Inductively Coupled Plasma Mass Spectrometry with Direct Injection Nebulization for Mercury Analysis of Drinking Water

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An improved technique has been developed to determine concentrations of mercury in drinking water. Inductively coupled plasma mass spectrometry (ICPMS) with direct injection nebulization (DIN) was used for the analysis. A characterization was conducted and optimum operating parameters found. The mercury detection limit with the DIN was comparable to a conventional pneumatic nebulizer (PN) while the inherent problems of memory effects were drastically reduced. The extent of spectral interference due to refractory oxide formations was compared using the DIN and the PN. Actual drinking water samples were spiked with varying concentrations of mercury and analyzed along with certified reference materials using DIN–ICPMS. Duplicate analysis was conducted between the DIN–ICPMS and the conventional technique of cold vapor atomic absorption spectrophotometry (CVAA) and a comparison made.

INTRODUCTION

The Ontario Ministry of the Environment has been monitoring mercury concentration levels in drinking water since the concern with mercury pollution began when hundreds of Japanese were poisoned at Minamata Bay in the mid 1960s.[1] Subsequently, environmental studies were conducted in Ontario, and high levels of mercury were found in water, fish, and wildlife close to anthropogenic sources. An event of mercury pollution in northern Ontario and the effect on the residents of the Grassy Narrows Indian reserve was the subject of much study.[2,3] Because of the toxicity of mercury to man, the Ontario government has recommended strict guidelines for mercury in drinking water.[4]

Many different analytical techniques for mercury have been developed over the years. They include wet chemistry,[5] fluorescence,[6] neutron activation.[7] and cold vapor atomic absorption spectrophotometry (CVAA).[8,9] The latter is the most sensitive of the techniques, giving detection limits close to 30 ng/L of Hg in aqueous solutions. However, the accuracy of the results are dependent on the effectiveness of the sample pretreatment. Several factors, such as incomplete conversion of Hg to Hg^{2+} prior to addition of a reducing agent and low results due to the presence of mercury as an organometallic compound, may influence the accuracy.[10]

Our laboratory has adapted the CVAA technique and developed a method for mercury analysis of drinking water because of the sensitivity and the fact that this technique had the shortest analysis time compared with other established techniques.[11] A fast analysis time is needed due to the large number of samples submitted to our laboratory.

Inductively coupled plasma mass spectrometry (ICPMS) has been used extensively in our laboratory for trace elemental analysis of drinking water (with the exception of mercury) for several years.[12] Until now, mercury analysis was not feasible with conventional ICPMS. The reason for this is the extensive memory effect or "wash-out" time needed for samples containing higher than typical concentrations of mercury.

The majority of drinking water samples in Ontario contain mercury levels at or below the 30 ng/L detection limit of CVAA; however, a smaller number of samples may range up to 50 μg/L. The analytical method must be rigorous enough to accommodate this varying range of concentration. Sample carry-over would cause substantial bias of the results. It seems that the mercury, even at relatively low concentrations, adheres to the walls of the spray chamber and the aerosol transfer tubing of the introduction system causing contamination of subsequent samples.[13] There have been attempts to minimize the memory effects seen in mercury analysis by ICPMS. Recently, workers have developed a technique to measure mercury in urine and whole blood by ICPMS.[14] This technique involves the use of a conventional sample introduction system.

However, dilution and chemical modification were conducted on the samples. This sample pretreatment would tend to lengthen analysis time and worsen detection limits as a result of a 30 times dilution factor.

Workers at the Ames Laboratory, IA, have developed a new version of a direct injection nebulizer (DIN).[15] The DIN is an concentric pneumatic nebulizer which fits directly in the torch replacing the injector tube. This eliminates the use of a spray chamber and aerosol transfer tubing. It has been shown to drastically reduce the analyte memory effects for

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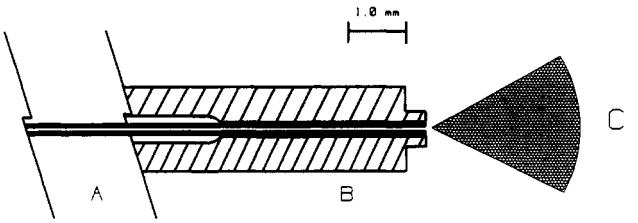

