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NG Sundin

University of Massachusetts Amherst

Julian Tyson

University of Massachusetts Amherst

C P. Hanna

S A. McIntosh

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The use of Nafion dryer tubes for moisture removal in flow injection chemical vapor generation atomic absorption spectrometry

NILS G. SUNDIN and JULIAN F. TYSON†

Department of Chemistry, University of Massachusetts, Box 34510, Amherst, MA 01003-4510, U.S.A.

CHRISTOPHER P. HANNA and SUSAN A. MCINTOSH

The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859, U.S.A.

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Abstract—A significant problem with flow injection chemical vapor generation atomic absorption spectrometry is a loss of sensitivity and blockage of transfer lines due to excessive moisture transported to the atom cell or lodged in the transfer line. A Nafion dryer tube was used to remove moisture from the wet carrier gas stream. The hygroscopic Nafion membrane removed water at 1.7 mg/min at an efficiency of $95 \pm 4\%$ when SnCl_2 was used as the reductant. When 0.4% (m/v) borohydride was used as the reductant, 2.3 mg/min of water was removed at an efficiency of $91 \pm 3\%$. No measurable change in precision was observed and a 5% reduction in peak height sensitivity (vs. PTFE) was seen for mercury when using the Nafion transfer line. At 60°C the Nafion dryer removed 4.9 mg/min of water vapor at an efficiency of $93 \pm 3\%$. The loss of mercury vapor through the Nafion membrane was no more than 0.04%. Only a 3% reduction in peak height sensitivity was observed for the determination of arsenic and selenium. Detection limits for mercury, calculated from calibration data, were 77 ppt, 20 ppt and 150 ppt for the PTFE tube, the model MD-250 dryer and the model MD-125 dryer, respectively.

1. INTRODUCTION

MERCURY and the metalloid elements (As, Bi, Sb, Se, Sn, Te) are most often determined by chemical vapor generation atomic absorption spectrometry. This method involves the use of reagents, such as tin(II) chloride or sodium borohydride, to convert the aqueous analyte to a gaseous product. The resulting elemental mercury or metalloid hydride is then stripped from solution in a gas-liquid separator using an inert carrier gas and directed to an atomic absorption spectrometer. Typically, the atomizer is a heated T-shaped quartz cell aligned in the optical light path. Several workers have noted problems such as loss of sensitivity and even blockage of transfer lines due to excessive moisture transported to the atom cell or lodged in the transfer line [1-3]. Several methods have been used to prevent carryover of moisture from the gas-liquid separator into the atom cell, most of which involve a desiccant. A radioactive tracer study of anhydrous calcium chloride showed that no more 4% of the hydride was lost [4]. Concentrated sulfuric acid [5], dry ice and methanol [6], silica gel and magnesium perchlorate [7] have been used. All of these agents remove moisture from the system but need periodic replenishment. More serious problems with this approach are that contaminants from the desiccant can be introduced and also that the analyte can be lost through trapping and/or adsorption, especially when silica gel is used.

Recently, CORNS *et al.* [8] showed that the incorporation of a Nafion drying tube between the gas-liquid separator and the atom cell in a continuous-flow atomic fluorescence system for the determination of mercury improved the long term stability and enhanced the sensitivity. Both of these effects were attributed to the continuous removal of water vapor. Similar effects were claimed by AIZPUN FERNANDEZ *et al.* [9] in the determination of mercury by both atomic absorption and atomic emission

† Author to whom correspondence should be addressed.

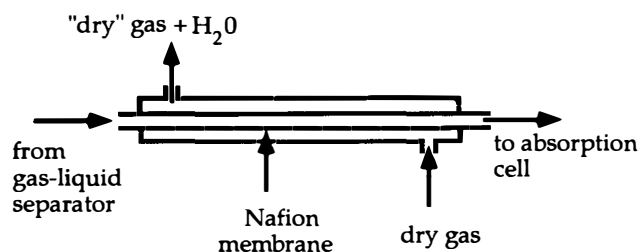


Fig. 1. Cross section of the Nafion dryer tube indicating the drying principle.

spectrometry procedures in which mercury vapor was generated by borohydride reduction from organized media and separated from the liquid phase by a grid nebulizer. CORNS *et al.* [10] have also described a hydride generation atomic fluorescence system for the determination of arsenic and selenium, in which a Nafion dryer tube was incorporated into the gas transfer line. The role of the dryer was not studied.

