A Technique for the Simultaneous Determination of Monomethyl and Monoethyl Mercury in Aqueous Samples

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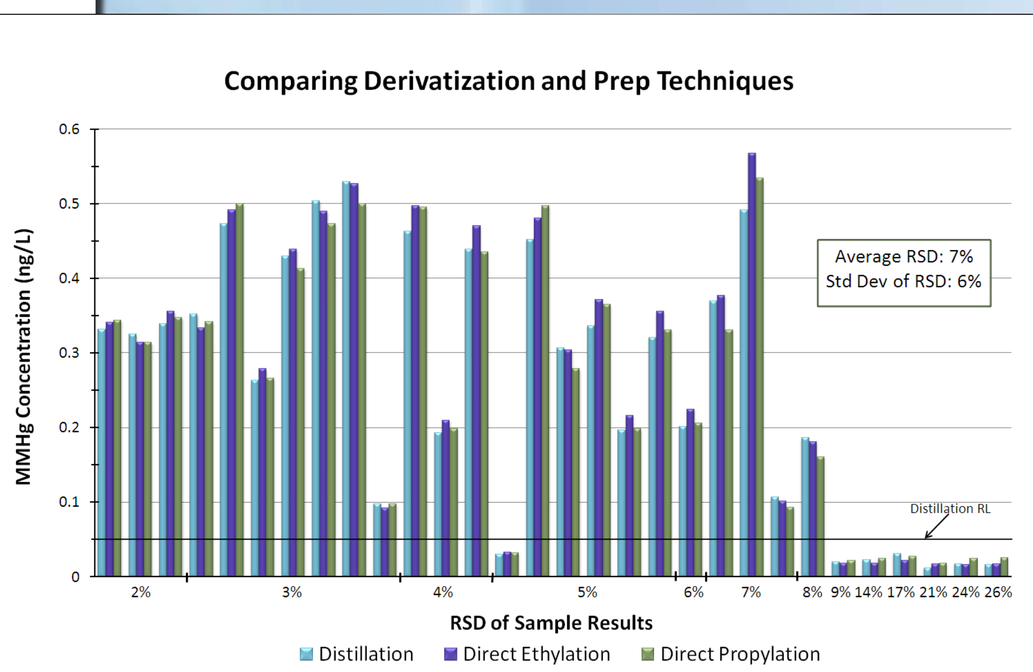
Monomethylmercury (MMHg) has been studied extensively since reliable methods for quantification were developed in the late 1980s. It has been well established that MMHg in the environment is often a byproduct of microbial metabolism, bioaccumulates in the food chain, and is one of the most toxic forms of mercury. Less attention has been given to another organic mercury species, monoethylmercury (EtHg).

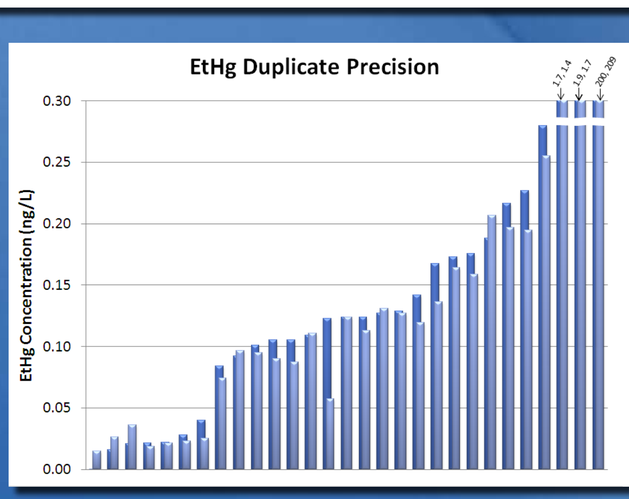
One of the sources of EtHg is as a metabolite of thiomerisol, a commonly-used preservative and antimicrobial in many vaccines. As awareness of the toxicity of alkylmercury compounds has increased, so has the concern over their presence in humans and the environment. To study EtHg at low-level concentrations, as are expected in most environmental samples, a robust and sensitive method for detection and quantification is required.

An analytical technique utilizing sodium tetra(n-propyl)borate ($NaBPr_4$) has been developed to determine MMHg and EtHg concentrations in prepared biological samples with great success (Gibičar, 2007). This method is similar to the EPA-approved methodology for MMHg analysis in waters, except that $NaBPr_4$ is used as the derivatization reagent. Additionally, a method has been developed for analyzing water samples for MMHg without a distillation step. In this method, sodium tetraethylborate ($NaBEt_4$) is added directly to a buffered sample just before analysis for determination by "direct ethylation" (Yu, 2006). The goal of this study was to combine those two techniques into a "direct propylation" method, allowing the simultaneous analysis of MMHg and EtHg in aqueous samples.