Figure 1. An enlarged view of the DIN tip. (A) fused silica sample transfer capillary (50-μm i.d.), (B) ceramic nebulizer support tube, (C) nebulizer aerosol.

mercury on a number of inductively coupled plasma atomic emission spectrometers (ICPAES)[16-18] and recently, ICPMS.[19]

This paper describes how DIN can be connected with ICPMS, characterized, and used as a technique to analyze mercury in drinking water. The study of this particular technique may lead to development of other methods in more complicated matrices such surface water and biota.

EXPERIMENTAL SECTION

Instrumentation. The ICPMS used was a Perkin-Elmer/Sciex Elan 5000. The conventional introduction system with this unit is a Perkin-Elmer crossflow nebulizer, Scott type Ryton spray chamber, and a demountable torch with a 2.0-mm-i.d. alumina injector. This PN was used for comparison of detection limits, memory effects, and oxide formation. The liquid sample was delivered via a Gilson Minipuls 2 peristaltic pump.

Data collection by the ICPMS was conducted using a dwell time of 800 ms at 3 points across the peak. Five replicates were taken for each sample for an estimated analysis time of 25 s. Mercury was monitored at 202 Da which is the most abundant isotope of mercury. Thallium, used as an internal standard, was monitored at 205 Da.

DIN Apparatus. A Cetac Microneb 2000 direct injection nebulizer was used for DIN studies. The ICP torch for this nebulizer was different from previously described DIN torches because it had no quartz injector tube. In addition, the present version of the DIN nebulizer is completely metal-free.

Liquid samples were delivered from a metal-free flow injection valve to the nebulizer through a 50-μm-i.d. × 25-cm-long fused silica quartz capillary tube. The internal volume of the nebulizer capillary was less then 1 μL. The acidic carrier stream was pumped through the sample delivery capillary by a gas displacement pump (GDP) with operating pressure of up to 500 psi. At 375 psi, the sample flow rate was approximately 100 μL/min. Figure 1 shows an enlarged view of the DIN tip.

To perform an analysis, the samples were first pulled into a loop on a metal-free flow injection valve by suction using a peristaltic pump. This eliminated contact between the sample and the peristaltic pump tubing to reduce memory effects. After the sample loop was filled, the valve was switched to inject the sample into the acidic carrier stream from the GDP. A 75-μL sample volume provided a steady-state analytical signal for the 35 s of data acquisition time. After the data were acquired, the injection valve was returned to the load position.

A peristaltic pump was then used to rinse the sample loop with a dilute nitric acid. To improve the rinse process, the sample injection valve position was cycled from the load position to the inject position three times. This was designated a wash cycle and "flushed out" any residual mercury in the sample loop. The system was then ready to be loaded with the next sample for injection. Figure 2 shows an enlarged view of the DIN system.

Reagents. The acid used for sample and standard preservation was Sea-Star purified nitric acid. All aqueous solutions used for standardization were made from labortory prepared stock solutions of 1000 mg/L. The stock solutions were then verified to NIST reference materials. Serial dilutions were made to meet the specific concentration level in the standard and the solution was acidified with 1% nitric acid.

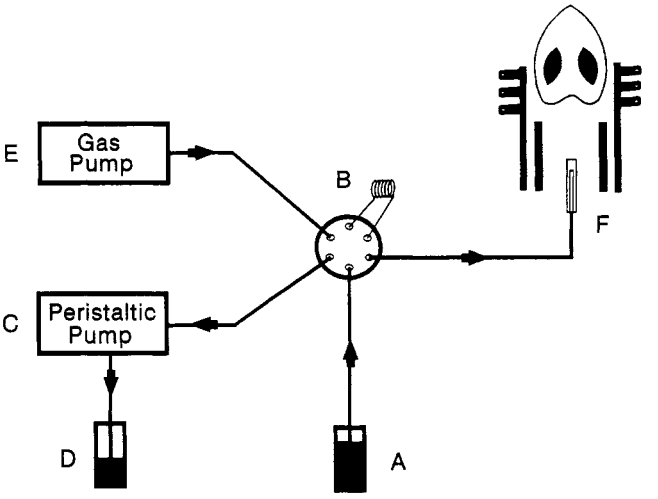

Figure 2. Flow diagram for the DIN. The sample solution (A) was pulled into the loop on the flow injection valve (B) using a peristaltic pump (C). The excess liquid went to waste (D). An acidic carrier stream from a gas displacement pump (GDP) (E), delivered the sample solution to the DIN (F).

