

METHOD STATEMENT



Determinand:

This method is applicable for the determination of Cadmium, Chromium, Copper, Lead, Nickel, Zinc, Arsenic, Selenium, Antimony, Silver, Barium, Beryllium, Cobalt, Lithium, Molybdenum, Tin, Strontium, Titanium, Thallium, Uranium, and Vanadium

Matrix:

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

Principle of Method:

This method uses the Agilent ICP MS and Nexion ICP-MS.

The method describes a technique for the simultaneous 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. Acidified samples are nebulised and the aerosol that is produced is transported to the plasma torch where excitation of the metal atoms occur. Excitation is due to the high temperatures (up to 6,000°C) 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 and fall on to the mass detector. The intensities of the currents produced are processed and controlled by a computer system.

Sampling and Sample Preparation:

Samples are normally collected in polyethylene (HDPE) bottles. RDT metals are also called "first draw" samples and should be the first litre of sample from a tap when it is turned on and hence should be received in 1000ml HDPE bottles. RDT samples usually contain higher levels of metals due to the fact that the water has stood in the tap and immediate pipework prior to sampling.

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 the sample is pre acidified or arrives in an STL25 no further acid is required. 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 $80 \pm 5^\circ\text{C}$. If the sample has been received in a RDT bottle this may be subbed into an azlon, acidified and microwaved for 1 minute. See method WPC44 for the metals preparation and digestion procedure. If particulate matter is observed in a sample after digestion, it must be filtered prior to analysis to avoid blocking the nebuliser or the tubing. Filter through a 0.45µm membrane filter. An acidified blank should also be filtered and analysed with the sample to prove there is no contamination from the filter from acidified solutions.

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

Careful choice of plasma conditions, internal standardisation, interference equations, collision or reaction gas settings and isotopes are all designed to minimise interference.

Potable waters do not tend to contain high levels of elements likely to cause adverse interferences.

Performance of Method:

Range of Application:

Agilent & Nexion ICPMS

Element	Calibration Range (µg/l)	Element	Calibration Range (µg/l)
Cd	LOQ - 6.25	Ba	LOQ - 500
Cr	LOQ - 62.5	Be	LOQ - 100
Cu	LOQ - 500	Co	LOQ - 100
Pb	LOQ - 31.25	Li	LOQ - 500
Ni	LOQ - 25	Mo	LOQ - 100
Zn	LOQ - 500	Sn	LOQ - 100
As	LOQ - 12.5	Sr	LOQ - 500

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Element	Calibration Range (µg/l)	Element	Calibration Range (µg/l)
Se	LOQ - 12.5	Ti	LOQ - 100
Sb	LOQ - 6.25	Tl	LOQ - 100
U	LOQ - 10	Ag	LOQ - 25
V	LOQ - 100		

All analytical ranges 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	Nexion LOQ	Agilent	Normal Reporting Limit
Cd	µg/l	0.011	0.006	0.025
Cr	µg/l	0.125	0.051	0.25
Cu	µg/l	0.812	0.276	2.5
Pb	µg/l	0.087	0.019	0.1
Ni	µg/l	0.407	0.030	0.5
Zn	µg/l	2.558	1.334	7.5
As	µg/l	0.045	0.011	0.25
Se	µg/l	0.156	0.246	0.25
Sb	µg/l	0.017	0.091	0.1
Ag	µg/l	0.193	0.200	1.0
Ba	µg/l	0.395	0.229	1.0
Be	µg/l	0.057	0.067	0.1
Co	µg/l	0.109	0.047	0.25
Li	µg/l	0.331	1.776	2.5
Mo	µg/l	0.154	0.175	0.25
Sn	µg/l	0.199	0.701	1.0
Sr	µg/l	0.510	0.189	2.5
Ti	µg/l	0.152	0.117	0.25
Tl	µg/l	0.334	0.154	0.5
U	µg/l	0.011	0.011	0.025
V	µg/l	0.064	0.045	0.25

Recoveries of Compounds:

Perkin Elmer Nexion ICPMS

	Soft Water		Medium Water		Hard Water		Raw Surface		Borehole Water		Filtered Hard Water	
	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD	%Rec	%Rec	%Rec	%RSD	%Rec	%RSD
Li	105.4	2.51	105.5	2.05	104.5	1.88	106.5	2.51	105.5	2.21	106.8	1.57
Be	104.1	4.07	107.4	2.69	107.6	2.6	106.1	3	106.9	3.14	108.2	2.4
V	105.2	1.64	105.5	1.16	105.6	1.17	104.5	2.02	105.4	1.44	105.4	1.33
Ti	103.6	2.23	104.2	1.42	104.2	2.27	103.7	1.97	103.8	1.69	104	1.78
Cr	101.1	1.56	101	1.04	100.3	1.34	100	1.93	100.3	1.87	100.4	1.16
Co	101.3	1.29	101.5	1.32	100.7	1.5	100.9	1.22	100.5	1.35	101.3	1.4
Ni	100.6	1.51	101.7	1.64	99.25	2.03	99.85	1.8	99.34	2.3	100.3	1.47
Cu	100.3	1.31	99.68	1.16	97.43	1.47	98.79	1.34	97.82	1.39	99.01	1.1
Zn	100.1	1.42	99.41	1.36	97.01	1.69	98.85	1.73	98.24	1.41	99.19	1.64
As	105	2	105.8	1.96	105.9	2.18	105.4	2.13	104.4	2.55	105.7	1.86
Se	104	2.88	104.5	3.12	105.3	3.59	104.6	3.94	104	3.73	103.6	2.72
Sr	104	1.93	104.3	1.72	101.2	3.36	101.1	1.71	101.8	1.74	101.4	2.91

