Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Talanta 68 (2006) 1366–1370

Talanta

www.elsevier.com/locate/talanta

Mercury determination by cold vapor atomic absorption spectrometry utilizing UV photoreduction

Ryan F. Bendl, Jeremy T. Madden, Allison L. Regan, Neil Fitzgerald*

Department of Chemistry, Biochemistry, and Physics, Marist College, 3399 North Road, Poughkeepsie, NY 12601, USA

Received 28 June 2005; received in revised form 28 July 2005; accepted 28 July 2005

Abstract

A method for the determination of mercury via UV photoreduction has been investigated. Mercury vapor was generated by the reduction of mercury species in an acetic acid solution using UV radiation. Detection of the volatile mercury was accomplished by atomic absorption spectrometry. An optimized system was found to provide a detection limit (defined as the concentration giving a signal equal to three times the standard deviation of the blank) of 2.1 $\mu g\,L^{-1}$ with a precision of 2.9% relative standard deviation ($n = 8$) for a 500 $\mu g\,L^{-1}$ mercury standard. The effect of various metal ions on the mercury signal was investigated and the method validated with a NRCC certified dogfish liver material (DOLT-3) using the method of standard additions. A reaction pathway is hypothesized for UV photoreduction.

Keywords: UV photoreduction; Mercury; Vapor generation; Atomic absorption spectrometry

1. Introduction

The high toxicity of inorganic and organic forms of mercury are well known to cause deleterious effects on the central nervous system in humans at low concentrations [1]. The extremely high toxicity and ability to bioaccumulate in the environment are driving the need for analytical techniques that are sensitive, rapid, inexpensive, and simple with the potential for portability for field analysis. Chemical vapor generation (CVG) achieves a number of these objectives. First reported in 1968 by Hatch and Ott [2], the generation of volatile mercury atoms at room temperature has been shown to be an extremely effective introduction method for atomic absorption spectrometry (AAS). CVG–AAS is often the preferred method for mercury determination due to its low detection limits and use of simple and inexpensive apparatus and reagents [3].

Most modern CVG methods employ flow injection manifolds to mix sample with reductant (typically sodium borohydride or stannous chloride) followed by separation of gas phase mercury product from the sample solution. This flow injection approach reduces sources of contamination and improves precision and speed of analysis. One drawback of the method is the requirement for a chemical reductant. As well as adding to the cost of analysis, the reductant needs to be freshly prepared and can lead to difficulties of liquid transport to the atomization cell due to the vigorous chemical reaction. An alternative to chemical reduction is the use of photoreduction. This approach has recently been reported by Guo et al. [4], who described the generation of volatile forms of a number of elements that were detected by inductively coupled plasma mass spectrometry (ICPMS). The method produces volatile species by irradiating a sample solution contained in a low molecular weight organic acid, such as formic or acetic acid, with a UV pen light. The technique appeared effective for Hg, Co, As, Sb, Bi, Se, and Te, but less efficient for Sn, Cu, Rh, Au, Pd, Pt, and Cd. The same authors investigated the reaction for selenium [5,6] suggesting that the mechanism consists of a photolytic cleavage of the organic acid resulting in hydrogen atoms and/or carbonyl radicals. These species are strong reducing agents that can reduce selenite species to elemental selenium followed by formation of volatile selenium species (presumably H_2Se). Wang et al. [7] used a UV/TiO_2

---

* Corresponding author. Tel.: +1 845 575 3000; fax: +1 845 575 3184.
E-mail address: neil.fitzgerald@marist.edu (N. Fitzgerald).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.07.061

photocatalyst reduction device to generate volatile species for the determination of selenium(VI) by atomic fluorescence spectrometry (AFS).