Nafion is a polymer similar to Teflon except that a sulfonic acid group is added to the chain giving the material a high affinity for water such that up to 13 molecules of water can be absorbed for every sulfonic acid group. Thus Nafion can absorb up to 22% of its weight in water. In addition, its Teflon backbone structure makes it very resistant to degradation from acids.

The dryer consists of a hollow tube of Nafion surrounded by a dry purge gas flowing in a coaxial sheath around the Nafion. When the carrier gas containing water vapor passes through the inside of the hollow tube, the water is absorbed by the Nafion material and moves through the walls of the material. If the dry sheath gas is passed over the exterior of the Nafion, water is continuously removed until the humidity of the carrier gas stream matches that of the purge gas. A cross section showing the operation of the Nafion dryer is shown in Fig. 1. The water removal process is driven by the humidity gradient between the interior and the exterior of the gas stream.

The aim of this work was to quantify the performance of the Nafion dryer in terms of moisture removal characteristics and to study the effect of the device on the sensitivities and precisions of the systems for the determination of mercury, arsenic and selenium.

2. EXPERIMENTAL

2.1. Instrumentation

A Perkin-Elmer FIAS 200 flow injection system was used. The system consisted of two peristaltic pumps, flexible pump tubing, PTFE connecting tubing (0.7 mm i.d.), injection valve, manifold connectors and a carrier gas flow regulator in a single housing. The timing of the valve, speed of the pumps, purge time, heating of the quartz atomizer, and data collection were all controlled through Perkin-Elmer GEM software supplied with the unit running on a Digital DECStation 316sx PC computer. This system was connected to a Perkin-Elmer 3100 atomic absorption spectrometer. The flow injection manifold used for this work is shown in Fig. 2 and the operating parameters are listed in Table 1. The argon carrier flow was optimized for the maximum signal for a 10 ppb standard solution.

A Perkin-Elmer Amalgam System was also used in some experiments to trap mercury vapor onto a rolled piece of gold/platinum gauze. The unit controls a purge gas for the manifold and an argon carrier for the vaporized mercury and pressurized air cooling gas. The gauze consisted of a wire mesh, 1.2 cm long, inside a 15 cm quartz tube (0.3 cm i.d.). Mercury is trapped onto the gauze when cooled and subsequently released by heating the gauze to approximately 600° C using two 10 W tungsten lamps.

Two models of Nafion dryer (Perma Pure, Toms River, NJ) were used in this study.

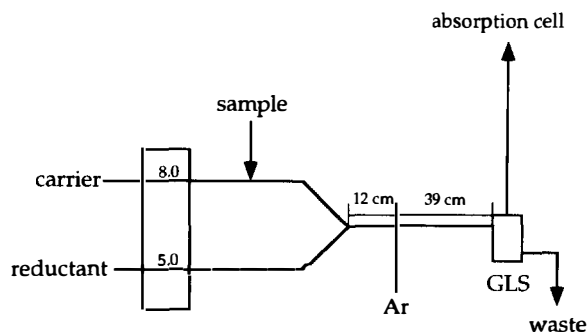


Fig. 2. Flow injection hydride-generation AAS manifold for the determination of mercury, arsenic or selenium. All manifold tubing is 0.7 mm i.d. GLS, gas-liquid separator; W, waste. Reagent flow rates are shown on the pump in ml/min.

Table 1. Instrument operating conditions

Parameter	Value
Mercury hollow cathode lamp current	6 mA
Mercury wavelength	253.7 nm
Arsenic hollow cathode lamp current	16 mA
Arsenic wavelength	193.7 nm
Spectral bandpass for mercury and arsenic	0.7 nm (reduced height)
Selenium electrodeless discharge lamp current	280 mA
Selenium wavelength	196.0 nm
Spectral bandpass for selenium	0.2 nm (reduced height)
Quartz tube atomizer temperature	200°C for Hg 900°C for As and Se
Volume injected	500 µl
Argon carrier flow	80 ml/min for Hg and As 100 ml/min for Se
Dry argon sheath gas flow rate	200 ml/min

Model MD-125 contained a Nafion membrane 30.5 cm long with an i.d. of 1 mm. Model MD-250 was also 30.5 cm long but had an i.d. of 2.2 mm.

Drierite drying tubes (Fisher) filled with a colored indicator and calcium sulfate were used to quantify the amount of moisture in various gas streams by gravimetry.