The double-distilled water used to prepare standards and blank solutions was made from first passing distilled water through a Barnstead deionizing system and then redistilling the water with a Corning distillation apparatus.

Certified References. Reference material was chosen to represent the sample matrix as best as possible. Environmental Protection Agency (EPA) pollution control standards were selected (EPA WP 287, EPA WP 476, and EPA WS 378). The solutions were prepared, as per instructions, from the sealed ampoule provided.

Standard Additions. A drinking water composite was obtained by combining drinking water samples compiled from several months of "left-over" samples. Mercury spikes at various concentrations were added to replicates of this composite to estimate the spike recovery. In addition, each sample was spiked with thallium which was used as an internal standard. Thallium was chosen because it is present at relatively low to virtually nondetectable concentrations in samples. Mass bias effects are also minimized because the Tl^{205}, the isotope measured, is close in mass to Hg^{202}.

RESULTS AND DISCUSSION

DIN Optimization. Although flow injection is used to introduce samples to the DIN, the signal observed is steady state rather than transient. This is because the internal volume of the nebulizer is small enough to minimize sample dispersion, even for samples of less than 0.1 mL.

The length of the steady-state signal produced by the sample injection was determined by the size of the sample loop. Initially, a sample loop of 300 μL was used which produced a steady-state signal of approximately 150 s. This length of time is more than adequate to take statistically representative data for one isotope of mercury and thallium. It was decided to reduce the size of the sample loop to 75 μL. A reduction to this loop size will speed wash-out between samples, without loss of sensitivity, and will decrease any potential matrix effects by reducing the sample size introduced into the plasma.

In previous studies, Houk experimented with sample loop sizes and their effect on sensitivity with the DIN have been characterized. They observed that by reducing the size of the sample loop, loss of sensitivity did not occur. Only the length of the steady-state signal decreased.

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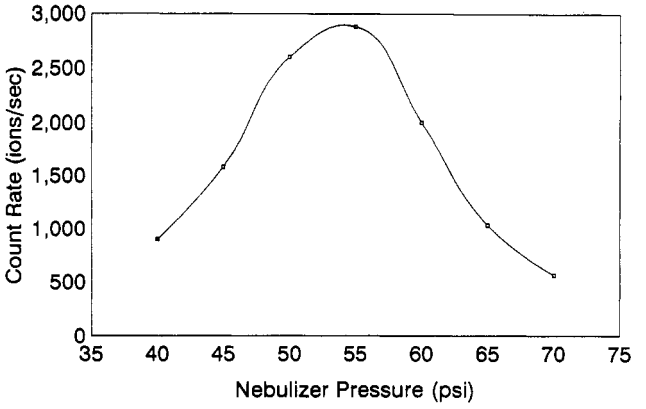

Figure 3. The response profile of a 10 μg/L Hg solution as the nebulizer pressure is varied.

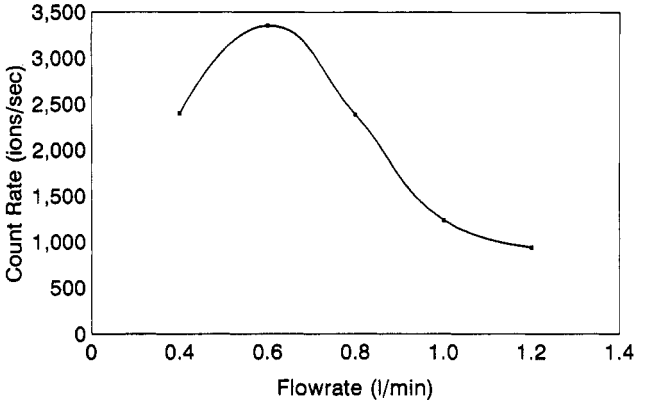

Figure 4. Variation in response profile as the auxiliary gas flow rate is changed.

