

Water Analysis Using ICP-OES with an Ultrasonic Nebulizer

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

Water quality has always been a primary concern because it directly affects human health and reflects on our living environment. One of the major areas of concern is the safety of public drinking water. Maximum contamination levels for many elements in drinking water has been legislatively assigned by the Water authorities or relevant environmental protection agencies such as the US EPA. Since the levels of contaminants in drinking water can be low, often approaching the detection limit of the instrument, a preconcentration step by evaporation [1,2], solvent extraction [3–5], ion exchange [6] or co-precipitation [7,8] may be required prior to the analysis.

In order to preconcentrate, the evaporation method is widely used, but it is tedious and prone to contamination. Solvent extraction is labour intensive and also prone to contamination. Ion exchange is not widely used and can be slower than the solvent extraction procedure. Co-precipitation is a very lengthy and laborious process with great risk of contamination and losses. Recently, an ultrasonic nebulizer has been developed and when combined with the ICP spectrometer offers generally an order of magnitude better detection limit compared to the conventional pneumatic nebulizer.

The principle of operation of the ultrasonic nebulizer is quite simple. The sample solution is continuously fed onto a transducer surface by a peristaltic pump. The piezoelectric transducer is coupled to an oscillator operated under RF frequency. The liquid sample stream is broken up into very fine droplets with high efficiency by this ultrasonic nebulizing process. The sample aerosol is generated with a mean droplet size of less than 10 μm and a narrow droplet size distribution. The rate of aerosol production is generally 10 times higher than that of the pneumatic nebulizers. Because of the high efficiency of this process, it is necessary to remove some of the liquid from the aerosol before it is transported into the plasma. This is achieved in a desolvation chamber and the overall result is an order of magnitude improvement in detection limit.

This work describes the use of an ultrasonic nebulizer with ICP-OES to determine trace elements in water samples. The method was assessed by analysing US EPA Pollution control samples and NIST SRM 1643b water sample.



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Experimental

Equipment

A Liberty 200 ICP spectrometer was used for all measurements. The spectrometer is equipped with a 0.75 m Czerny-Turner monochromator with a 1800 groove/mm holographic grating. The grating can be used from the 1st up to the 4th order with a typical resolution of 0.018 nm at 1st order and 0.006 nm at 4th order. The wavelength range covers from 160–940 nm. The RF generator is crystal-controlled with direct serial coupling for higher efficiency, and operates at a frequency of 40.68 MHz. The instrument was controlled by an IBM PS/2 Model 30/286 personal computer. The instrument operating parameters are listed in Table 1. The concentric glass nebulizer used was a C type with a gas flow rate of 1.0 L/min.

Table 1. Instrument Operating Conditions

Power	1.5 kW
Plasma gas flow	12.0 L/min
Auxiliary gas flow	0.75 L/min
Pump rate	15 rpm
Sample uptake rate	1.8 mL/min
Viewing height	Optimized
Integration time	5 seconds
Replicates	3
Grating order	Default
Filter position	Default
PMT voltage	800 V
Background correction	Dynamic
Snout	High

The ultrasonic nebulizer used was a model U-5000AT (Cetac Technologies Inc., Omaha, Nebraska USA). A schematic diagram of the device is shown in Figure 1. The operating conditions are listed in Table 2.

Table 2. Operating Conditions for the U-5000AT Ultrasonic Nebulizer

Transducer frequency	1.4 MHz
Transducer type	Piezo ceramic
Current	5 A
Heating temperature	140 °C
Cooling temperature	5 °C
Nebulizer gas flow	0.7 L/minute

Reagents and Standards

All laboratory ware was washed with deionized distilled water from a Milli-Q system (Millipore, Bedford, MA, USA). Chemicals were of analytical reagent grade.

All multi-element stock solutions were made up using single element standard solutions (Spectrosol, BDH Chemicals). The multi-element working standards were prepared by dilution of the multi-element stock solutions. All calibration standards and blank solution were acid matched with the sample solution. The acid contents are 0.1 M HCl and 0.7 M HNO₃.

The Australian water samples were collected from domestic household supplies and were acidified soon after collection.