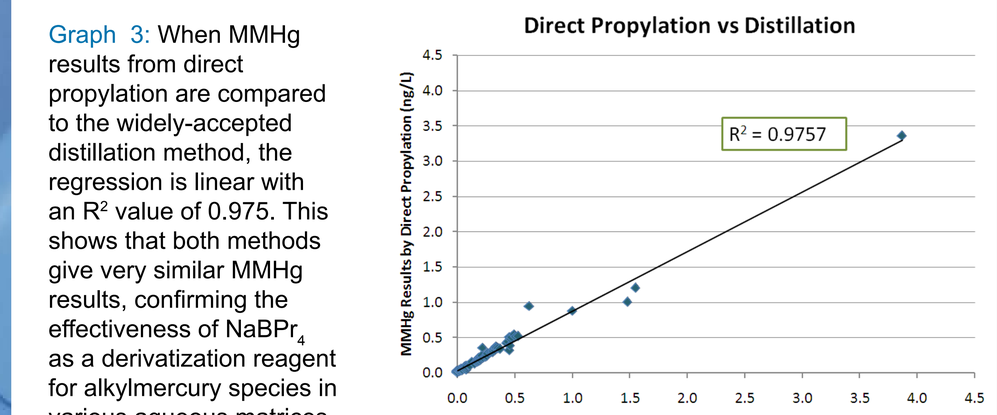
For this direct propylation method, an acid-preserved water sample is buffered just prior to zero-headspace derivatization with $NaBPr_4$, followed by cold vapor pre-concentration onto a Tenax™ trap, isothermal gas chromatography (GC) separation, thermal decomposition, and atomic fluorescence spectrometric detection. All analyses were performed using a Brooks Rand Labs MERX™ system configured for automated MMHg analysis.



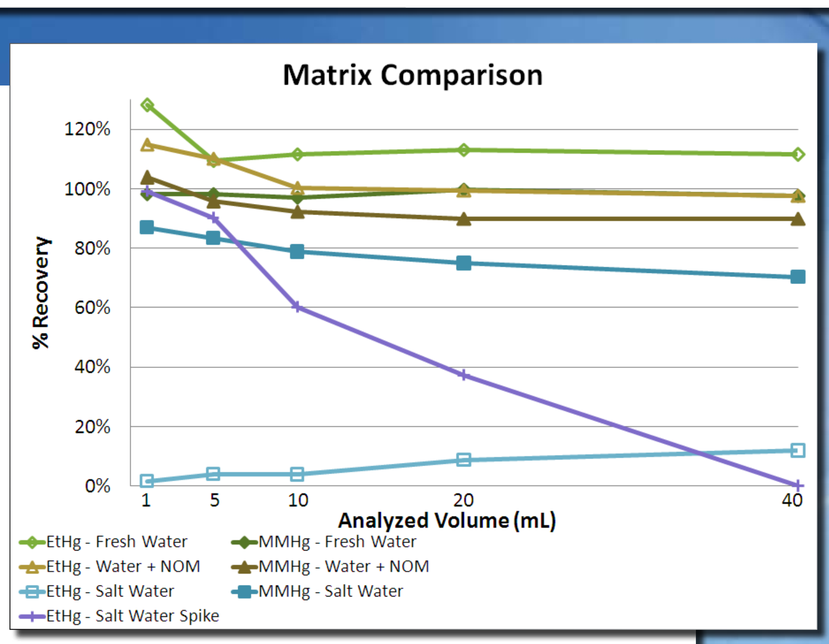
Graph 1: To verify the efficiency of the derivatization using $NaBPr_4$, a side-by-side comparison of the results for three different MMHg analysis methods was performed: *Distillation* – results for distillation followed by derivatization with $NaBEt_4$, *Direct Ethylation* – results for direct ethylation with $NaBEt_4$, and *Direct Propylation* – results for direct propylation with $NaBPr_4$. The RL for the distillation method (0.050 ng/L) was assumed for all techniques.



Graph 2: The samples were analyzed for EtHg twice on different days. Both results are graphed. Most samples had acceptable duplicate precision with RPDs of < 20%. Only two samples that were above the EtHg RL had poor duplicate precision. The corresponding MMHg results for those samples had excellent duplicate precision indicating the direct propylation technique is not the cause of the variability seen in these samples results.



Graph 3: When MMHg results from direct propylation are compared to the widely-accepted distillation method, the regression is linear with an R^2 value of 0.975. This shows that both methods give very similar MMHg results, confirming the effectiveness of $NaBPr_4$ as a derivatization reagent for alkylmercury species in various aqueous matrices.



Graph 4: Three common environmental water matrix types were tested: *Fresh Water* (preserved to 0.4% with HCl), *Water + NOM* (reagent water high in dissolved organic carbon, spiked with ~10 mg/L of natural organic matter preserved with HCl), and *Salt Water* (preserved with H_2SO_4). All of the test samples were fortified with MMHg and EtHg, since the naturally occurring levels were very low. They were analyzed in triplicate two months after fortification and preservation. They were analyzed at 1, 5, 10, 20, and 40 mL aliquot sizes to investigate the influence of the matrix on analyte recovery. For the *Fresh Water* and *Water + NOM* matrices, both MMHg and EtHg recoveries were ≥ 90% at all analysis volumes. MMHg recoveries in the *Salt Water* matrix were biased low (70-87%), even at the lowest aliquot size, and continued to decrease with increasing analysis volumes. EtHg showed extremely low recoveries at all analysis volumes in *Salt Water*. As a result of the low recoveries, additional *Salt Water* samples were fortified with known amounts of EtHg just previous to derivatization, the results are graphed as *Salt Water Spike*. The recoveries for the *Salt Water Spike* samples were good at the 1 mL and 5 mL aliquot sizes, and decreased sharply at greater analysis volumes, indicating some interference from the *Salt Water* matrix. This matrix may be dealkylating the EtHg, which is an occurrence that has been previously reported (Suda, 1993).