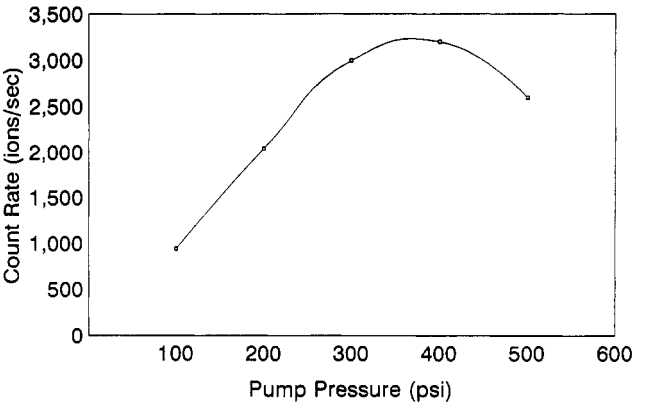

Figure 5. Change in signal profile when the GDP pump pressure is increased.

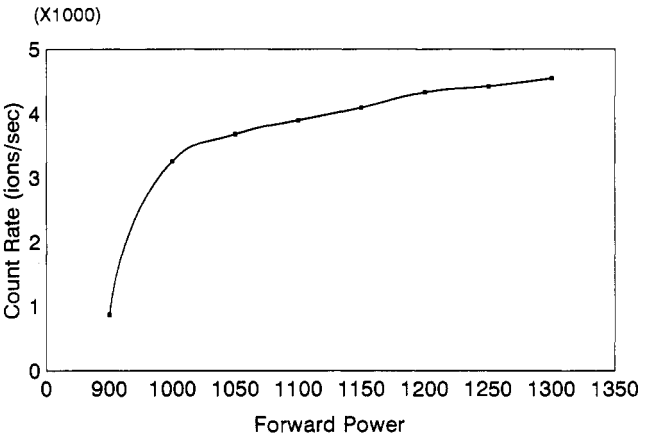

Figure 6. A signal profile for a 10 μg/L Hg solution as the forward power varies.

DIN optimization was conducted by varying several parameters of the DIN and the ICPMS. The physical placement of the DIN in the ICP torch was such that the DIN was approximately 1 mm below the middle tube of the ICP torch. In previous work, this position produced the best analyte signal.[19] Positioning of the torch was conducted using the X, Y, Z adjustments available on the ICPMS. These adjustments centered the plasma to the sampling orifice and could be maximized by monitoring the signal produced by aspirating a 10 μg/L mercury solution.

Nebulizer flow rate/pressure is a major consideration in optimizing signals for all ICP systems. The DIN nebulizer pressure is relatively high when compared to most nebulizers. This is the result of the design of the nebulizer which minimizes droplet size at higher pressures.

Figure 3 shows the change in mercury signal profile when the DIN nebulizer pressure was changed. The response curve indicates the optimum signal occurs at 55 psi and then rapidly falls as the pressure is increased. As with other nebulizers, a change in flow/pressure has the effect of moving the initial radiation zone in the plasma, thus affecting sensitivity.[20]

The auxiliary gas flow rate also has the effect of changing the viewing position of the initial radiation zone. However, increasing or decreasing the auxiliary gas flow moves the entire plasma with respect to the load coil rather than moving just the initial radiation zone in the inner channel when nebulizer pressure/flow rate changes are made. Figure 4 shows the change in analyte signal response as changes in auxiliary flow rate were made. An optimum was obtained at 0.6 L/min. Increased flow rate beyond this point decreased the signal.