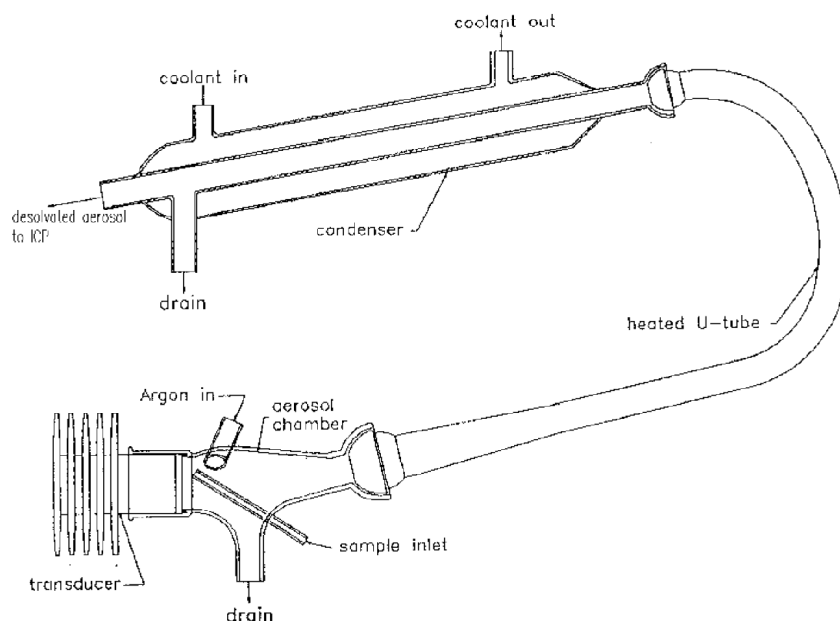


Figure 1. Schematic diagram of the ultrasonic nebulizer.

Results

Detection Limit

The detection limits of the system were measured as twice the standard deviation of a blank solution and are listed in Table 3. The detection limits of the ultrasonic nebulizer were compared with those measured for the concentric glass nebulizer, and an improvement factor ranging from 5 to 50 times was achieved.

Drinking water regulations, expressed as maximum contaminant level (MCL) by US EPA [11,12] and EEC [13], are also shown in Table 3. The detection limit of the ultrasonic nebulizer is well below the MCLs. Therefore, determination of trace elements in drinking water is superior with the ultrasonic nebulizer.

The contract required detection limit (CRDL) [9], specified by the US EPA as the minimum level of detection acceptable under the contract Statement of Work (SOW) is also given in Table 3.

A signal comparison for the ultrasonic nebulizer and the concentric nebulizer with 1 mg/L solution of Cd, Pb and Ni is shown in Figure 2. In general, the emission intensity obtained from the ultrasonic nebulizer is at least 10 times more intense than that from the concentric nebulizer.

Scan traces of 10 µg/L solutions of Fe and Mn are also shown in Figure 3.

Table 3. USN Detection Limit, Drinking Water Regulations and CRDLs

	Wavelength (nm)	USN (µg/L)	Concentric (µg/L)	MCL (µg/L)		CRDL [9] (µg/L)
				US EPA [11,12]	EEC [13]	
Ag	328.068	0.2	3	50	10	10
Al	167.079	0.15	1.5	–	200	200
Al	396.152	0.4	4	–	200	200
As	188.979	2.5	12	50	50	10
Ba	455.403	0.0012	0.07	1000	1000	200
Be	234.861	0.006	0.2	1	–	5
Cd	228.802	0.06	1.5	10	5	5
Co	228.616	0.15	5	–	–	50
Cr	267.716	0.08	4	50	50	10
Cu	324.754	0.16	5	1000	–	25
Fe	259.940	0.08	1.5	300	200	100
Mn	257.610	0.02	0.3	100	50	15
Ni	231.604	0.3	6	50	50	40
Pb	220.353	1	14	50	50	5
Sb	217.581	0.9	18	–	10	60
Se	196.026	3.6	37	10	10	5
Sr	407.771	0.002	0.02	–	–	–
Tl	190.801	1.4	14	–	–	10
V	292.402	0.2	4	–	–	50
Zn	213.856	0.04	0.9	5000	5000	20