Chemical vapor generation reaction mechanisms have traditionally been described in terms of the generation of a nascent hydrogen species which is considered a strong reducing agent [8]. Recently, some questions have been raised over the validity of the term ‘nascent hydrogen’. Laborda et al. [9] suggested that ‘reactions thought to be due to nascent hydrogen arise from hydrogen atoms or excited hydrogen molecules’. It would seem reasonable, therefore, that similar species are produced in the UV photoreduction process. Guo et al. [5,6] proposed the generation of hydrogen atoms as the most likely process in the production of volatile selenium species by UV photoreduction. There are, however, some inconsistencies between this proposed mechanism and experimental results. For example, published results from Guo et al. [4] demonstrate a discrepancy in generation efficiencies for different elements. Several elements (Hg, Co, As, Sb, Bi, Se, and Te) show signal-to-background ratios of greater than 1500 for a 1 or 5 ng/mL standard while other elements (Cu, Rh, Au, Pd, Pt, and Cd) have signal-to-background ratios of 20 for a 10 ng/mL standard. If the reducing agent is atomic hydrogen, it would be expected to reduce all of these elements with differences in the signal-to-background ratios due primarily to the ability of the reduced form to produce volatile species. This does not appear to be the case, for example, cadmium is known to form volatile cadmium atoms at room temperature by chemical vapor generation [10] but does appear to be generated readily by UV photoreduction.

The replacement of chemical reduction by UV photoreduction is attractive. A UV system eliminates the need for freshly prepared chemical reductant, can simplify the flow-injection manifold by removing a reductant line and should lead to a smoother, less violent reduction process. In this work we setup, optimize and evaluate a UV photoreduction AAS system in order to investigate its usefulness as a mercury detection method. To our knowledge the analytical characteristics of UV photoreduction have not been previously reported for mercury. We also suggest an alternative reaction pathway for UV photoreduction.

2. Experimental

2.1. Instrumentation

The experiments were preformed using a SOLAAR M5 (ThermoElemental, Franklin, MA) atomic absorption spectrometer fitted with a mercury hollow cathode lamp (model 2128005, Unicam, Cambridge, UK). A wavelength of 253.7 nm was used during the course of the investigation. The instrument was operated in flame mode with a T-cell quartz tube (Perkin-Elmer, Shelton, CT) placed on top of the burner. The air/acetylene flame remained off for the duration of the experiment. Volatile mercury was generated using the system shown in Fig. 1. The reduction to the elemental mercury form was accomplished with the assistance of a UV Pen Light (model 90-0012-01, UVP Inc., Upland, CA). The sample was exposed to the UV light by tightly wrapping 0.8 mm i.d. FEP tubing around the illuminated portion of the pen light in order to achieve a total irradiated volume of 2.6 mL. The acetic acid carrier stream was constantly pumped through the tubing with Delrin® fittings (Upchurch Scientific Inc., Oak Harbor, WA) by an Ismatec Model 78016-10 peristaltic pump with silicon pump tubing (yellow/blue, Cole-Palmer, Vernon Hills, IL). Sample was introduced into the carrier stream via a rotary injection valve (Rheodyne, Rohnert, CA). The UV irradiated sample–reactant mixture entered the top inlet of a low-volume MSIS™ (Marathon Scientific, Niagara Falls, Ontario, Canada) with the lower inlet clamped closed, which served as the gas–liquid separator. The low-volume MSIS™ has been described previously [11]. Argon gas was used to strip volatile species from the reaction mixture. The gas forced any volatile species into the T-cell as to be determined by AAS. Simultaneously, liquid waste was pumped from the MSIS using an identical peristaltic pump.

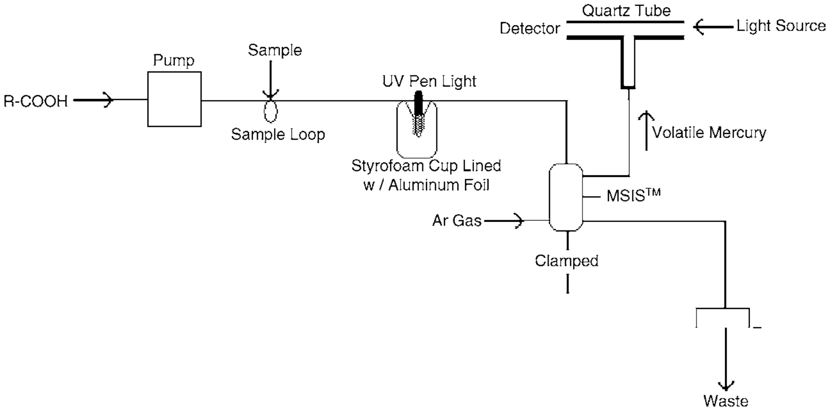

Fig. 1. Mercury UV photoreduction system schematic.

