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UV/spray chamber for generation of volatile photo-induced products having enhanced sample introduction efficiency

R. E. Sturgeon,* S. N. Willie and Z. Mester

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A combined spray chamber/UV photolysis unit is described which is shown to substantially enhance sample introduction efficiency for several elements in the presence of 1–5% concentrations of formic, acetic and propionic acids. Enhancement factors of 2–40-fold were achieved for Ag, As, Se, Sb, Hg, I, Bi, Pb and Sn when the aerosol field within the cyclonic chamber produced during conventional concentric nebulizer sample introduction was illuminated by an axially placed 6 W mercury pen lamp. UV photolysis of the organic acids likely initiates radical reactions, generating volatile analyte species.

Introduction

Enhancement of sample introduction efficiency is currently pursued by many practitioners of atomic spectrometry. Fruitful avenues of activity include design of improved nebulizers and spray chambers, frequently operating at low sample uptake and ultimately relying on their integration or complete elimination of the latter so as to achieve 100% efficiency¹ or utilizing chemical vapor generation (CVG) to convert the analytes of interest to volatile species, thereby achieving similar results.² CVG is undergoing a resurgence of interest in the past decade following the report of a volatile species of copper generated during merging of an acidified solution of the analyte with that of sodium tetrahydroborate reductant.³ Subsequently, a number of transition and noble metals have been detected based on similar reactions, but typically under conditions facilitating rapid separation of the relatively unstable product species from the liquid phase.⁴ This requirement is most easily met when the sample and reductant solutions are merged at the end of a concentric or cross-flow nebulizer, the resultant aerosol providing a unique atmosphere for rapid release of the volatile product from a large surface-to-volume phase into an inert transport gas.^{5–13} The recent introduction of the MSIS system by McLaughlin and Brindle¹⁴ should prove useful for this application.

A simplified and potentially “cleaner” arrangement for vapor generation can be realized with use of ultraviolet irradiation.^{15–26} Although UV has been widely deployed to assist with oxidative sample preparation (*e.g.*, ref. 27–29), its application as a tool for vapor generation of a number of metals is only recently emerging. Radical induced reactions in irradiated solutions of low molecular weight organic acids provide small

ligands capable of reacting with a number of elements¹⁹ to yield volatile products. This has been studied in both continuous flow and batch systems. Ideally, its incorporation into an integrated nebulizer/spray chamber unit should result in optimal benefit with no perturbation to conventional pneumatic sample introduction. This communication briefly summarizes initial experiences with such a system, which suggest improvements in sample introduction efficiency by more than an order of magnitude can be readily achieved for a number of elements.

Experimental

Instrumentation

A 50 ml internal volume water-jacketed Twister cyclonic spray chamber (Glass Expansion, Hawthorn, VIC, Australia) was used for this study. The standard waste removal line was modified to accommodate the mounting of a 6 W UVC mercury pen lamp (Analamp, Claremont, CA, model 81-1057-51 λ_{\max} 253.7 nm) having a 50 mm lighted length and 5 mm o.d. This was achieved by removing the handle and mounting the lamp barrel in the ground glass fitting of the waste line using epoxy resin. In operation, the lamp thus extended along the vertical central axis of the spray chamber and did not impede the normal pneumatic operation of the device. The spray chamber was fitted with a Conikal concentric glass nebulizer (Glass Expansion, model 70115) and fed with sample *via* a peristaltic pump at a nominal flow rate of 1 ml min⁻¹.

The nebulizer/spray chamber was mounted on the end of the torch with a socket attachment and supported an ICP in an Optimass 8000 TOF-MS instrument (GBC Scientific Equipment Pty. Ltd., Dandenong, VIC, Australia). Typical operating conditions for the ICP-TOF-MS instrument are summarized elsewhere.³⁰

Materials and reagents

Formic, acetic and propionic low molecular weight organic (LMW) acids were obtained from Anachemia and BDH and used without purification. Reverse osmosis water was further purified by deionization in a mixed-bed ion-exchange system (NanoPure, model D4744, Barnstead/Thermoline, Dubuque, IA) and nitric and hydrochloric acids were purified in-house from commercial stocks by sub-boiling distillation. Five ng ml⁻¹ multielement solutions containing Ag, As, Ba, Bi, Cd, Cu, Pb, Hg, I, Sb, In, Ni, Sn and Se were prepared in high purity water containing either 0.5% (v/v) HNO₃ or nominally 1 and 5% (v/v) LMW acids.