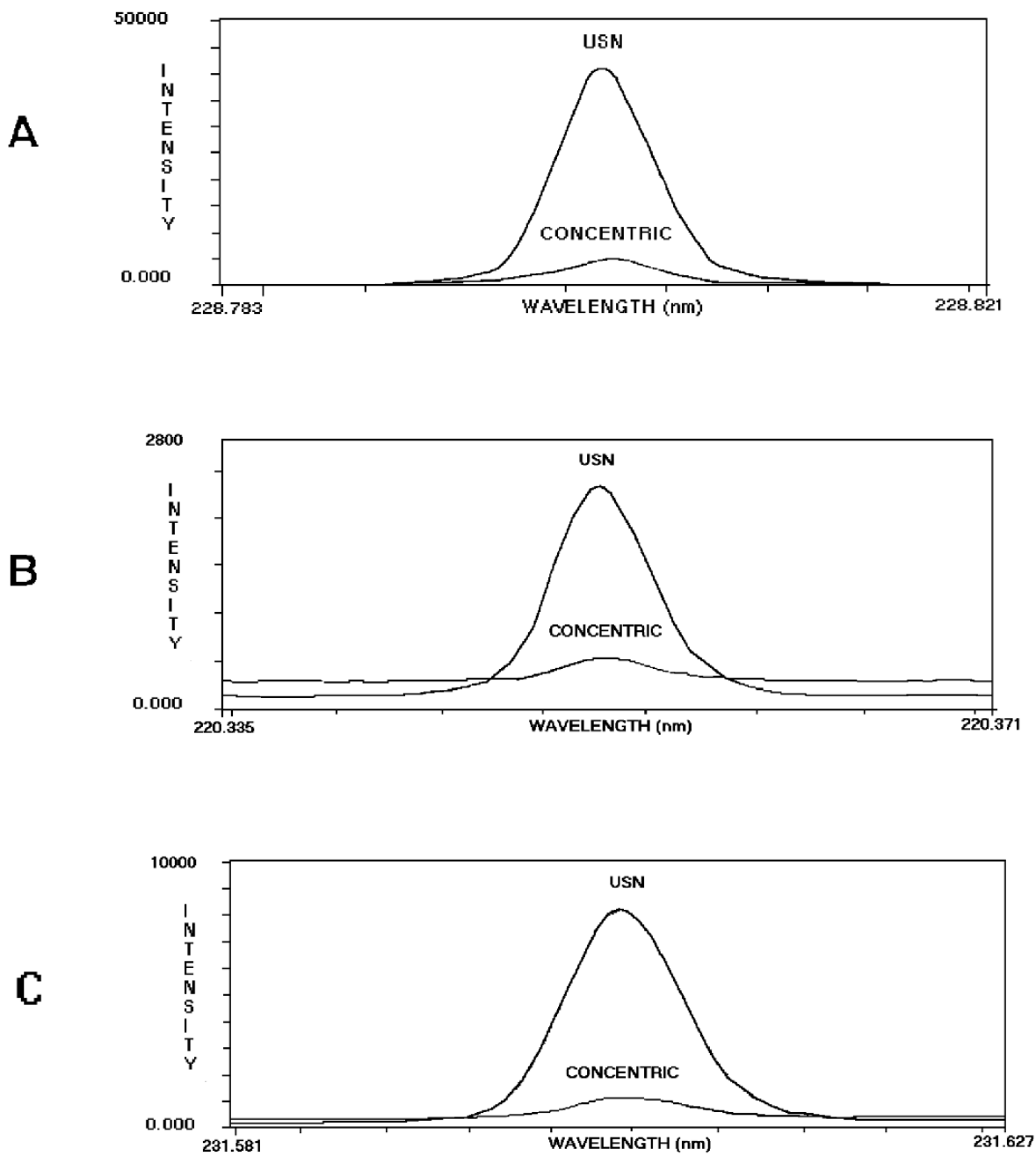


Figure 2. Signal comparison between the ultrasonic nebulizer and the concentric nebulizer on a 1 mg/L solution of (a) Cd 228.802 nm, (b) Pb 220.353 nm and (c) Ni 231.604 nm.