2.2 Reagents

All solutions were prepared with distilled, deionized water produced from a E-pure system (Barnstead). The mercury carrier stream solution was prepared by diluting ACS grade HCl (37% mm, Fisher) to a concentration of 3% (v/v) with distilled, deionized water. The carrier stream solution for both the arsenic and selenium studies was 10% HCl (v/v). Tin(II) chloride reducing agent solution (1% m/v) was prepared by dissolving 10.0 g of tin(II) chloride dihydrate (Fisher) in 100 ml of concentrated HCl and diluting to 1000 ml. Sodium borohydride solutions were prepared by dissolving 4.0 g of the powder in 1000 ml of 0.05% sodium hydroxide (pellet form, Fisher) and then filtering through a Whatman No. 42 filter paper under suction. Standard solutions were prepared by dilution of 1000 mg/l stock solutions of Hg(II) As(V) or Se(VI) (Fisher). The mercury standards were preserved with 0.5% (v/v) nitric acid and 0.005% (m/v) potassium dichromate. The tin(II) solutions were used to reduce mercury while the borohydride was used as the hydride transfer reagent for the arsenic and selenium studies.

Any experiments requiring As(III) solutions were prepared by appropriate dilution of the As(V) standard and pre-reducing the As(V) to As(III) with 10 ml of 10%

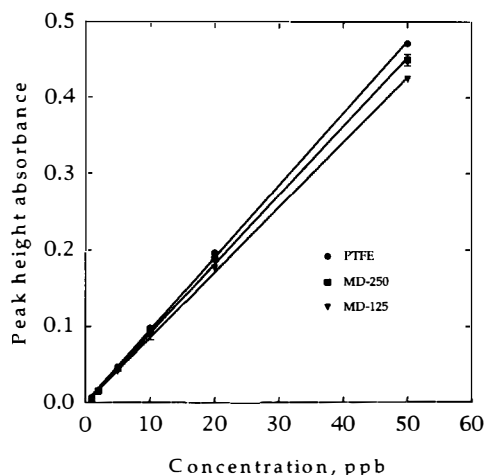


Fig. 3. Effect of type of transfer tubing on peak height sensitivity of mercury. See text for abbreviations.

(m/v) potassium iodide/10% ascorbic acid with 10 ml of concentrated hydrochloric acid for every 100 ml of As(III) needed.

Experiments employing Se(IV) solutions were prepared by pre-reducing 500 μ l of a 1000 ppm Se(VI) standard in 80 ml of 1 : 1 HCl. Working standards were prepared by appropriate dilution of a 500 ppb stock solution of Se(IV). The working standards also contained 10% HCl (v/v).

All standards and reductants were prepared fresh daily.

2.3. Parameters studied

The effect of the Nafion dryer on the following performance characteristics were investigated: (1) peak height sensitivity for mercury, arsenic and selenium; (2) rate of moisture removal for both ambient and elevated temperatures; (3) precision of repeated measurements; and (4) possible loss of analyte through the Nafion membrane.

3. RESULTS AND DISCUSSION

3.1. Effects of Nafion dryer tubes on peak height sensitivity of mercury by flow injection atomic absorption spectrometry

Initially, the two Nafion dryer tubes were compared with the standard 1 mm i.d. polytetrafluoroethylene (PTFE) transfer tubing on the basis of peak height sensitivity. Peak height absorbances were measured for six standards (1, 2, 5, 10, 20 and 50 ppb) as well as a blank for each of the three transfer lines for five replicate injections of 500 μ l. The blank corrected peak height absorbance for each replicate was used to construct a calibration curve for each type of transfer tube. These are shown in Fig. 3. The PTFE calibration curve had a slope of 0.0095 ± 0.0001 ppb⁻¹ (all quoted error values are 95% confidence intervals) while the MD-250 dryer gave a slope of 0.0090 ± 0.0001 ppb⁻¹. The smaller dryer (MD-125) produced a calibration curve with a slope of 0.0085 ± 0.0001 ppb⁻¹. All slopes were calculated by a first order linear regression procedure. Thus the Nafion transfer line produces a reduction in sensitivity of about 5% when compared with that of the PTFE transfer line. On the basis of visual inspection, all the calibration curves were linear up to 50 ppb. The MD-250 was used for future experiments as it gave the better sensitivity. Detection limits, calculated from the calibration data [11], were 77 ppt, 20 ppt, and 150 ppt for the PTFE tube, the model MD-250 dryer, and the model MD-125 dryer, respectively.