2.2. Reagents and sample preparation

All solutions were prepared in 18 MΩ distilled–deionised water (DDW) prepared using a Barnstead Nanopure II system (Bedford, MA). Mercury reference standard (1000 mg L^{-1}) was obtained from Banco Standardized (Fort Worth, TX). Samples and standards were prepared in acetic acid prepared by dilution of glacial acetic acid (99.7% Mallinckrodt, Paris, KY). Sample preparation was achieved by stirring approximately 1 g of SRM Dogfish Liver (DOLT-3, NRCC, Ontario, Canada) with 10 mL of 25% (v/v) tetramethylammonium hydroxide (Alfa Aesar, Ward Hill, MA) in a 125 mL polypropylene bottle for 3 h. Approximately 10 mL of DI water was then added and the solution stirred for approximately 25 min. The mixture was then transferred to a 50-mL volumetric flask and acidified with 10 mL of cold 6 M HCl (Fisher Scientific, Pittsburgh, PA). Acetic acid and DI water were then added in order to produce a 50 mL solution with a final acetic acid concentration of 3 M. This solution was then centrifuged and 8 mL portions decanted into separate 10-mL volumetric flasks. The appropriate amount of mercury standard was added to each flask for standard addition calibration and the solutions made up to volume with 3 M acetic acid.

2.3. Investigation of reaction mechanism

The reducing power of the system was investigated by illuminating metal ion solutions ($CuSO_4 \cdot 5H_2O$, Fisher Scientific, Fair Lawn, NJ and $Co(NO_3)_2 \cdot 6H_2O$, Mallinckrodt, Paris, KY) of varying concentrations (between 10 and 100 mg L^{-1} in 3 M acetic acid) inside a glass jar with a UV pen light shielded inside a 1-cm quartz cuvette. The metal solutions were evaluating in terms of their appearance (change in color and presence of particulates) and UV–vis spectra (obtained using Beckman/Coulter Model DU-600) after approximately 10 min of UV illumination. For evaluation by UV–vis spectra, the absorbance was obtained prior to illumination, at the maximum absorbance wavelength in the visible region, and immediately after irradiation at the same wavelength. Any change in appearance and absorbance was assumed to be due to a reduction process.

3. Results and discussion

3.1. Optimization

The chemical and physical variables of the manifold were optimized to achieve the best analytical performance by investigating each variable in turn with all other variables kept constant. These parameters included acetic acid concentration, acetic acid carrier stream flow rate, sample loop volume, and argon flow rate. All optimization studies were performed with a 500 μg L^{-1} Hg standard in the continuous signal mode using peak height measurements.

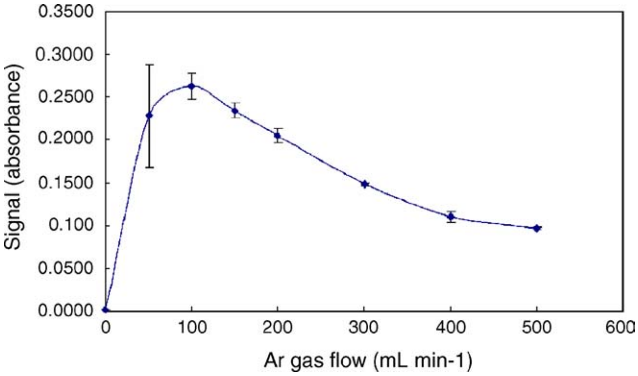

Fig. 2. Effect of argon gas flow on peak height.