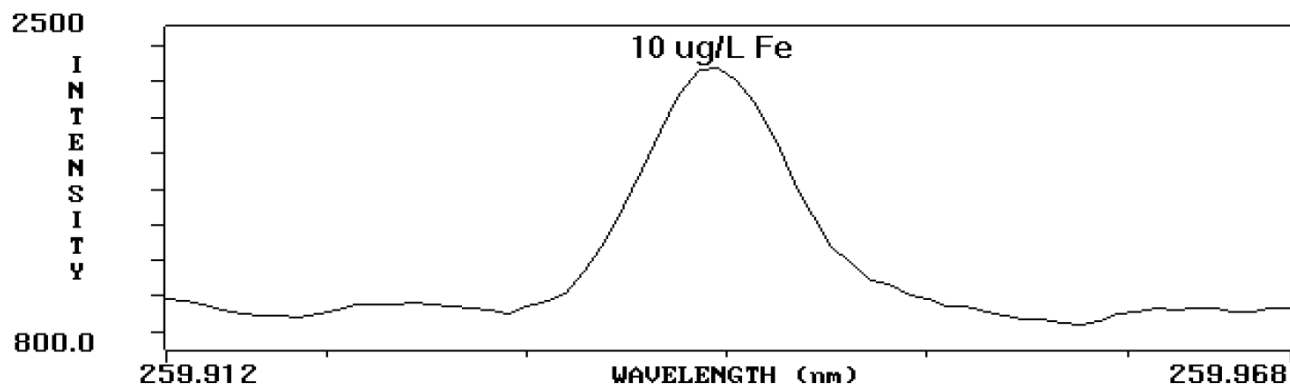


Figure 3(a). Wavelength scans of 10 µg/L solution of Fe 259.940 nm using the ultrasonic nebulizer.

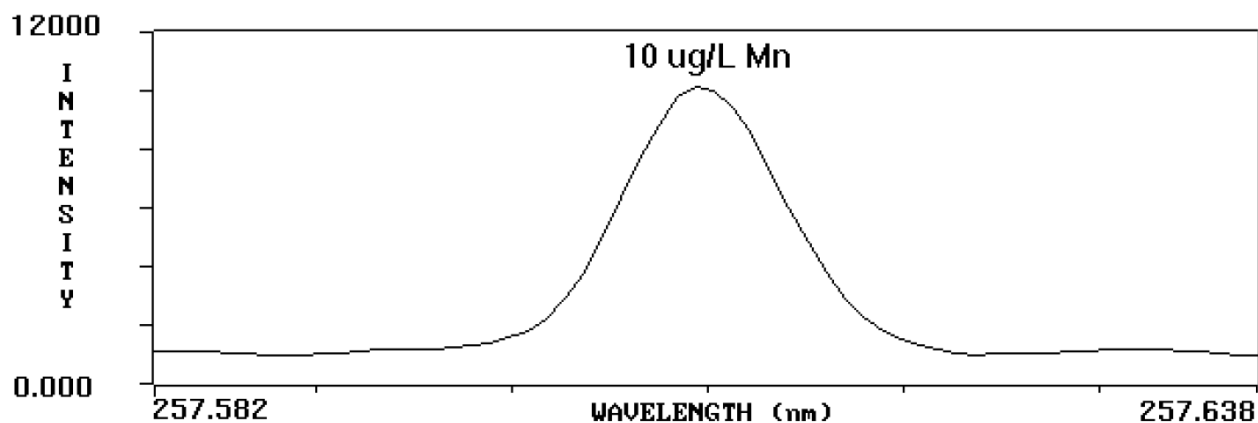


Figure 3(b). Wavelength scans of 10 µg/L solution of Mn 257.610 nm using the ultrasonic nebulizer.

Memory Effect

Memory effect is expressed as the wash out time measured by aspirating 1000 mg/L Cu solution for about 3 minutes. This is followed by a rinse using a blank solution while continuously monitoring the decay of Cu signal intensity at 324.754 nm. Three wash out profiles were measured under the following conditions :

- Normal pump speed with a solution uptake rate of 1.8 mL/min., selected under software control
- Fast pump speed with a solution uptake rate of 5 mL/min., selected under software control
- The auxiliary rinse, manually operated with a plastic rinse bottle, delivering liquid directly onto the transducer surface.

The wash out profiles can be seen in Figure 4, and the wash out times are listed in Table 4. The wash out time to achieve 0.1% signal decay under fast pump and auxiliary rinse are closely similar. This time (of about 33–39 secs) is comparable to the washout time (30 secs) for the conventional pneumatic nebulizer sample introduction system.

Table 4. Wash Out Time for the Ultrasonic Nebulizer with Liberty ICP-OES

	Wash out time (seconds)		
	Normal pump	Fast pump	Auxiliary rinse
1% decay	33	21	16
0.1% decay	59	39	33