National Research Council Canada, Institute for National Measurement Standards, Ottawa, Canada. E-mail: Ralph.sturgeon@nrc.ca

Procedure

The ICP-TOF-MS was first optimized for response by introducing an approximately 1 ml min^{-1} 10 ng ml^{-1} solution of Ho in 0.5% (v/v) HNO_3 . Steady-state response from a multielement solution containing HNO_3 and from each of the three LMW acids was measured with and without the mercury discharge lamp on. In each case, the average response from 3 replicate 5 s integration periods was used. The temporal characteristics of the signals were also monitored using 1 s continuous integration readings.

Results and discussion

Sensitivities for all elements in the presence of the LMW acids were significantly lower than achieved with a nitric acid solution (5–50-fold), in part because instrument performance was optimized using a nitric acid solution and the changes in density, viscosity, wetting characteristics and decomposition products associated with the LMW acid solutions created non-optimum aerosol characteristics. It is possible that the benefits accruing from the use of the UV field, described below, could be enhanced if sample introduction had first been optimized for each solution.

Fig. 1 and 2 illustrate the time dependence of the evolution of the enhanced signals for ^{78}Se , ^{127}I and ^{202}Hg when the mercury lamp is powered, exposing the introduced aerosol to UV photolysis. Pronounced changes in the intensities of the signals for many elements were noted; these are summarized in Table 1. The suite of elements included in this study was not meant to be comprehensive, but rather a representative selection of elements that had earlier been shown to be amenable to vapor generation.¹⁹ It should be noted that the aim of this communication is to present preliminary proof-of-principle experiments; a full evaluation of pertinent parameters was not undertaken and will be the focus of a more intensive follow-up study.

Most notable are the enhanced signals for elements such as Se, Bi, I, Hg and Pb in all LMW acids and Sb and Sn in formic

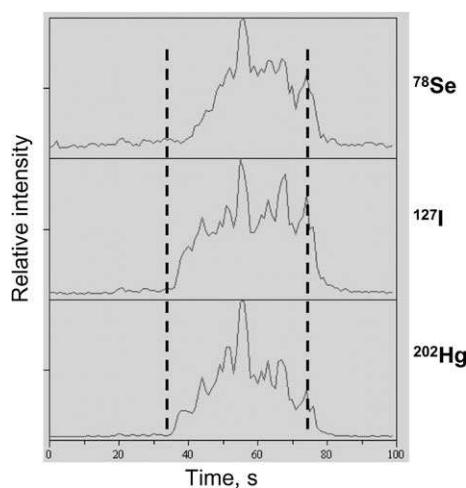


Fig. 1 Effect of UV field on response from ^{78}Se , ^{127}I and ^{202}Hg during steady-state introduction of a 5 ng ml^{-1} multielement solution containing 5% propionic acid. Vertical bars indicate onset and termination of UV discharge.

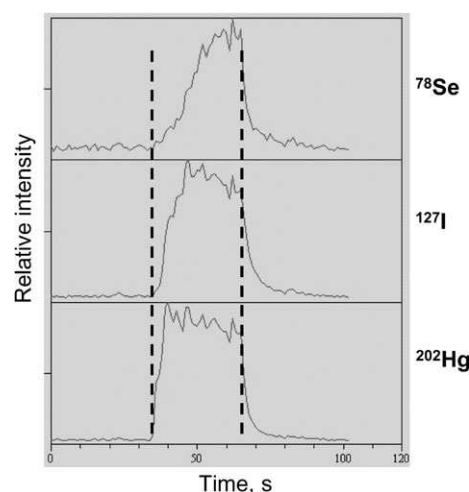


Fig. 2 Effect of UV field on response from ^{78}Se , ^{127}I and ^{202}Hg during steady-state introduction of a 5 ng ml^{-1} multielement solution containing 5% acetic acid. Vertical bars indicate onset and termination of UV discharge.

and acetic acids. Barium was monitored as it is assumed to be unaffected by any radical reactions and changes in its intensity in the presence of the UV field likely reflect physical alterations in the measurement system. Evolution of carbon oxides as well as hydrogen and perhaps hydrocarbons may occur during photolytic oxidation of the LMW acids which will change the optimum sampling depth of the plasma and give rise to fluctuations in the baseline and sensitivity of the system. Thus, to some degree, the effects noted for Ba may be used to infer other physical changes in the detection system that occur over and above those associated with real enhancements in sample introduction efficiency for some elements. The same observation is evident with the introduction of analytes in 1% nitric acid. Table 1 shows that, with the exception of Hg, UV photolysis results in a nearly uniform 25% suppression in response for all elements. It may thus be inferred that evolution