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	Soft Water		Medium Water		Hard Water		Raw Surface		Borehole Water		Filtered Hard Water	
Mo	102.7	1.03	103.1	1.21	103.1	1.28	102.6	1.31	103.2	1.37	103.1	0.97
Ag	100.8	1.69	99.52	2.06	98.87	2.37	97.88	2.76	98.19	3.18	100.6	1.46
Cd	102.3	2.54	102.3	2.85	101.4	2.61	102.1	1.61	102.1	1.57	103.2	2.01
Sb	103.7	1.92	103.7	1.68	104	1.85	103.5	1.71	103.4	1.53	103	2.02
Sn	103.4	1.62	103.7	1.34	103.8	1.43	103.5	1.24	103.6	1.56	103.2	1.07
Ba	102.6	1.48	102.7	1.77	102.7	1.84	102.5	1.81	98.61	1.91	97.84	2.83
Tl	103.4	1.03	103.9	1.16	104.3	1.18	103.8	1.18	104.2	1.29	103.7	1.01
Pb	107	1.06	107.2	1.06	107.1	1.08	106.9	0.99	107.2	1.52	107.2	1.06
U	105.6	1.16	106.4	1.37	107.6	1.11	106	1.09	106.6	1.37	105.8	0.95

Agilent ICPMS

	Soft Water		Medium Water		Hard Water		Raw Surface		Borehole Water		Filtered Hard Water	
	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD	%Rec	%Rec	%Rec	%RSD	%Rec	%RSD
Li	98.31	1.04	97.68	1.27	95.57	1.35	97.08	1.62	97.21	1.76	95.64	1.46
Be	101.7	0.88	101.2	1.49	98.99	1.04	99.44	1.17	100.27	1.85	99.11	1.34
V	102.23	0.94	101.65	1.35	101.98	0.78	101.55	1.31	101.89	1.88	101.93	1.15
Ti	100.48	1.36	100.32	1.27	100.72	1.35	100.05	1.87	100.29	1.74	100.94	1.47
Cr	99.73	1.16	99.31	1.13	98.63	1.27	98.98	1.11	99.12	1.38	98.48	1.32
Co	99.11	0.90	98.72	1.20	98.26	0.96	99.46	0.92	97.02	1.43	98.36	1.13
Ni	97.11	1.19	96.24	1.43	95.28	0.95	96.62	1.27	94.30	1.39	95.06	1.42
Cu	97.84	1.26	96.61	1.51	94.74	1.22	97.13	1.18	93.42	1.93	94.44	1.27
Zn	102.3	1.16	101.57	1.69	99.79	0.96	101.66	0.88	99.14	1.94	99.67	1.21
As	101.02	1.00	100.98	1.16	102.36	0.87	100.82	1.20	100.87	1.53	102.09	1.02
Se	98.77	1.37	99.21	1.35	101.21	1.08	99.15	1.50	100.56	1.85	100.99	1.23
Sr	97.78	0.87	99.17	1.17	98.55	1.10	97.34	2.50	99.34	0.91	99.47	2.23
Mo	100.7	1.23	100.55	1.42	101.68	0.88	100.14	1.14	101.03	1.46	101.54	1.21
Ag	97.41	1.76	95.93	2.53	94.54	2.38	95.09	2.83	93.93	2.23	95.03	2.01
Cd	99.65	1.02	98.76	1.18	98.06	1.35	99.05	1.18	98.54	1.32	97.96	1.40
Sb	102.51	0.93	101.84	1.69	109.20	3.37	112.5	5.45	113.71	4.55	107.16	1.75
Sn	100.89	0.83	100.31	1.06	100.99	0.85	95.17	2.43	99.7	1.06	101.17	1.23
Ba	103.54	2.06	103.69	1.54	105.01	1.49	105.11	0.89	101.39	0.98	104.75	1.55
Tl	102.27	0.83	101.9	1.19	102.77	1.14	102.31	1.04	102.54	1.43	102.83	1.02
Pb	102.18	0.91	101.55	1.08	102.13	1.08	102.16	0.71	100.06	2.22	102.05	1.27
U	99.89	1.07	99.57	1.25	99.7	1.12	99.11	1.17	99.27	1.38	99.94	1.54

References:

In house method based on SCA bluebooks.

Nexion 300 ICP-MS System Customer Hardware Documentation (Software CD) Part No. W1032732-C

DWI Guidance note Sample Preservation and Preparation for Metals Analysis of Drinking Water

In-house Method WPC44- Metals Digestion Procedure