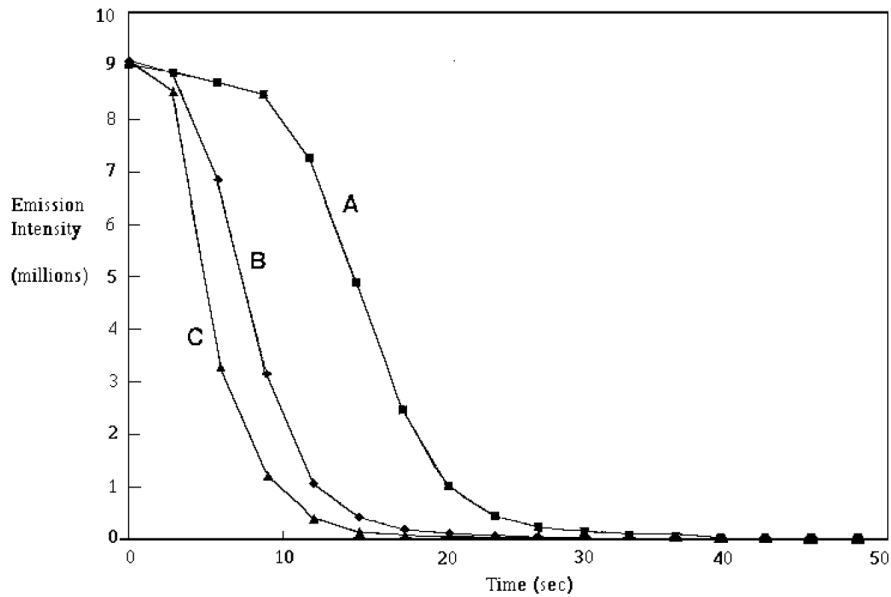


Figure 4. Washout profile of a 1000 mg/L Cu solution by the ultrasonic nebulizer with (a) normal pump, (b) fast pump and (c) auxiliary rinse.

Short Term Precision and Long Term Stability

Short term precision of the ultrasonic nebulizer is typically 0.5–2 %RSD.

Long term stability was measured by performing a calibration on a multielement standard and a reagent blank, then continuously measuring the standard solution as a sample every 5 minutes without recalibration or reslope. Figure 5 shows that the long term reproducibility over 18 hours ranged from 1.1 to 1.9 %RSD.

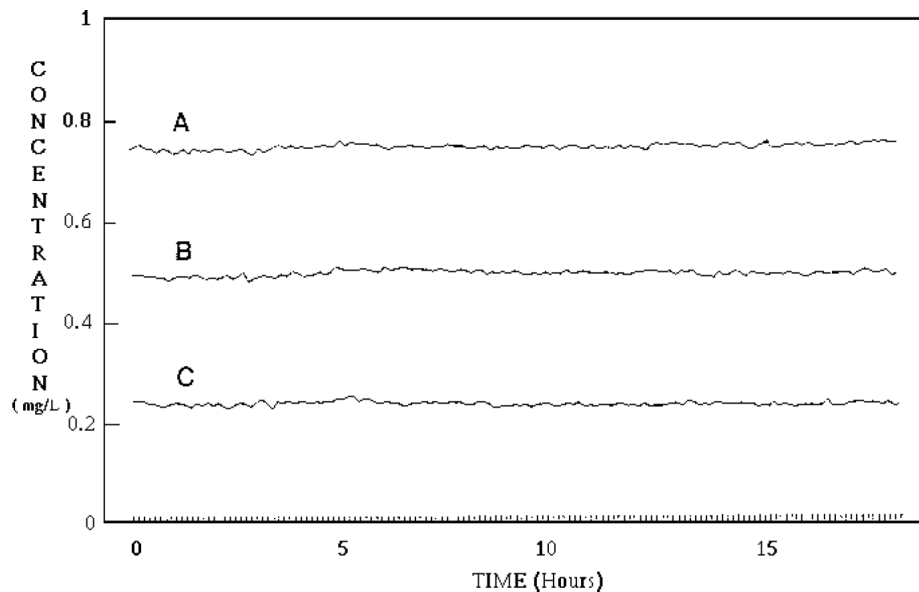


Figure 5. Long term stability over 18 hours for (a) Cu 324.754 nm, (b) Al 396.152 nm and (c) Ba 455.403 nm with an ultrasonic nebulizer.

Water Analysis

US EPA Water Samples

The results of the analysis of US EPA Water Pollution Quality Control samples 4, 5 and 6 are listed in Table 5. The values obtained are in good agreement with the certified values, except for the Fe value of sample 4. The sample was rerun several times and a similar result was found. It was subsequently confirmed by an independent analysis (graphite furnace AAS) that the sample was contaminated.