Table 1 Relative intensity enhancement factors in response to UV photoalkylation^a

Element	Low molecular weight acid concentration						
	% Formic		% Acetic		% Propionic		% Nitric
	1	5	1	5	1	5	
Cu	1.0	0.9	1.4	3.3	1.7	1.8	0.66
Ag	1.8	1.2	7.6	6.4	2.5	2.6	0.67
Cd	1.0	1.2	2.0	3.9	1.9	2.0	0.70
As	1.1	1.7	1.6	4.4	2.0	2.6	0.71
Se	2.8	16	19	29	5.6	6.3	0.78
Ba	<i>1.0</i>	<i>1.1</i>	<i>1.5</i>	<i>3.6</i>	<i>1.8</i>	<i>1.7</i>	<i>0.72</i>
Sb	1.0	9.3	2.9	4.6	2.0	2.3	0.75
Hg	18	17	5.1	16	17	17	11
I	2.2	3.1	12	38	12	16	0.84
Bi	0.9	4.2	43	18	3.3	9.7	0.77
Pb	1.0	2.0	7.0	5.9	2.5	3.1	0.78
Ni	1.1	1.7	1.6	2.9	1.6	1.7	0.67
Sn	1.0	5.6	3.2	5.2	2.1	2.1	0.69
In	1.0	0.9	1.5	3.9	1.9	1.9	0.69

^a Based on the relative intensity change in the signal in the presence/absence of the UV field.

of molecular gases, such as nitrogen oxides, and/or the presence of the heated lamp post in the spray chamber give rise to an alteration in the aerosol distribution or composition, inducing a change in plasma chemistry/optimum sampling depth.

Photo-oxidation is a radical mediated reaction and response to the presence/absence of the UV field should be immediate. Reaction of such products with a number of elements may lead to production of hydrides, methyl and ethyl analogues in formic, acetic and propionic acids, respectively.¹⁹ The relatively slow rise and fall of the signals for these elements in response to the lamp being turned on and off is likely a consequence of the wetting of the internal walls of the spray chamber and the release of the volatile analyte species from the liquid phase. This is consistent with the increasingly longer time required to achieve steady-state response for Se, for example, as the LMW acid is changed from formic to acetic to propionic the “rise time” of the signal increases from 9 to 14 to 18 s. Earlier studies^{16,18} have shown that such radical reactions lead to substitution onto the metal, resulting in hydride, dimethyl- and diethyl-Se compounds which are expected to have correspondingly decreasing vapor pressures. Thus, a delay time, characteristic of sample wash-in and wash-out for a spray chamber, is evident in these experiments in response to powering the UV lamp on and off.

Mass 220 Da was also monitored in each system to reveal any changes in the background over time. The influence of the UV field was difficult to detect as the total counts acquired were relatively small at this mass. All effects were significantly smaller than noted for Ba.

Table 1 summarizes the relative enhancement factors attained in the various LMW acids in response to the presence of the UV field. No statistical evaluation of the results is presented as these data are based on only a few numbers of experiments in each system. Data highlighted in bold face indicate those elements for which an enhanced sensitivity is accorded to the presence of the UV field, the magnitude of the effect surpassing any signal changes noted for Ba and assigned to plasma effects accompanying photolysis reactions.

Conclusion

The combination of UV irradiation with pneumatic sample introduction of solutions containing LMW organic acids appears to offer a simple and convenient approach by which the benefits of photo-generated yield of volatile analytes can be easily realized. The full extent of the scope of these reactions is currently unknown as are, with the exception of As, Se and Ni, the precise identities of the photolysis products. The influence of the intensity of the UV field requires study as only a low power lamp was used for these experiments. Redesign of the spray chamber to create a full annular discharge within the space currently used for the water jacket or use of a larger surface area Scott-type spray chamber may enhance efficiencies and minimize the “wash-in and wash-out” effects. A systematic study of all experimental parameters, expansion of the range of elements investigated and an in-depth examination of the chemistry of this system will be the focus of future work.

The concepts discussed in this study have been subject to patent protection.