Figure 5 shows the effect on analyte signal when the GDP pump pressure was changed. The sample liquid flow rate increases as the pump pressure increases. An optimum signal was obtained at 375 psi. Beyond this pressure the signal falls steadily which is likely due to higher sample loading. Variations in forward power while monitoring the signal strength for mercury are shown in Figure 6. As the power was increased, the analyte signal rapidly increases, almost exponentially, to point at roughly 1000 W and then slowly increases and levels off thereafter. A maximum, in this case, was not reached because a forward power above 1300 W moved the plasma down in the load coil bringing it too close to the DIN tip. This overheated the nebulizer tip and resulted in poor nebulization. The optimum forward power chosen was 1200 W. The mass spectrometer ion lens settings and applied voltage to the detector were optimized by monitoring the 10 μg/L mercury standard.

All the optimum operating conditions are listed in Table I. After the DIN and the ICPMS were optimized, a 1000 mg/L Y solution was introduced using the DIN. The initial radiation zone formed was at least as intense as the one produced by conventional PN. Although no spray chamber was used with the DIN, the plasma was visually very stable with no "flickering" in the central channel. The distance between the tip of the initial radiation zone and the tip of the sampling orifice was approximately 4 mm.

Detection Limits and Precision. After optimization, the detection limits were determined as 3× the standard deviation of the blank value. The detection limits were found to be similar and are listed in Table I.

It is possible to achieve better absolute detection limits from the DIN because the sample volume required is 1 order of magnitude smaller. The short-term precision for the DIN was improved over the PN, typically 1% RSD for a 10 and a 35 μg/L mercury solution. The improved short-term

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Table I. Conditions Which Produced the Optimum Signal for a 10 μg/L Standard Solution for Both Nebulizers[a]

parameter	DIN–ICPMS	PN–ICPMS
	Argon Gas Flows	
nebulizer pressure, psi	55	28
nebulizer flow rate, L/min	1.0	0.920
coolant flow, L/min	12	12
auxiliary flow, L/min	0.6	0.8
	Sample	
GDP pump pressure	375 psi	
carrier solution	1% HNO_3/HCl	
sample size	75 μL	uptake, 1.2 mL/min
	Instrument	
ICP forward power, W	1200	1050
ion lens settings		
*E*1, V	5.05	5.15
*S*2, V	−9.98	−10.61
P, V	−64.67	−67.89
*b*1, V	9.76	10.12
detector voltage, kV	−3.300	−3.300

[a] Detection limits: PN, 40 ng/L; DIN, 30 ng/L.

precision of the DIN maybe due to the elimination of "dead volume areas" such as the spray chamber, PN housing, and drain tube. Other nebulizers suffer from turbulence and pressure pulses from the waste drain which have been shown to cause imprecision in aerosol transport.[21]

Oxide Formation and Spectral Interference. Formation of refractory oxides, particularly from alkaline earth metals, in an ICPMS may lead to possible spectral interferences.

The mechanisms of oxide formation in a plasma are documented;[22,23] however, the study of molecular re-formation around the sampler of the ICPMS is still not well understood.

Operating conditions, specifically in the ICP source, contribute greatly to the extent of oxide formation.[24] Solutions of cerium when introduced into an ICP develop refractory oxides of a level that is usually higher than other oxide-forming elements and can be used as a "diagnostic oxide reference" for many ICPMS experiments. An experiment was conducted to determine the extent oxide formed with the DIN as opposed to the PN. A 100 μg/L cerium solution was used. Cerium oxide formed at a (MO^+/M^+) ratio of 10.1% for the DIN and 8% for the PN. Further reduction of the MO^+/M^+ ratio may be obtained by adjusting ICP operating conditions; however, lower sensitivity may occur.

In this study, the element of interest is mercury at 202 Da. Any spectral interference (isobaric or oxide) at this mass will cause a higher than normal background which would lead to erroneous quantitative results. Fortunately, there are no isobaric interferences at 202 Da; however, a metal oxide interference could be observed if tungsten is present in the sample. An experiment was conducted to determine the levels of tungsten necessary to be present to cause a significant rise in the background of Hg^{202} at the chosen operating conditions. Tungsten at a concentration of 100 μg/L was introduced using the DIN, and the tungsten oxide signal was measured. Tungsten oxide formed at Hg^{202} only slightly above background (approximately 300 counts).

