Recent Improvements in Analysis of Aqueous Samples for Methyl Mercury: Improvements in Accuracy, Precision, and Detection Limits

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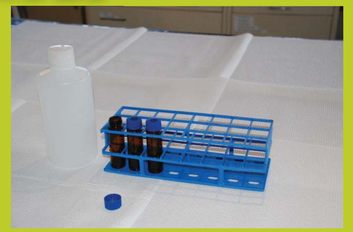
Introduction

Very few substantial improvements have been made in the preparation of aqueous samples for MMHg analysis in the last ten years. A distillation procedure was developed in 1993 by Horvat et al. and is still the commonly used method for preparing aqueous samples for analysis of MMHg by cold vapor - atomic fluorescence spectrometry (CVAFS) and is specified in the Draft EPA Method 1630. Distillation has some advantages. Distillation eliminates interferences from sulfide and organic carbon compounds in the aqueous matrix. It also reduces the amount of divalent mercury, Hg(II), in the sample, which can interfere with MMHg determination (Bloom and von der Geest, 1995). Disadvantages of the distillation process include the introduction of a substantial amount of variability, the increased chance of carryover, the large amount of time it takes, and the extra equipment that is needed.

A potentially substantial improvement in sample preparation, called direct ethylation, was developed at the Florida Department of Environmental Protection (FDEP) and presented at the Eighth International Conference on Mercury as a Global Pollutant. Direct ethylation is a procedure for analyzing an aqueous sample for methyl mercury without a distillation step. With direct ethylation, the sample matrix is only modified by the addition of citrate buffer at the time of analysis. Currently, direct ethylation can only be preformed on an automated methyl mercury analytical system. A technique for using the manual purge-and-trap system has not yet been developed. The elimination of the distillation step makes analysis of aqueous samples for methyl mercury much faster and more efficient.

Methods

Distillation. Approximately 50 mL of sample preserved to 0.4% (v/v) with HCl is weighed out in a Teflon™ vial. To this, 0.5 mL of 9 M H_2SO_4 and 0.2 mL of 20% (w/v) KCl/0.2% (w/v) L-cysteine are added. The sample vial is then put in a 138 °C hot block and attached via 1/8"-in Teflon tubing to a second vial that is kept in ice, with nitrogen gas flowing from the hot block to the chilled vial. The samples distill for 2-4 hours and are then ready for analysis.



Direct Ethylation. No preparation is required. The preserved sample is weighed out directly into the analytical vial.

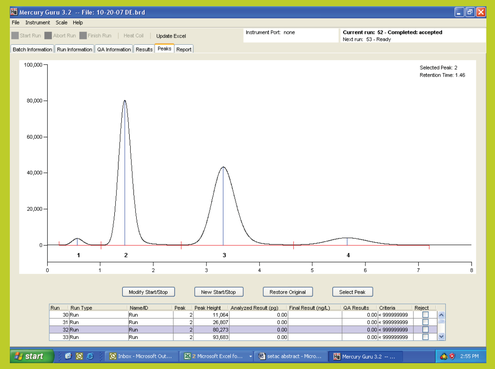
Analysis. The sample to be analyzed is weighed out into a 40-mL amber borosilicate glass vial with a septum-topped lid. To this, 4 mL of citrate buffer and 0.05 mL of a 1% (w/v) sodium tetraethylborate ($NaBEt_4$)/ 2% (w/v) potassium hydroxide (KOH) solution are added. The vial is then filled the remainder of the way with reagent water. The sample is capped and put on the MERX autosampler for analysis.

Discussion

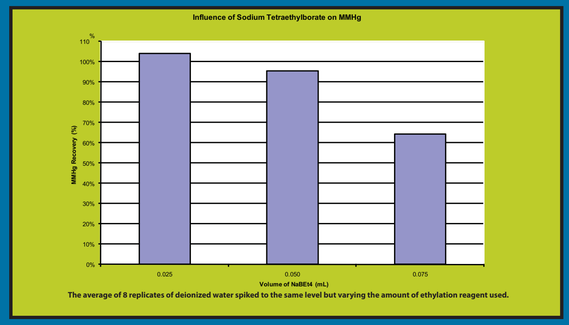
There are mercury cations in the aqueous sample, primarily CH_3Hg^+ and Hg^{2+}. $NaBEt_4$ works by adding ethyl groups to the mercury cations in the sample, making them volatile and available for pre-concentration onto a Tenax™ trap. The ethylated mercury species can then be desorbed from the pre-concentration trap and separated by the use of a gas chromatography (GC) column. The mercury species are pyrolyzed as they elute from the GC column, reducing to elemental mercury, which is detected using CVAFS. $NaBEt_4$ is the critical component in analysis for MMHg. In order to achieve consistent results, it is imperative that the pH of the sample is between 4.5 and 5.0. If the correct pH range is not obtained, the MMHg recovery will be low. The addition of citrate buffer plays a key role in achieving and maintaining the correct pH.