These results may be contrasted with those obtained by AIZPUN FERNANDEZ *et al.* [9] who found that the incorporation of the dryer tube improved the sensitivity of

their atomic absorption determination by a factor of 20% to 0.007 ppb⁻¹. No reasons were proposed for this effect, and insufficient experimental details were given to allow further speculation.

3.2. *Effect of Nafion dryer tubes on precision by flow injection atomic absorption spectrometry*

For both the PTFE transfer line and MD-250, twenty one replicate injections of a 10 ppb mercury standard were made. The percentage relative standard deviations were 1.0% for PTFE and 0.98% for MD-250. The values are not significantly different (*F* test). For ten replicate determinations of a 50 ppb solution AIZPUN FERNANDEZ *et al.* [9] reported relative standard deviation values of 2.5% and 1.9%, for systems without and with the drier, respectively. These values are not significantly different. Similar results were reported by CORNS *et al.* [8] for the short term atomic fluorescence determination but a considerable improvement in the precision after prolonged use was obtained when the Nafion dryer was used.

3.3. *Efficiency of water removal through the use of Nafion dryers*

For the study of water removal, water was pumped continuously in both channels for 2 h. The wet argon carrier gas was directed through the Nafion dryer and then through a pre-weighed Drierite drying tube. The sheath gas flowing around the outside of the Nafion was directed to a separate pre-weighed Drierite tube. The MD-125 removed water at the rate of 1.25 mg/min while MD-250 removed water at 1.71 mg/min. The efficiency of water removal for MD-250 was determined to be $95 \pm 4\%$.

To simulate the conditions when a large amount of water vapor is generated, as has been observed in certain kinds of flow injection manifolds [12], the reaction coil and gas liquid separator were heated to 60°C in a water bath. The Nafion dryer and Drierite were employed as described above to measure the amount of water removed by the dryer. Water vapor was removed at a rate of 4.9 mg/min. Under these conditions water droplets were observed to form on the outside of the Nafion membrane. The efficiency was $93 \pm 3\%$.

Similar experiments were also performed using an acid carrier stream and a borohydride reducing stream. These experiments were carried out in order to ensure that the performance of the Nafion dryer did not suffer when a more vigorous reaction took place. Solutions of 10% HCl and 0.4% sodium borohydride were prepared as described in the experimental section. Again, the carrier gas and sheath gas were directed through Drierite drying tubes. The rate of water removal was 2.3 mg/min at an efficiency of $91 \pm 3\%$.

The performance of the PTFE transfer line was variable. On some occasions water droplets would form immediately on starting an analysis and within minutes the quartz windows of the absorption cell would become fogged. On other occasions, 2–3 h of satisfactory operation would be obtained before the build up of water droplets and vapor became a problem.

3.4. *Effect of Nafion dryer on the recovery of mercury*

Two sets of experiments were performed in order to determine if any mercury was lost through the Nafion membrane which could account for the small reduction in peak height absorbance noted previously in Section 3.1.

3.4.1. *Indirect measurement of mercury loss.* The amalgam system was used to trap the mercury vapor from the transfer line. If no mercury is lost, then the same peak height and peak area should be measured for both the PTFE and the Nafion. Four replicate injections of 500 µl were performed at each of six different mercury concentrations (1, 2, 5, 10, 20 and 50 ppb) and resulting mercury vapor was trapped onto the gold–platinum gauze and subsequently released through heating. The resulting peak heights and peak areas were measured. A two way analysis of variance (ANOVA) showed no statistically significant difference between either peak height or peak area when comparing PTFE with Nafion. Results are shown in Tables 2 and 3 for peak area and peak height, respectively.

Table 2. Results of a two way ANOVA comparing PTFE and MD-250 using blank corrected peak area values

Source*	DF‡	Sum of squares	Mean square	F	p Value
A	1	0.001	0.001	0.923	$p > 0.25$
B	5	90.353	18.071	13228.4	$p \leq 0.0001$
A × B	5	0.049	0.001	0.562	$p > 0.25$
Error	36	0.049	0.001		
Total	47	90.407			

* 'A' represents the two factors under comparison (PTFE and Nafion) and 'B' symbolizes the six concentration levels.

‡ DF is number of degrees of freedom.