This is not considered a major interference in our study. However, a certified method for mercury determinations in drinking water should require that tungsten be monitored

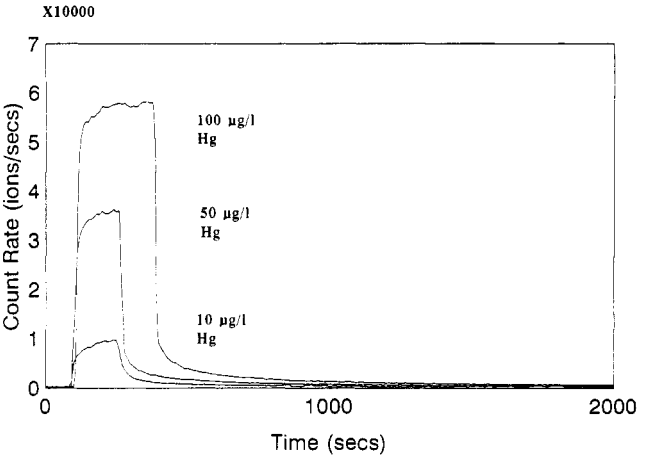

Figure 7. Wash-out time of the PN with three different concentration levels.

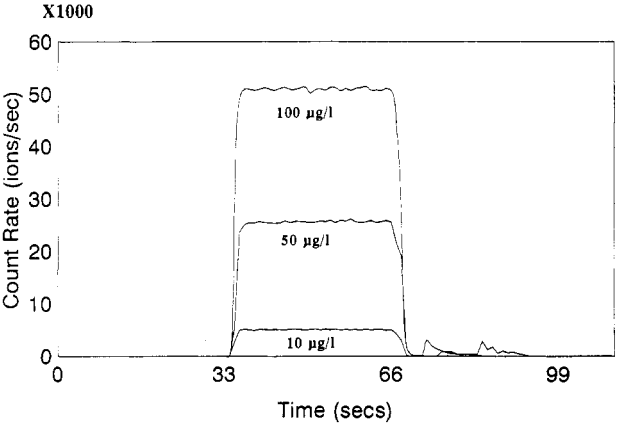

Figure 8. Mercury wash-out time for the DIN at three different concentration levels.

and an appropriate background correction be applied if the concentration reaches a predetermined level.

Memory Effects. Various concentration levels of mercury standard were aspirated into the PN, and the steady-state signal was monitored. Figure 7 shows the signal produced when three different concentrations of mercury solution were aspirated. As observed, from time zero, a steady-state signal was not reached until at least 200 s into the analysis for the 50 and 100 μg/L concentration levels. The lower concentration level (10 μg/L) did not actually reach steady state. The possibility of mercury accumulating in the PN introduction system, giving a false positive increase in the signal, should not be ruled out. Once the best steady-state signal was reached, the introduction system was washed out.

The response profile indicated that for all concentration levels an inordinately long time to wash-out the system to background levels was required. In fact, the 100 μg/L concentration level did not reach a background until after 2000 s.

Figure 8 shows the same three mercury concentration levels introduced into the ICP using the DIN. In each case, the sample was injected at a time equal to 33 s. The response profile indicates a steady-state signal was reached in approximately 2 s for all concentration levels.

The analytical data were gathered during the steady-state signal. At time is equal to 66 s, the flow injection valve was returned to the "load" position and the mercury signal rapidly decreased as the nebulizer was rinsed. Simultaneously, the peristaltic pump rinsed the valve and flow injection loop with dilute hydrochloric acid. The valve position was then cycled between "load" and "inject" to aid in completely rinsing the sample introduction system. The small peaks observed in

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Table II. Comparison of Low-Level Concentrations of Hg in Certified References

reference ID	certified value, μg/L	cold vapor, μg/L	DIN-ICPMS, μg/L
EPA WP 287	5.50 ± 0.6	2.12 ± 0.04	3.34 ± 0.05
EPA WS 378	4.0 ± n/a	3.97 ± 0.04	4.31 ± 0.08
EPA WP 476	7.6 ± n/a	8.02 ± 0.07	7.79 ± 0.07

Figure 8 between 60 and 100 s represent a small mercury signal as the incompletely rinsed valve was cycled. After the rinse procedure, no mercury was detected on subsequent injections of blank solutions. This indicates that a method for routine analysis should incorporate a wash cycle to ensure that the sample loop is completely rinsed before the next sample injection is made. The entire rinse procedure, including rinse-out of the valve and sample loop, was less than 40 s. For the 100 μg/L mercury solution, the DIN washout time was about 50 times faster than for the PN. During this study, nitric acid was substituted with hydrochloric acid as a carrier solution because it was found that rinsing of the sample loop could be done more efficiently with less wash injections. A possible answer for this is that any mercury retained in the sample loop could form mercuric chloride which would be more efficiently rinsed from the loop.

