

Analysis of Urine and Seawater Samples by Ultrasonic Nebulization With a High Resolution ICP Spectrometer

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

Because of the low detection limit capability of the ultrasonic nebulizer when combined with an ICP spectrometer, it has been widely used to determine trace and ultratrace levels in water samples [1]. The purpose of this work was to evaluate the ability of the ultrasonic nebulizer to handle samples with significant amounts of dissolved solids, such as urine and seawater.



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Experimental

Instrumentation

All measurements were carried out on Varian Liberty 200 ICP spectrometer. The ultrasonic nebulizer was a Cetac U-5000 AT.

The operating conditions of the instrument system are listed in Table 1.

Table 1. Instrument Operating Parameters

Power	1.20 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	2.25 L/min
Torch type	Demountable torch with 1.8 mm id injector tube
Pump rate	15 rpm
Sample uptake rate	1.8 mL/min
Integration time	5 sec
Replicates	3
Viewing height	Optimized
Background correction	Dynamic
PMT voltage	800 V
Grating order	Default
Filter position	Default
Snout purge	High
USN Ar flow	0.7 L/min
USN heating temperature	140 °C
USN cooling temperature	10 °C

For optimum operation, the use of a higher auxiliary Ar flow of 2.25 L/min lifts the plasma away from the injector tube to minimize the possibility of salt build up at the tip of the injector tube. The use of a 1.8 mm id injector tube can also minimize salt build up at the injector tube, especially while running seawater samples.

Lowering the torch by 1 mm (compared with the normal position) can also minimize salting up at the injector tip. The distance from the injector tip to the top of the intermediate tube is normally set to 3 mm with a demountable torch.

Reagents

All chemicals used were analytical grade. The multi-element stock solution was made up from single element standard stock solutions (Spectrosol, BDH Chemicals). The multi-element working standard was prepared by dilution of the multi-element stock solution and contained 0.14 M HNO₃.

Matrix matched standards and blank were employed in this work. As an alternative, the method of internal standardiza-

tion could also be used, to compensate for differences in transport efficiencies between different sample types.

For Seronorm urine analysis, the standard and blank were prepared in synthetic urine solution. Synthetic urine solution [2] contains 14.1 g NaCl, 2.8 g KCl, 17.3 g urea, 1.9 mL of 25% v/v ammonia solution, 0.6 g CaCl₂ and 0.43 g MgSO₄, made up to 1 L with 0.02 M HCl solution.

For seawater analysis, the standard and blank were prepared in artificial seawater solution. Artificial seawater solution [3] contains 25.4 g NaCl, 5.083 g MgCl₂, 1.104 g CaCl₂, 0.722 g KCl, 0.026 g H₃BO₃ and 0.203 g SrCl₂, made up to 1 L with distilled de-ionized water.

Results

Long Term Stability

Long term stability was evaluated by performing a calibration on a multi-element standard and a blank, both being made up in 1% w/v NaCl solution. The standard was then measured as a sample continuously for a period of an hour. After an hour, the reproducibility ranged between 0.8 to 2 %RSD for the measurements plotted in Figure 1.

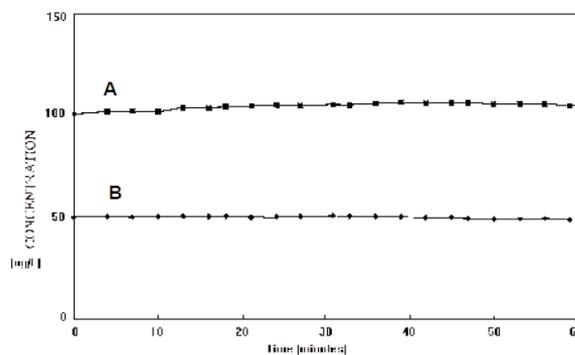


Figure 1. Signal stability over an hour for (A) Mn 57.610 nm, (B) Cd 228.802 nm in 1% w/v NaCl solution.

An additional stability test was performed on a seawater solution, as shown in Figure 2. The reproducibility over an hour ranged from 2 to 5 %RSD. It was noted that after continuously aspirating the seawater solution for over an hour, the injector tube gradually showed signs of blockage due to salt deposition. Further experimentation confirmed that rinsing between samples is desirable to minimize any potential clogging of the tube and improve the long term stability of the analysis.

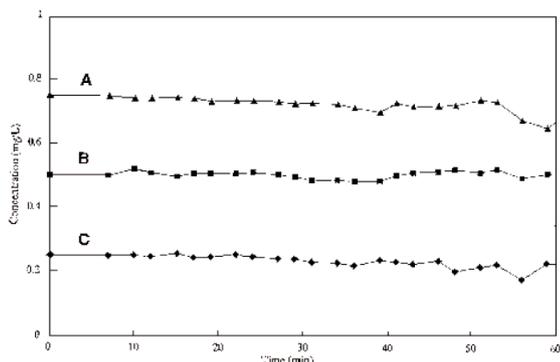


Figure 2. Signal stability over an hour for (A) Cu 324.754 nm, (B) Pb 220.353 nm (C) Cd 228.802 nm in seawater solution.