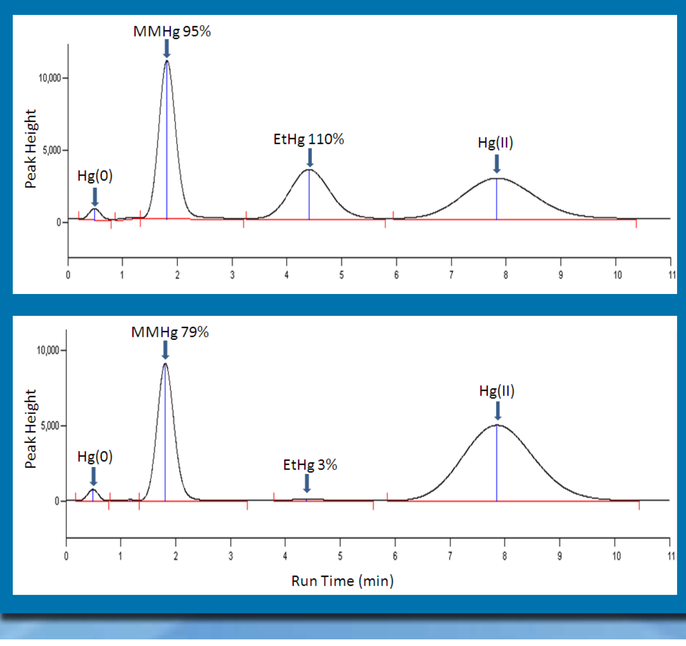
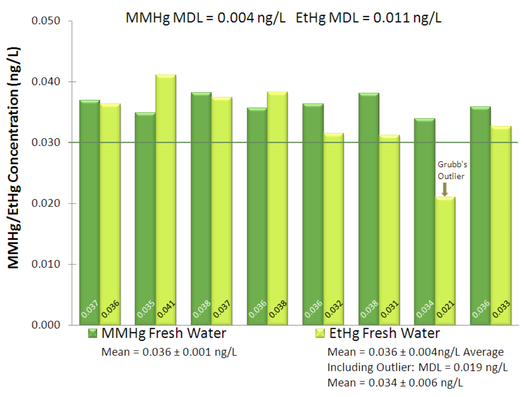
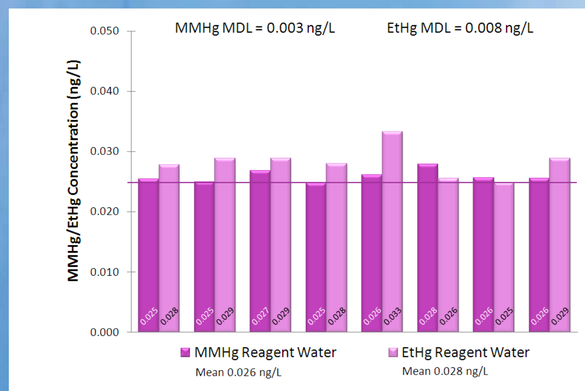


Figure 1: Chromatograph for analysis of *Water + NOM*, demonstrating good spike recoveries for both MMHg and EtHg.

Figure 2: Chromatograph for analysis of *Salt Water*, demonstrating good spike recovery for MMHg and poor spike recovery for EtHg.

Graph 5: MDL study of MMHg and EtHg in *Fresh Water* fortified with 0.030 ng/L of each analyte. Results slightly higher than the fortified value are expected due to the ambient level of the analytes in the *Fresh Water* sample.





Graph 6: MDL study of MMHg and EtHg in reagent water fortified with 0.025 ng/L of each analyte.

Conclusions

Direct propylation of samples was an excellent derivatization method for simultaneous MMHg and EtHg determination.

- There were very few issues caused by matrix interferences.
- The MMHg concentrations determined by direct propylation compared very well to both direct ethylation and distillation prior to ethylation.
- The EtHg analyses demonstrated excellent precision.
- Low method detection limits (MDL) were obtained for both MMHg and EtHg using direct propylation.

Pros

- simultaneous determination of MMHg and EtHg, and potentially Hg(II)
- low MDLs for both MMHg and EtHg
- quick and easy
- good accuracy and precision, as demonstrated through matrix spike recoveries
- can use commercially available instrumentation - Brooks Rand Lab MERX™

Cons

- $NaBPr_4$ is expensive
- matrix effects noted for salt water matrix; potentially other interferences for matrices other than fresh waters
- broad peaks for EtHg and Hg(II) – a GC with temperature ramping capabilities would produce sharper peaks

References

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