Method Comparison. Concerns over matrix effects in ICPMS are well founded and have been extensively studied.[25,26]

Any discussion of the mechanism behind the cause and elimination of matrix effects in ICPMS is beyond the scope of this paper. However, the DIN was assessed on its performance with respect to potential matrix effects from a drinking water matrix.

To ensure matrix effects do not affect the accuracy when the DIN is used, an accuracy study and a technique comparison between DIN-ICPMS and CVAA was conducted. Table II shows an accuracy comparison between the two techniques using EPA water pollution control samples. One of the three references had a low bias in results for both the CVAA method and DIN-ICPMS analysis. It is possible that the length of storage for WP 287 would have an effect on the accuracy to the certified value, and in this case WP 287 was out of date. However, this would not explain the discrepancy between the DIN analysis and the CVAA method. All three certified references were analyzed using standard addition, and the matrix for all three reference materials are the same. This would seem to reduce the possibility of a matrix effect. The reason for this variation is still under investigation.

Drinking water composite samples were spiked with mercury in varying concentrations. By doing this, a wide concentration range can be simulated to represent a worst possible sample scenario. As well, to minimize any potential matrix effects, thallium was used as an internal standard and was added to the samples prior to analysis. Table III shows a comparison of 20 samples by the two techniques.

There is some statistically significant disagreement between the two techniques. This difference could be attributed to variations in standards between the two techniques and the accuracy and precision of spiking. The greatest discrepancy occurs at the low concentration spike which is very close to the detection limit value.

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Table III. Comparison of Analysis Techniques: Cold Vapor Atomic Absorption vs Direct Injection ICPMS[a]

sample ID	theoretical, μg/L	cold vapor, μg/L	DIN-ICPMS, μg/L
1	0	0.00	0.00
2	0	0.00	0.00
3	0.05	0.05	0.02
4	0.05	0.05	0.06
5	0.1	0.10	n/a
6	0.1	0.10	0.09
7	0.5	0.47	0.40
8	0.5	0.49	0.44
9	1.0	1.01	1.00
10	1.0	1.03	1.00
11	2.5	2.50	2.70
12	2.5	2.52	2.71
13	5.0	5.06	5.79
14	5.0	5.05	5.66
15	10.0	9.81	11.4
16	10.0	9.81	10.9
17	25.0	25.3	26.1
18	25.0	25.6	26.5
19	50.0	49.0	53.8
20	50.0	49.5	52.4

[a] Samples listed are drinking water composites spiked with a varying range of Hg.

As well, there is some significant variation between the DIN-ICPMS and the theoretical value. This variation could be due to error in standard preparation. We do not suspect any matrix effects since variation in concentration from the theoretical value does not have a consistant bias between samples (i.e. some spikes are closer than others). As method development progresses, more comparison data will be generated to understand the discrepancy in accuracy.

CONCLUSIONS

The potential for developing a method for determining trace amounts of mercury in drinking water by DIN-ICPMS is very promising. The substantial reduction of memory effects and the advantage of a smaller sample size are a definite benefit for mercury analysis by DIN-ICPMS.

Using the FI valve to introduce the sample to the DIN will also reduce potential matrix effects by decreasing the amount of sample transported to the plasma.

The DIN system is also quite adaptable to an automated sampling system which would increase the efficiency of sample throughput. The detection limits between the DIN and PN are very comparable. The speed of analysis and the freedom from sample pretreatment make DIN-ICPMS a feasible choice for mercury analysis as compared with the CVAA method.

Ongoing investigations into the use of the DIN for multielement capability are being conducted.

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