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References

- 1 J. M. Mermet and J. L. Todoli, *Anal. Bioanal. Chem.*, 2004, **378**, 57–59.
- 2 R. E. Sturgeon and Z. Mester, *Appl. Spectrosc.*, 2002, **56**, 202A–213A.
- 3 R. E. Sturgeon, J. Liu, V. J. Boyko and V. T. Luong, *Anal. Chem.*, 1996, **68**, 1883–1887.
- 4 R. E. Sturgeon, X.-M. Guo and Z. Mester, *Anal. Bioanal. Chem.*, 2005, **382**, 881–883.
- 5 A. S. Luna, R. E. Sturgeon and R. C. de Campos, *Anal. Chem.*, 2000, **72**, 3523–3531.
- 6 C. Moor, J. W. H. Lam and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2000, **15**, 143–150.
- 7 H. Sun, R. Suo and Y. Lu, *Anal. Chim. Acta*, 2002, **457**, 305–310.
- 8 P. Pohl and W. Zyrnicki, *J. Anal. At. Spectrom.*, 2003, **18**, 798–801.
- 9 P. Smichowski, S. Farias and S. Perez Arisnabarreta, *Analyst*, 2003, **128**, 779–785.
- 10 Y.-L. Feng, J. W. Lam and R. E. Sturgeon, *Spectrochim. Acta, Part B*, 2004, **59**, 667–676.
- 11 S. Xu and R. E. Sturgeon, *Spectrochim. Acta, Part B*, 2005, **60**, 101–107.
- 12 S. Xu and R. E. Sturgeon, *Ann. Chim.*, 2005, **95**, 491–499.
- 13 Y.-L. Feng, R. E. Sturgeon, J. W. Lam and A. D’Ulivo, *J. Anal. Spectrom.*, 2005, **20**, 255–265.
- 14 R. L. J. McLaughlin and I. D. Brindle, *J. Anal. At. Spectrom.*, 2002, **17**, 1540–1548.
- 15 X. M. Guo, R. E. Sturgeon, Z. Mester and G. J. Gardner, *Appl. Organomet. Chem.*, 2003, **17**, 575–579.
- 16 X. M. Guo, R. E. Sturgeon, Z. Mester and G. J. Gardner, *Environ. Sci. Technol.*, 2003, **37**, 5645–5650.
- 17 X. M. Guo, R. E. Sturgeon, Z. Mester and G. J. Gardner, *Anal. Chem.*, 2003, **75**, 2092–2099.
- 18 X. M. Guo, R. E. Sturgeon, Z. Mester and G. J. Gardner, *Appl. Organomet. Chem.*, 2004, **18**, 205–211.
- 19 X. M. Guo, R. E. Sturgeon, Z. Mester and G. J. Gardner, *Anal. Chem.*, 2004, **76**, 2401–2405.
- 20 X. Guo, R. E. Sturgeon, Z. Mester and G. J. Gardner, *J. Anal. At. Spectrom.*, 2005, **20**, 702–708.
- 21 C. Zheng, Y. Li, Y. He, Q. Ma and X. Hou, *J. Anal. At. Spectrom.*, 2005, **20**, 746–750.
- 22 R. F. Bendl, J. T. Madden, A. L. Regan and N. Fitzgerald, *Talanta*, 2006, **68**, 1366–1370.
- 23 S. McSheehy, X. Guo, R. E. Sturgeon and Z. Mester, *J. Anal. At. Spectrom.*, 2005, **20**, 709–716.
- 24 R. Figueroa, M. Garcia, I. Lavilla and C. Bendicho, *Spectrochim. Acta, Part B*, 2005, **60**, 1556–1563.
- 25 S. Fragueiro, I. Lavilla and C. Bendicho, *Talanta*, 2006, **68**, 1096–1101.
- 26 T. Nakazato and H. Tao, *Anal. Chem.*, 2006, **77**, DOI: 10.1021/ac051783f.
- 27 D. L. Tsalev, M. Sperling and B. Welz, *Analyst*, 1998, **123**, 1703–1710.
- 28 X. Wei, C. A. Brockhoff-Schwegel and T. J. Creed, *J. Anal. At. Spectrom.*, 2001, **16**, 12–19.
- 29 D. Mazej, I. Falnoga, M. Veber and V. Stibilj, *Talanta*, 2006, **68**, 558–568.
- 30 S. N. Willie and R. E. Sturgeon, *Spectrochim. Acta, Part B*, 2001, **56**, 1701–1716.