The acetic acid concentration was varied between 0 and 12 M. The results failed to yield a notable trend although the absence of acetic acid was observed to completely remove the signal. A concentration of 3 M was used for subsequent experiments as the standard deviation was significantly better than any of the other tested concentrations. Investigation of acetic acid concentrations between 0 and 3 M was thought to be unlikely to produce significant improvements in peak height or precision and was not investigated. The carrier stream flow rate was varied between 0.5 and 3.0 mL min^{-1}. The signal increased as the flow rate was increased up to 1.5 mL min^{-1}. As the flow rate was increased above 1.5 mL min^{-1}, the signal rapidly decreased. A sample loop volume of 500 μL was found to be the most efficient sample loop size for this system. Unlike chemical vapor generation systems, the signal shape is independent of diffusion rates between the sample and reagent, therefore, double peaks are not observed. Using sample loops larger than 500 μL produced flat-topped peaks. The argon gas served to strip volatile mercury species from the modified $MSIS^{TM}$ and carry it to the light path. The effect of the argon flow rate on peak height was found to be critical and can be seen in Fig. 2. Argon flow rates were varied between 0 and 500 mL min^{-1}. The optimum flow rate was found to be 100 mL min^{-1}. This flow rate provided an optimal signal with relatively good precision. The conditions that were determined to provide optimum peak height with acceptable precision are summarized in Table 1.

3.2. Validation and figures of merit

Under optimized conditions, a detection limit (defined as the concentration giving a signal equal to three times the standard deviation of the blank) of 2.1 μg L^{-1} was obtained. Calibration curves were observed to be linear up to 500 μg L^{-1}.

Table 1
Optimized conditions for UV photoreduction vapor generation of mercury

Argon gas flow (mL min^{-1})	100
Carrier stream flow (mL min^{-1})	1.5
Sample loop volume (μl)	500
Acetic acid concentration (M)	3.0

Table 2
Results for SRM Dogfish Liver (DOLT-3)

Total mercury (certified value, $\mathrm{mg\,kg^{-1}}$)	3.37 ± 0.14
Methyl mercury (certified value, $\mathrm{mg\,kg^{-1}}$)	1.59 ± 0.12
Measured values ($\mathrm{mg\,kg^{-1}}$)	3.11, 2.58, 3.37

A precision of 2.9% (R.S.D., $n = 8$) was demonstrated for a $500\,\mu\mathrm{g\,L^{-1}}$ Hg standard. The method was validated using DOLT-3 Dogfish Liver SRM by standard additions calibration. The results (Table 2) suggest that the system is reducing both inorganic and organic mercury to volatile mercury.

3.3. *Interference study*

The effect of adding metal ion species to a $1\,\mathrm{mg\,L^{-1}}$ mercury solution can be seen in Table 3. Significant interferences were observed for transition metals Cr(VI), Fe(III), Cu(II), and Pb(II). Little effect was observed for Zn(II), Mn(II), and Mg(II), while an enhancement effect was observed for Ni(II) and Co(II). These results are consistent with previously reported interference effects for chemical vapor generation [12], suggesting that the mechanism of interference is independent of the generation method (chemical or photoreduction). The sensitivity increase for cobalt and nickel has been described previously as a catalytic effect [12,13] although the mechanism of the enhancement does not seem well understood.

3.4. *Reaction mechanism*

In a series of simple experiments, we have found UV photoreduction in a batch mode capable of reducing copper(II) ions but not cobalt(II). This evidence is not consistent with the production of hydrogen atoms with an estimated reduction potential of −2.106 V [9]. This observation and literature results raise some question of the validity of the previously published reaction mechanism for UV photoreduction, namely the photolytic cleavage of low molecular weight organic acids by UV radiation [5].

$$\mathrm{RCOOH} + h\upsilon \rightarrow \mathrm{R}^{\bullet} + {}^{\bullet}\mathrm{COOH}$$

Table 3
Effect of metal ions on the mercury signal for $1\,\mathrm{mg\,L^{-1}}$ mercury solution

Species	Concentration ($\mathrm{mg\,L^{-1}}$)	Effect (%)
Cr(VI)	100	−97
Cr(VI)	10	−55
Co(II)	100	+25
Fe(III)	100	−25
Ni(II)	100	+16
Mg(II)	100	+1
Cu(II)	100	−11
Mn(II)	100	−6
Zn(II)	100	0
Pb(II)	100	−79

Effect (%) calculated as measured mercury concentration minus nominal concentration divided by nominal concentration, multiplied by 100.