Table 3. Results of a two way ANOVA comparing PTFE and MD-250 using blank corrected peak height values

Source*	DF‡	Sum of squares	Mean square	F	p Value
A	1	1.0×10^{-6}	1.0×10^{-6}	0.106	$p > 0.25$
B	5	1.272	0.254	26535.5	$p \leq 0.0001$
A × B	5	3.4×10^{-5}	6.9×10^{-6}	0.716	$p > 0.25$
Error	36	3.5×10^{-4}	9.6×10^{-6}		
Total	47	1.273			

* 'A' represents the two factors under comparison (PTFE and Nafion) and 'B' symbolizes the six concentration levels.

‡ DF is number of degrees of freedom.

These results indicate that no mercury was lost through the Nafion membrane (on the assumption that no mercury is lost through the PTFE transfer tube).

3.4.2. *Direct measurement of mercury loss.* In a separate experiment the sheath gas was directed to the amalgam unit to determine if mercury was transferred across the membrane. A continuous flow experiment was performed with 250 ml of a 50 ppb Hg standard as "carrier" stream and 1% Sn(II) as the reductant. The generated mercury vapor was directed to the fume hood while the sheath gas was passed over the gauze. The mercury collected on the gold-platinum gauze after 1 h was vaporized and the resulting signal was measured. The resulting signal (for both peak height and peak area) corresponded to between 2.5 and 5.0 ng and thus no more than 0.04% of the mercury was lost through the Nafion membrane.

3.5. *Effect of Nafion dryer tube on peak height sensitivity of arsenic*

Five replicate injections of arsenic(III) standards were made at six different concentrations (1, 2, 5, 10, 20, 50 ppb) for both the PTFE tube and the Nafion tube. A 10% HCl carrier stream was merged with a 0.4% borohydride solution. The resulting peak heights and peak areas were measured. A two way ANOVA calculation showed that there was a statistically significant difference, for both peak height and peak area, between the two transfer lines. The slopes of the peak area calibration curves were 0.079 ± 0.004 s ppb⁻¹ and 0.075 ± 0.004 s ppb⁻¹ for PTFE and Nafion, respectively.

The ANOVA indicates a difference between the two transfer lines while the 95% confidence intervals of the regression procedure overlap (indicating no statistical significance between the transfer lines). This is because the regression procedure fits the best straight line through the data and there is always some "error" in this process. That is, the y residuals (the difference between the fitted line and the individual data points) indicates the lack of fit between a linear model and the data. ANOVA, however, simply calculates the total variance in a set of data and partitions this among the various factors (concentration, type of transfer line, inherent variability and

interaction). It does not fit a model to a set of data nor does it adjust parameters to minimize differences between the model and the data.

The results may indicate that some of the arsine is lost through the Nafion membrane. However, as shown from the mercury studies, the reduction in sensitivity is not necessarily due to loss of analyte, but may instead be due to a gas phase dilution because the MD-250 has an internal diameter of 2.2 mm in comparison with an i.d. of 1 mm for PTFE. In addition, SINEMUS *et al.* [13] point out that a typical flow injection hydride generation peak has a half-width of several seconds and a tail extending for more than 20 s. This means that a significant area under the absorption profile is measured under a relatively low signal-to-noise ratio making such a measurement less reliable.

3.6. Effect of Nafion dryer tube on peak height sensitivity of selenium

Five replicate injections of selenium(IV) standards were made at six different concentrations (1, 2, 5, 10, 20, 50 ppb) for both the PTFE tube and the Nafion tube. A 10% HCl carrier stream was merged with a 0.2% borohydride reductant solution. A two way ANOVA calculation shows that there was a statistically significant difference between peak height results but not between the peak area results. The slopes of the peak area calibration curves were $0.059 \pm 0.003 \text{ ppb}^{-1}$ and $0.058 \pm 0.003 \text{ ppb}^{-1}$ for PTFE and Nafion, respectively. The peak height difference indicated by ANOVA may again be an indication of a gas phase dilution or a carrier gas flow rate variation. The slopes of the calibration curves and the peak area ANOVA data indicate no loss of SeH_2 through the Nafion membrane.

4. CONCLUSION

Nafion dryer tubes remove moisture efficiently from a wet carrier gas stream in a flow injection hydride generation AAS system. In comparison with the use of chemical desiccants, use of a dryer tube has the advantages of avoiding (a) the introduction of contaminants and (b) significant analyte loss. In addition, there is no need for a shut down procedure to dry the system. The Nafion dryer removes over 90% of the moisture in the carrier gas both at room and elevated temperatures and does not adversely affect the performance characteristics of the hydride generation technique.

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