Urine Analysis

Urine samples can be analyzed directly by ultrasonic nebulization. Analysis was performed on a Seronorm urine sample. The standard and blank were prepared in a synthetic urine solution. The results of the analysis and the calculated detection limits (2 sigma) are listed in Table 2. The measured values are in good agreement with the certified values. The precision of the measurements ranged from 0.5 to 3 %RSD.

Wavelength scans of standard, blank and urine sample on Cd and Cr are illustrated in Figure 3.

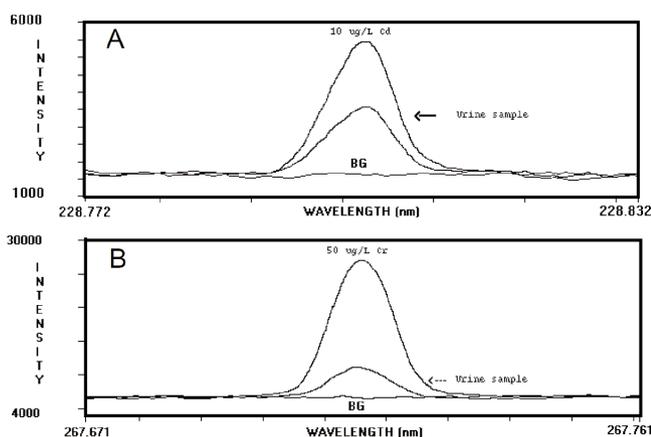


Figure 3. Wavelength scans of (A) 10 µg/L Cd standard, blank and urine sample, (B) 50 µg/L Cr standard, blank and urine sample.

Table 2. Results of Seronorm Urine Sample Analysis

	Wavelength (nm)	DL in urine (µg/L)	Measured value (µg/L)	Certified value (µg/L)
Al	167.079	1.2	160	161
As	188.979	7	201	200
Cd	228.802	0.3	5.5	6.2
Co	238.812	0.8	12	11
Cr	267.716	0.3	25	22
Cu	324.754	0.2	44	45
Fe	259.940	0.4	70	72
Mn	257.610	0.06	20	20
Ni	231.604	1.2	38	40
Pb	220.353	5	90	88

Seawater Analysis

This study has shown that seawater samples can be analyzed directly following ultrasonic nebulization. To demonstrate the accuracy of the method, a known amount of analytes were added to the sample and the recovery calculated.

The dissolved solids content of seawater can be up to 3.5% w/v. Because of the relatively high salt content in seawater, it is recommended that longer washout times are required between samples to clean out any possible salt deposition in the injector tube and improve long term stability. The use of an auxiliary rinse, which delivers rinsing agent directly onto the transducer surface, can speed up the washout process and reduce the analysis time.

The results of the seawater analysis, the percentage spike recovery and the calculated detection limit (2 sigma) are given in Table 3. The percentage recoveries ranged from 90–103%. The precision of the measurements ranged from 0.5 to 3 %RSD.

Wavelength scans of 50 µg/L of Pb and Ni in seawater sample are shown in Figure 4.

Table 3. Results of Seawater Analysis

	Wavelength (nm)	DL in seawater (µg/L)	Measured value (µg/L)	Spiked value (µg/L)	Found value (µg/L)	% Recovery
Al	167.079	1.2	15.2	200	196	98
Cd	228.802	0.5	< 2.5	50	45	90
Cr	267.716	0.7	< 3.5	50	50	100
Cu	324.754	0.2	< 1	50	49	99
Fe	259.940	1	< 5	100	103	103
Mn	257.610	0.07	0.8	200	194	97
Ni	231.604	2	< 10	200	194	97
Pb	220.353	5	< 25	50	49	99

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

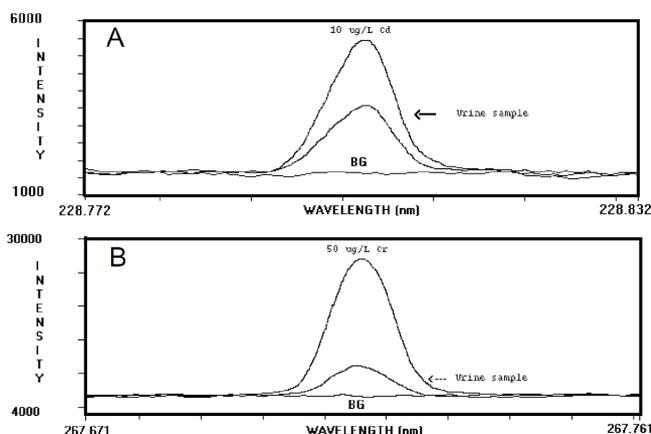


Figure 4. Wavelength scans of (A) 50 µg/L Ni, (B) 50 µg/L Pb in seawater solution.

Summary

The Liberty ICP and ultrasonic nebulizer combination can be used for the direct determination of trace elements in samples such as urine and seawater. The measured values are in good agreement with the certified values and the percentage recoveries ranged from 90 to 103%.

References

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2. T. Tanaka, Y. Hayashi, "Determination of silicon, calcium, magnesium and phosphorus in urine using inductively coupled plasma emission spectrometry and a matrix matching technique", Clin. Chim. Acta, 1986, 156, 109-114.
3. C. R. Parker, "Water analysis by Atomic Absorption", Varian Techtron, Springvale, Victoria, 1972.

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