Table 5. Results of US EPA Pollution Quality Control Water Sample Analysis

	EPA No.4		EPA No.5		EPA No.6	
	Found (µg/L)	True	Found (µg/L)	True	Found (µg/L)	True
Al	65	60	500	450	803	800
As	33	22	60	60	326	300
Be	25	20	274	250	824	900
Cd	3	2.5	12.5	13	65	70
Co	22	20	77	80	570	600
Cr	12	10	81	80	249	250
Cu	13	11	48	50	341	350
Fe	31	20	81	80	891	900
Mn	18	15	74	75	489	500
Ni	28	30	75	80	283	300
Pb	30	24	123	120	401	400
V	78	70	242	250	876	850
Zn	20	16	85	80	407	400

NIST SRM 1643b Water Sample

The results of the analysis of NIST SRM 1643b water samples are listed in Table 6. The measured values compared well with the certified values.

Table 6. Results of NIST SRM 1643b Water Analysis

	Found (µg/L)	Certified (µg/L)
As	42 ± 0.2	(49)
Ba	40 ± 0.4	44 ± 2
Be	22 ± 0.5	19 ± 2
Bi	11 ± 0.2	(11)
Cd	20 ± 0.2	20 ± 1
Co	24 ± 0.4	26 ± 1
Cr	17 ± 0.1	18.6 ± 0.4
Cu	21 ± 0.4	21.9 ± 0.4
Fe	96 ± 0.4	99 ± 8
Mn	31 ± 0.6	28 ± 2
Mo	89 ± 0.2	85 ± 3
Ni	47 ± 0.1	49 ± 3
Pb	23.5 ± 0.4	23.7 ± 0.7
Sr	229 ± 3	227 ± 6
V	43.1 ± 0.4	45.2 ± 0.4
Zn	68 ± 0.4	66 ± 2

* Values in parenthesis are uncertified.

Domestic Drinking Water Samples

Drinking water samples from several Australian capital cities were analyzed for trace and major elements.

In a study of matrix effects, a Melbourne drinking water sample was spiked with 400 mg/L Ca and 100 mg/L Mg, in order to simulate a typical hard water sample. Results in Table 7 show that the addition of a high level of Ca and Mg has a negligible matrix effect. The percentage recovery of Ca and Mg was 98.2 and 97.9%, respectively.

Table 7. Results of Melbourne Water Sample With and Without Spikes of 400 mg/L Ca and 100 mg/L Mg

	Direct analysis (µg/L)	With Ca and Mg spike (µg/L)
Al	110	103
As	< 12.5	< 12.5
Ba	13.2	12.7
Be	< 0.03	< 0.03
Cd	< 0.3	< 0.3
Cr	< 0.4	< 0.4
Cu	261	250
Fe	128	112
Mn	5.5	5.4
Ni	< 1.5	< 1.5
Pb	< 5	< 5
Sr	16.2	16.1
Zn	9.1	10.7
	mg/L	mg/L
Ca	2.9	396
K	0.49	0.42
Mg	1.2	99.1
Na	4	3.9

Results for domestic Australian water sample analyses and the guideline levels [10] for major and trace elements are listed in Table 8. The measured values are within the guideline levels. It should be noted that the measured values do not necessarily represent typical levels found in the municipal water.

Summary

The ultrasonic nebulizer used with the Liberty ICP spectrometer has provided 5 to 50 times better detection limits than the pneumatic nebulizer. The short and long term stability are excellent. The measured values of the reference water samples are in good agreement with the certified values.

Both the Liberty ICP-OES 100 and 200 combined with an ultrasonic nebulizer can be used for the direct analysis of water samples, and meets the requirements of both US EPA and EEC water quality regulations.

Table 8. Results of Domestic Drinking Water Analysis

Water samples	Adelaide (µg/L)	Brisbane (µg/L)	Melbourne (µg/L)	Perth (µg/L)	Sydney (µg/L)	Guideline values [10] (µg/L)
Al	95	36.9	110	42.4	200	200
As	< 12.5	< 12.5	< 12.5	< 12.5	< 12.5	50
Ba	20	20.4	13.2	23.4	13.3	–
Be	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	–
Cd	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	5
Cr	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	50
Cu	310	25.6	261	74.4	18	1000
Fe	8	48.4	128	61.2	60	300
Mn	3.8	6.8	5.5	0.55	10.4	100
Ni	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	50
Pb	< 5	< 5	< 5	< 5	< 5	50
Sr	211	122	16.2	40.6	47	–
Zn	43.6	17.5	9.1	12.8	10.8	5000
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Ca	35	23	2.9	6.1	8.1	–
K	5.8	2.8	0.49	1.7	1.4	–
Mg	24	12	1.2	4.8	4.7	–
Na	98	27	4	41	10.8	300
SO ₄	58	28	1.3	7.4	20.5	400

< Values are expressed as 10 times the standard deviation of background emission.

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