Su et al. [14] studied the photodissociation of formic acid experimentally and theoretically. They concluded that H_2O and CO formation is energetically favored over radical formation.

$$\mathrm{HCOOH} + h\upsilon \rightarrow \mathrm{HCOOH}^{*} \rightarrow \mathrm{H_2O} + \mathrm{CO}$$

For acetic acid, the analogous mechanism would result in the formation of ketene (CH_2CO).

$$\mathrm{CH_3COOH} + h\upsilon \rightarrow \mathrm{CH_3COOH}^{*} \rightarrow \mathrm{H_2O} + \mathrm{CH_2CO}$$

We, therefore, hypothesize that CO (for formic acid) or CH_2CO (for acetic acid) may the reducing species in the UV photoreduction process. It should be emphasized that this pathway is purely speculation on our part but appears to be consistent with experimental results and ongoing computation studies [15]. We report this pathway at this stage only to serve as a basis for further discussion.

4. Conclusions

The method of mercury analysis developed in this work has several practical advantages to the more common methods of mercury analysis. The system eliminates the need for freshly prepared chemical reductant, simplifies the flow-injection manifold by removing the reductant line and leads to a smoother, less violent reduction process. The problems encountered with strong reducing agents, such as droplet transport to the measurement cell, were not observed. The method maintains a useful detection limit with reasonable precision. The analysis of DOLT-3 suggests that UV photoreduction is able to reduce both inorganic and organo-mercury.

Acknowledgements

This work was partly funded by the Merck/AAAS Undergraduate Science Research Program. The authors wish to acknowledge Tait Takatani and Dr. John Galbraith (Marist College, Department of Chemistry, Biochemistry, and Physics) for their work and discussions regarding reaction mechanisms. We also acknowledge Marathon Scientific for donation of the MSIS™.

References

[1] C. Baird, M. Cann, Environmental Chemistry, W.H. Freeman, New York, 2005, p. 519.
[2] W.R. Hatch, W.L. Ott, Anal. Chem. 40 (1968) 2085.
[3] J.D. Ingle, S.R. Couch, Spectrochemical Analysis, Prentice Hall, Englewood Cliffs, 1988, p. 280.
[4] X. Guo, R.E. Sturgeon, Z. Mester, G.J. Gardner, Anal. Chem. 76 (2004) 2401.
[5] X. Guo, R.E. Sturgeon, Z. Mester, G.J. Gardner, Anal. Chem. 75 (2003) 2092.

[6] X. Guo, R.E. Sturgeon, Z. Mester, G.J. Gardner, Environ. Sci. Technol. 37 (2003) 5645.
[7] Q. Wang, J. Liang, J. Qiu, B. Huang, J. Anal. At. Spectrom. 19 (2004) 715.
[8] J. Dedina, D.L. Tsalev, Hydride Generation Atomic Absorption Spectrometry, Wiley, New York, 1995.
[9] F. Laborda, E. Bolea, M.T. Baranguan, J.R. Castillo, Spectrochim. Acta B 57 (2002) 797.
[10] A. Sanz-Medel, M.C. Valdes-Hevia y Temprano, N. Bordel Garcia, M.R. Fernandez de la Campa, Anal. Chem. 67 (1995) 2216.
[11] E.T. Ritschdorff, N. Fitzgerald, R.L.J. McLaughlin, I. Brindle, Spectrochim. Acta B 60 (2005) 139.
[12] C. Vargas-Razo, J.F. Tyson, Fresenius J. Anal. Chem. 366 (2000) 182.
[13] H.W. Sun, R. Suo, Anal. Chim. Acta 509 (2004) 71.
[14] H. Su, Y. He, F. Kong, W. Fang, R. Liu, J. Chem. Phys. 113 (2000) 1891.
[15] T. Takatani, J.M. Galbraith, Alternate Mechanisms for the Formation of Volatile Selenium Species, Presented at the National Conference on Undergraduate Research, Lexington, Virginia, 2005.