As part of the direct ethylation study, a surrogate spike (n-propyl mercuric chloride) was used. The surrogate mirrors the performance of MMHg in the sample. Adding a surrogate spike to each of the samples is helpful because it will indicate poor ethylation or matrix interferences.

The volume of ethylation reagent added was also found to be critical. Fifty percent more ethylation reagent significantly inhibited MMHg recoveries. Fifty percent less ethylation reagent made very little difference. For the purposes of this study, 0.05 mL of the ethylation reagent solution was used.



Typical chromatogram using Guru 3.2. Peak 1 is Hg (0), peak 2 is the monomethyl mercury peak, peak 3 is the Hg (II) peak, and peak 4 is the surrogate n-propyl mercury peak.

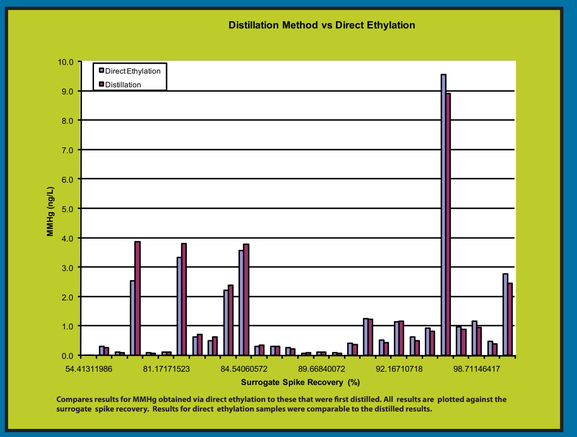


The average of 8 replicates of deionized water spiked to the same level but varying the amount of ethylation reagent used.

With direct ethylation, there is a risk of contaminating the GC column with a variety of organic compounds that may be present in the samples, because there is no distillation step that cleans up the sample prior to analysis. A solution to this problem would be to use a capillary GC column with a ramping program set to increase after every run. The ramping of temperature has two positive effects; it thoroughly cleans the GC column between analyses and it helps the larger compounds elute from the column, resulting in sharper peaks even as retention times increase. An isothermal GC packed with OV-3 was used in this experiment, as it is less expensive and is the standard equipment on the Brooks Rand Labs MERX MMHg autoanalyzer. The isothermal GC gave good MMHg peaks throughout the experiment. The MMHg peaks were sharp and symmetrical with a retention time of 1.4 minutes. The MMHg recoveries did not degrade throughout the analytical run, even though a cleaning step was not done after each analysis. If the GC column is not cleaned, it could lead to interferences in the future. As a maintenance measure, the GC column should be heated to at least 180 °C weekly. The surrogate peaks, with a retention time of 6 minutes, were short and broad but symmetrical. The surrogate peaks could not be integrated using peak height as the MMHg peaks are. However, integration of the surrogate peaks using peak area gave adequate calibrations and was reproducible.

Conclusion

Direct ethylation greatly increases the efficiency of MMHg analysis in water without compromising the quality of the data. Achieved MDLs were 2-3 times lower than what was achievable by distillation. The addition of a surrogate spike was useful to assessing recovery and ethylation efficiency. The relative percent difference, RPD, between distilled samples and directly ethylated samples were generally less than 10% when the surrogate spike recovery was more than 80%. When the surrogate spike recovery was greater than 80%, the results for directly ethylated samples were generally slightly higher than the results for the same samples that had been distilled. As the surrogate spike recovery decreased, the results from the direct ethylation samples were lower than those that had been distilled, indicating the sample needed to be reanalyzed at a dilution.



Compares results for MMHg obtained via direct ethylation to these that were first distilled. All results are plotted against the surrogate spike recovery. Results for direct ethylation samples were comparable to the distilled results.

The MDL was calculated by multiplying the standard deviation of a number of replicates (n), by the student-t value (n-1) at the 99% confidence level. Using direct ethylation, MDLs of 0.004 to 0.009 ng/L were regularly obtained. For distilled samples, MDLs ranged from 0.011 to 0.014 ng/L under optimal conditions. It was found that in order to get MDLs less than 0.015 ng/L for distillation, an extra cleaning step for the distillation vials was needed. Without that extra cleaning step, the MDLs would be slightly higher, though consistently below 0.020 ng/L. Direct ethylation allows for reproducible results that are very similar to those achieved by distilling the sample first, but has the added advantage of achieving lower MDLs with a much higher throughput.

References

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