	x

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Element	LOD (µg/l)	MRV (µg/l)		Final Effluent (Sutton)		Trade Discharge		Untreated Raw		Dissolved Det
				Low Spike	High Spike	Low Spike	High Spike	Low Spike	High Spike	
			%rsd	2.30	1.72	1.48	1.51	-	-	
Mo	0.206	1.9	%recovery	100.49	100.87	100.77	101.08	96.14	98.15	-
			%rsd	1.85	1.89	1.84	1.68	3.24	2.84	
Cd	0.0837	0.12	%recovery	100.92	100.69	104.44	103.09	102.67	102.33	x
			%rsd	1.68	1.69	1.53	1.30	1.44	1.17	
Tl	0.196	0.20	%recovery	99.23	99.36	101.28	101.57	99.93	100.17	-
			%rsd	1.64	1.56	1.33	1.28	1.31	0.90	
Pb	0.109	0.81	%recovery	100.42	100.69	103.40	104.06	101.55	102.55	x
			%rsd	1.60	1.59	3.25	1.29	1.16	0.95	

References:

In house method based on SCA bluebooks

Perkin Elmer ELAN DRC-e Hardware guide manual.

ISO 17294-2:2016: Water quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2: Determination of selected elements including uranium isotopes

Agilent ICP-MS: ISIS 3 (Integrated Sample Introduction System).

Agilent ICP-MS: MassHunter Workstation User Guide.

Agilent ICP-MS: Familiarization Guide

Agilent 7800/7900 ICPMS: Hardware Maintenance Manual

Agilent SPS 4 Autosampler: User's Guide

ISO 17294-2:2003 Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements.