Evaluation of the Grid-type Nebuliser for the Introduction of High Dissolved Salt and High Solids Content Solutions into the Inductively Coupled Plasma

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The Hildebrand grid nebuliser (Leeman Labs) was evaluated for inductively coupled plasma (ICP) use with high solids content solutions. The nebuliser provided good long- and short-term stability for introducing synthetic ocean water (2.7% *m/V* dissolved solids) and a 5% dissolved solids solution into the ICP. The nebuliser exhibited no clogging problems or memory effects and a linear dynamic range of at least 3–4 orders of magnitude was obtained.

Keywords: *Grid-type nebuliser; inductively coupled plasma; sample introduction; high salt and solids content solutions; synthetic ocean water*

One of the active areas of analytical research is the quantitative determination of metal species in a variety of sample matrices. The increased commercial availability of reasonably priced inductively coupled plasma (ICP) spectrometers, in the past several years, has heightened interest in exploring their usefulness for difficult and complex sample analyses. The ICP has good sensitivity for the detection of metals and a large number of elements can be excited simultaneously under one set of conditions.[1–3] The selectivity of spectrometric techniques for metal species, and the potential for obtaining speciation information (the individual metal species present in the sample), make the ICP particularly attractive. Matrix effects and interferences, which can pose serious problems with d.c. plasma emission, are reduced or eliminated. In addition, the ICP gives linear dynamic ranges of up to five orders of magnitude.

There are several methods of sample introduction into an ICP, the most common being pneumatic nebulisation of liquid samples. These pneumatic nebulisers can be a limiting factor in utilising ICP emission spectrometry, especially when the solution being nebulised contains a large amount of suspended particulate matter and dissolved solids. Both the cross-flow and concentric nebulisers exhibit short-term noise and long-term drift and are inefficient in sample transport.[4] The concentric nebuliser is particularly prone to clogging when aspirating a solution with a high dissolved solids content.[5]

The glass-frit nebuliser operates by passing gas through a sintered frit. The sample liquid passes over the frit and the carrier gas shears the liquid into a fine aerosol. The glass-frit nebuliser is highly efficient and has been used for organic solvent sample introduction.[6] However, it exhibits memory effects and can also become clogged when aspirating solutions with a high dissolved solids content.

There have been many nebulisers designed specifically for introducing high dissolved solids content solutions into the ICP. Suddendorf and Boyer[7] reported using a V nebuliser for high dissolved solids content solutions, yielding detection limits comparable to a conventional pneumatic nebuliser. Garbarino and Taylor[8] reported on the use of a Babington nebuliser that was insensitive to suspended particulate matter and yielded detection limits equivalent to, or better than, pneumatic nebulisers. Thelin[9] reported on another variation of a V nebuliser that was used for high salt (10%) content steel samples. Variations of the Babington nebuliser that could utilise solutions containing as high as 20% *m/V* of dissolved solids or slurries have been reported by Ebdon and Cave[10] and Wichman *et al.*[11] Baginski and Meinhard[12] have reported the use of a Meinhard Type C nebuliser with a recessed capillary-tip nozzle that is used for high dissolved solids content solutions. Walton and Goulter[13] described a new slotted maximum dissolved solids content nebuliser (MDSCN) and compared it with the Meinhard nebuliser in terms of sensitivity, precision, clean out and drift.

Leeman Labs (Lowell, MA, USA) developed the Hildebrand grid nebuliser for use with high dissolved solids content solutions. The grid nebuliser design features a fine-mesh grid of inert material positioned in front of a high-velocity argon stream. The sample is introduced into the grid through a large cross-section tube, and the liquid flows over the grid past the stream of high-velocity gas. Nebulisation of the sample takes place as a result of shearing from the wetted surface. As the sample is introduced through a large cross-section tube, dissolved or suspended solids are less prone to clog the inside.

The objective of this study was to evaluate further the suitability of the grid nebuliser for use with high salt and high dissolved solids content matrices. The performance criteria that were used in the evaluation were stability, detection limit (multi-element mode), clogging, memory effects, use with difficult to nebulise samples and linear dynamic ranges. The grid nebuliser was compared with a fixed cross-flow nebuliser in terms of stability and detection limits.

Experimental

The experiments were carried out using a Leeman Labs Plasma Spec ICP 2.5. The Plasma Spec incorporates an échelle grating spectrometer and uses a Huth - Kuhn free running tuned cavity oscillator as the r.f. power supply.

Some minor modifications were made to the Leeman Labs instrument for this work. Solution uptake was with a Gilson Minipuls-2 peristaltic pump (Rainin Instruments, Woburn, MA, USA) using PVC manifold pump tubing for solution uptake. The tubing was calibrated prior to use.

The grid nebuliser used was developed and supplied by Leeman Labs. Fig. 1 depicts this nebuliser and the fixed cross-flow nebuliser used. The second (downstream) grid is

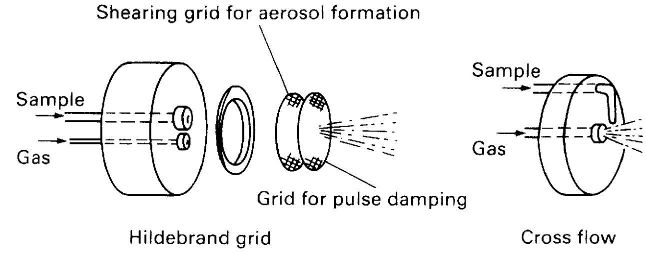

Fig. 1. Hildebrand grid and cross-flow nebulisers

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for pulse damping purposes. A Pyrex conical spray chamber was used. Reagents for synthetic ocean water and the 5% *m/V* dissolved solids solutions were obtained from Fisher Scientific. Metal solutions were prepared and stored in glassware that had been rinsed in nitric acid prior to use. Standard solutions were prepared by serial dilutions of certified atomic absorption standards (Fisher Scientific).

Optimising ICP Viewing Conditions

In performing sequential multi-element detection, compromise viewing conditions must be used, as the optimum viewing height is not the same for all elements. The Leeman Labs spectrometer automatically maximises the signal intensity of a selected element in both the horizontal and vertical directions by initialising the auto-peaking function of the instrument. In this study, Cu was the element that was so optimised, when using the sequential multi-element mode.

Results and Discussion

Short-term Stability

Short-term stability was determined by nebulising solutions of 2% *V/V* nitric acid, synthetic ocean water and a solution containing 5% *m/V* solids content solution for 30 min. The composition of synthetic ocean water and the 5% *m/V* dissolved solids solutions is described in Table 1.

During the 30 min nebulisation time, 25 data points were taken and the percentage relative standard deviation (% RSD) calculated. Stabilities of the grid and fixed cross-flow nebulisers were determined for both 2% nitric acid and synthetic ocean water solutions and are listed in Tables 2 and 3. The emission lines of Pb, Ni, Cd, Mn, Zn, Cu and Fe were used. In addition, the short-term stability (% RSD) of the grid nebuliser using a 5% *m/V* solids content solution was determined to be 2.6 and 1.86% for a blank and a 10 p.p.m. solution, respectively.

The data in Table 2 indicate that the short-term stabilities of the cross-flow nebuliser used in the study and the grid nebuliser are comparable for the 2% nitric acid solution. For the fixed cross-flow nebuliser the average RSDs (of various metal species) are 0.78, 1.87 and 2.21% for a blank, 1 p.p.m. and 10 p.p.m. solutions, respectively. For the grid nebuliser, the average RSDs for the blank, 1 p.p.m. and 10 p.p.m. solutions are 0.58, 1.38 and 1.72%, respectively, an improvement over the cross-flow nebuliser.

The data in Table 3 indicate that the short-term stability of the Hildebrand nebuliser for the synthetic ocean water (SOW) solution surpasses the short-term stability of the fixed cross-flow nebuliser for the same solution. The average RSDs of the grid nebuliser for a blank, 1 p.p.m. and 10 p.p.m. SOW solution (Cu, Cd, Ni, Fe, Ni, Mn and Zn) are 0.91, 1.26 and 2.37%, respectively. In comparison, the average RSDs of the cross-flow nebuliser for the blank, 1 p.p.m. and 10 p.p.m. solutions are 1.0, 2.89 and 7.3%, respectively.

Detection Limit

The 3σ detection limits were calculated from a total of 25 data points. As the data were acquired in the sequential multi-element mode, compromise viewing conditions were used. Improved detection limits could be obtained by optimising for each element.

Detection limits determined for both the grid and the fixed cross-flow nebulisers were comparable. Table 4 shows the generally comparable detection limits obtained, using the grid and the fixed cross-flow nebulisers, for the 2% *V/V* nitric acid and synthetic ocean water solutions.

Table 5 shows the detection limits obtained using the grid nebuliser for a variety of elements in a 5% dissolved solids solution. The detection limits of elements in a 5% dissolved

Table 1. Composition of synthetic ocean water and 5% *m/V* dissolved solids solution

Component	Synthetic ocean water, %	5% dissolved solids, %
NaCl (*m/V*)	2.11	3.0
$MgCl_2$ (*m/V*)	0.41	1.0
$CaCl_2$ (*m/V*)	0.12	0.5
KCl (*m/V*)	0.08	0.5
H_2SO_4 (*V/V*)	0.2	0.2
HCl (*V/V*)	0.4	0.4
Total dissolved solids (*m/V*)	2.7	5.0

Table 2. Short-term stability (30 min) for 2% nitric acid solution

		% RSD (25 replicates)					
		Blank		1 p.p.m.		10 p.p.m.	
Element line	Wavelength/nm	Grid	Cross flow	Grid	Cross flow	Grid	Cross flow
Cu I	324.75	0.33	0.62	0.64	0.97	1.12	1.62
Mn II	257.75	0.41	0.66	1.75	1.60	1.92	2.10
Zn I	213.86	0.61	1.17	2.39	2.03	2.54	2.24
Cd II	214.44	1.08	0.94	1.28	2.37	1.58	2.82
Ni II	221.65	0.63	0.89	1.11	2.16	1.47	2.34
Fe II	238.20	0.42	0.42	1.11	2.08	1.71	2.15

Table 3. Short-term stability (30 min) for synthetic ocean water

		% RSD (25 replicates)					
		Blank		1 p.p.m.		10 p.p.m.	
Element line	Wavelength/nm	Grid	Cross flow	Grid	Cross flow	Grid	Cross flow
Cu I	324.75	1.00	0.62	1.00	1.30	2.30	6.82
Mn II	256.61	0.64	0.34	1.04	2.98	1.68	4.00
Zn I	213.86	0.93	1.04	1.97	3.93	2.69	11.61
Cd II	214.44	0.87	1.09	1.22	4.92	4.21	7.72
Ni II	221.65	1.06	0.59	1.37	2.28	1.85	6.60
Fe II	238.20	0.96	2.42	0.96	1.92	1.48	7.56

Table 4. Detection limits (p.p.b.) obtained for the grid and cross-flow nebuliser

	2% nitric acid		Synthetic ocean water	
Element	Grid	Cross flow	Grid	Cross flow
Cu	13.1	22.2	49.9	27.6
Mn	0.94	1.5	2.3	1.1
Zn	3.1	6.1	7.1	7.5
Cd	3.9	3.3	3.1	3.8
Ni	7.4	11.7	21.0	11.3
Fe	3.7	5.8	13.2	32.2

Table 5. Detection limits for the 5% dissolved solids solution

Element	Detection limit, p.p.b.
Pb	24.7
Ni	46.4
Cd	10.2
Mn	7.4
Zn	33.8
Cu	72.6

Table 6. Matrix for FDA samples (1983)

Sample	Matrix
Spinach	20% H_2SO_4
	1500 p.p.m. Ca, Mg, Na
Pork chops	4% HNO_3
	600 p.p.m. Na, Ca, Mg, K
Femurs	10% $HClO_4$
	2000 p.p.m. Ca

solids solution are degraded by as much as one order of magnitude compared with a 2% nitric acid solution.

This degradation in detection limits can be attributed, in part, to the increased continuum and background noise of the 5% dissolved solids blank solution. Further, the ion emission line intensity is suppressed when the solution contains a high amount of dissolved ionic species. Fig. 2 shows the emission line suppression of five manganese emission lines when comparing a 10 p.p.m. Mn solution in 2% nitric acid with a 10 p.p.m. Mn in 5% *m/V* dissolved solids solution. Emission line suppression may be more pronounced for ionic lines than for atomic lines.[14] Lines Mn(1), Mn(2) and Mn(3) are ion lines and the emission line suppression is 75, 74 and 45%, respectively. This can be compared with the atomic emission line suppression of Mn(4) (87%) and Mn(5) (73%).

Clogging

When nebulising high dissolved solids content solutions, an important consideration is the effect of clogging. When using either a conventional Meinhard concentric nebuliser, a glass-frit or a cross-flow nebuliser, clogging can occur. The grid nebuliser never clogged with either the synthetic ocean water or the 5% *m/V* dissolved solids solutions. These solutions were continually nebulised over an 8-h period and the nebuliser remained unclogged. However, continual nebulisation for 1.5–2 h of the synthetic ocean water solution deposited salt crystals on the ICP torch injector tip which prevented a sufficient amount of aerosol from reaching the plasma. Deposition was prevented by alternating nebulisation with a 10-min nitric acid wash cycle. Others have used humidified argon to prevent salt build-up on the injector tip.[13]

Memory Effects

Fig. 3 depicts the procedure used to determine the memory effects of the grid nebuliser. A 2% nitric acid solution containing 1 p.p.m. of Cu, Mn, Zn, Ni and Fe was nebulised into the ICP for 20 min. During this time data were collected.

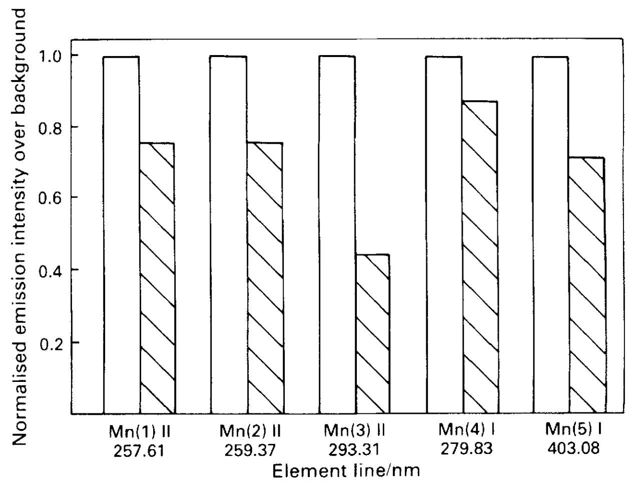

Fig. 2. Emission line suppression for 10 p.p.m. of Mn in a 5% solids solution (shaded area) compared with a 2% nitric acid solution (unshaded area)

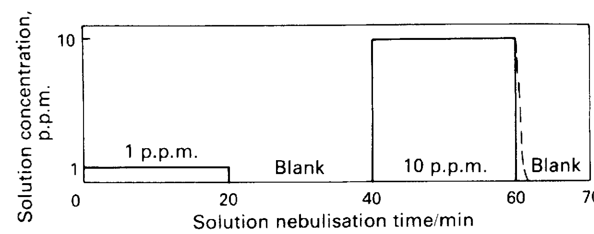

Fig. 3. Long-term stability and memory effects for 1 and 10 p.p.m. solutions of Cu, Mn, Zn, Ni, Fe and Cd in 2% nitric acid. Observed concentrations (p.p.m.) 1.5 min after switching to blank: Mn, 0.000; Cu, 0.003; Zn, 0.000; Fe, 0.001; Ni, 0.001; and Cd, 0.000

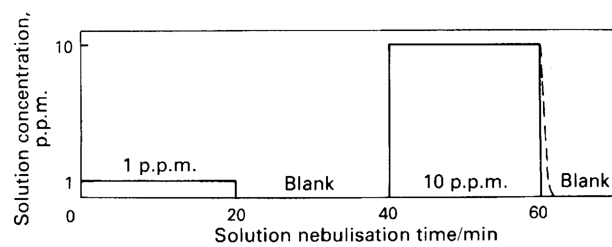

Fig. 4. Long-term stability and memory effects for a synthetic ocean water containing 1 and 10 p.p.m. of Cu, Mn, Zn, Ni, Fe and Cd. Observed concentrations (p.p.m.) 1.5 and 10 min after switching to blank, respectively: Zn, 0.018 and 0.009; Cu, 0.060 and 0.005; Mn, 0.002 and 0.000; Fe, 0.022 and 0.013; Ni, 0.027 and 0.003; and Cd, 0.016 and 0.005

Afterwards a blank 2% nitric acid solution was nebulised for 20 min, data were collected and a calibration graph was generated. Then a 2% nitric acid solution containing 10 p.p.m. of Cu, Mn, Zn, Ni and Fe was nebulised into the ICP for 20 min, after which a blank solution was nebulised for 90 s and data were collected and compared with the calibration graph. Fig. 3 shows how the 10 p.p.m. emission signal decays in 90 s to within the % RSD of the initial blank.

The same procedure was used for the synthetic ocean water solution. Fig. 4 shows that the values for Cu, Zn, Ni, Fe and Cd were no more than five standard deviations from the initial blank values after 90 s. After 10 min the values were within one to three standard deviations of the initial blank values.

The grid nebuliser exhibited virtually no memory effects from a 2% nitric acid solution but requires a slightly longer washout time (5–10 min) for solutions containing high dissolved solids. This test also demonstrated that the nebuliser provides good long-term stability. After 1 h of continual nebulisation, the blank solution is still within the % RSD of the initial blank solution.

Table 7. Comparison of results (p.p.m.)

Sample	Method of determination	Element: Al	Cd	Cu	Fe	Mg	Ni	Mn	Sr	Ti	Zn
California spinach	FDA	—	0.01	0.18	3.4	>100	0.04	1.5	—	—	0.5
	Hildebrand	2.7	0.01	0.19	3.0	—	0.08	1.4	1.3	0.2	0.5
Texas spinach	FDA	—	0.30	0.30	6.0	>100	0.3	1.5	—	—	0.65
	Hildebrand	3	0.28	0.27	4.7	—	0.3	1.4	—	0.3	0.59
Pork chops	FDA	—	—	—	0.8	2.0	—	—	—	—	2.4
	Hildebrand	—	—	—	—	—	—	—	—	—	2.3
Femur 3979	FDA	—	—	—	—	2.9	—	—	—	—	0.07
	Hildebrand	—	—	—	—	2.7	—	—	—	—	0.07
Femurs 3974	FDA	—	—	—	—	2.9	—	—	—	—	0.14
	Hildebrand	—	—	—	—	3.0	—	—	—	—	0.16

Table 8. Correlation coefficients, slopes and intercepts for log - log calibration plots

Element	Slope	Intercept	Correlation coefficient
Fe	0.95	1.442	0.9999
Zn	0.98	1.390	0.9999
Cd	1.02	1.300	0.9998
Mn	1.00	1.810	0.9999

Use with Digested Samples

The Food and Drug Administration (FDA) of Cincinnati provided samples which were difficult to nebulise into the ICP. These were digested food samples of spinach, pork chops and digested rat femurs. These samples were analysed using the grid nebuliser for comparison with FDA results. Table 6 shows the various matrices of the digested samples. Table 7 shows a comparison of our recent results with those of the FDA (ICP emission) obtained in 1983. Results for the Femur 3974, 3979 and the California spinach agree very closely. The Fe- and Zn-content results from the Texas spinach disagree slightly. Magnesium was not determined and no iron was found in the pork chop sample.

Although there are small discrepancies in the comparison (which may be because the FDA samples were 3 years old), this study demonstrated that the Hildebrand grid nebuliser may be effectively used for real samples containing high dissolved solids.

Linear Dynamic Range

The Hildebrand nebuliser exhibited at least a 3–4 order of magnitude linear dynamic range (LDR) for elements (Cd, Fe, Mn and Zn) in a solution of synthetic ocean water. Table 8 shows some of the statistics for these investigations.

Conclusion

The grid nebuliser is suitable for use with high dissolved solids content solutions. Using a 2% nitric acid solution the short-term stabilities of the grid and the fixed cross-flow nebulisers are comparable, but the grid exhibited much better % RSD for the synthetic ocean water solution which contains approximately 2.7% *m/V* dissolved solids. The grid nebuliser exhibited no clogging for SOW or a 5% dissolved solids solution. Further, there were no memory effects for the 2% nitric acid solution but a slight memory effect for the synthetic ocean water solution was observed, which could be prevented by using a 5–10 min 2% nitric acid wash cycle. Long-term stability was very good.

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