

Introduction

Mercury is one of the most widely known toxic elements existing in the environment. It is released into the atmosphere naturally from coal-fired power plants and can also be released from industrial activities such as mining. Metallic element, inorganic salts, and organic compounds are three existing forms of mercury¹. Mercury released into the atmosphere deposits into bodies of water and soils and where it can be converted into methyl mercury by microbial activity. Methyl mercury, an organic form of mercury, is one of the most toxic forms. Methyl mercury bioaccumulates up the food chain, ultimately resulting in consumption in large concentrations by humans². Ingestion of fish is the most common human exposure to methyl mercury. For example, a devastating incident occurred during mid 1950s in Minamata Bay, Japan, where factory effluent caused the bay to become contaminated with methyl mercury. People in Minamata Bay ingested the contaminated fish, which caused symptoms such as numbness in limbs, slurred speech, brain damage, insanity, deaths and deformed and mentally impaired newborn babies. The incident in Minamata Bay exposed many of the serious affects of methyl mercury poisoning.

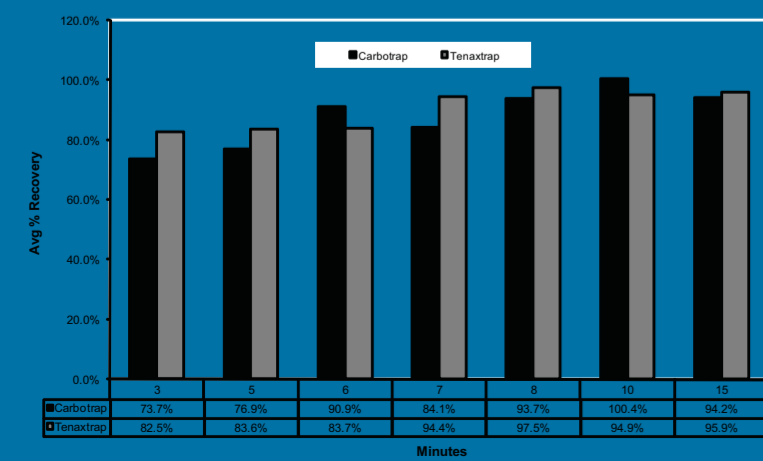
EPA Draft Method 1630 is used to determine methyl mercury in water samples by purge and trap preconcentration followed by cold vapor atomic fluorescence spectrometer (CVAFS). In the EPA method, Carbotrap™ is mentioned as means of preconcentrating mercury species from the sample during the cold vapor generating step. Carbotrap™ is graphitized carbon that relies on electrostatic attraction to its high surface area of bulky-balls and nano tubes³. Although Carbotrap™ is mentioned in method 1630, the method is performance based and equipment modifications are allowed. Due to the difficulty in obtaining Carbotrap™ material of consistent quality, many laboratories stated using use Tenax™, a proprietary trapping material. Tenax™, a porous polymer based on 2,6-diphenylene oxide, is a chromatographic media used as a trapping agent. Both traps are weak absorber and are used to determine the concentration of various volatile organic compounds including methyl mercury.

There are various pros and cons between two materials. For example, Tenax™ seems to be manufactured to a more consistent level of quality than Carbotrap™. Carbotrap™ has been noted to last less than a month of normal use, while Tenax™ generally lasted approximately six months. On the other hand, Tenax™ gives a broader, more rounded peak shape by CVAFS than Carbotrap™ (figure 1). Tenax™ material can degrade with exposure to high temperatures, however the material is white and turns tan when it degrades. This benefit allows an analyst to determine when a trap is diminishing in quality and can be discarded before it affects the data. Carbotrap™ is black and has to first be analyzed to observe the peaks and recoveries before being able to determine the quality of the trap.

Though Tenax™ is used by many laboratories as a trapping agent for methyl mercury, a formal comparison of the two trapping materials does not exist in research literature. Therefore, a study was undertaken to evaluate the strengths and weaknesses of Carbotrap™ compared to Tenax™ trapping material for methyl mercury analysis. Several parameters were evaluated and compared. Recoveries of known quantities of methyl mercury spiked standards over a variety of conditions (e.g., breakthrough, carryover, purging times, and drying times) were also tested.

Purging Time

Each trap was spiked with 25pg of methyl mercury standard and was purged for three, five, six, seven, eight, ten, and fifteen minutes with four replicates on each trap type at each purge time. Results are shown in (figure 2) as average % recoveries. Carbotrap™ had about 15% and Tenax™ about 10% lower recoveries at three to five minutes of purging. Unlike Carbotrap™, Tenax™ seems to give more consistent results with around 95% accuracy after seven minutes of purging. Carbotrap™ did give results above 90% after six minutes but were less consistent. Both traps at 15 minutes of purging time showed excellent recoveries.



A Comparison of Preconcentration Trap Materials for Use in Determination of Monomethyl Mercury by Cold Vapor Atomic Fluorescence Spectroscopy

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Methods

EPA Method 1630 (Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS) was used for this study. About 50mL of deionized water with known concentration of methyl mercury spiked standards were buffered with 0.300mL of 2 M Acetate buffer in a purge vessel (bubbler). Then 0.050mL of 1% sodium tetraethyl borate (NaBEt4) and 2% potassium hydroxide (KOH) solution was added to the purge vessels as an ethylation reagent. Purge vessels were left alone for fifteen minutes to ensure complete ethylation of the sample. After ethylation, the methyl mercury molecules, now methylethyl mercury become volatile and are swept out of the solution onto the trap by purging with mercury free nitrogen (N₂) at a flow rate of 40 psi fifteen minutes. Traps were then dried with N₂ for five minutes to ensure that moisture was not trapped within the material. The trapped methylethyl mercury was thermally desorbed from the traps into an argon gas stream at 45 psi that carried it into the gas chromatography column (GC column), through a pyrolytic coil, and then into the cell of a cold-vapor atomic fluorescence spectrometer detector.

The traps were tested using a Brooks Rand Model III AFS with an isothermal GC oven set at 95 °C and a 50-cm GC column packed with OV-3 by Brooks Rand Labs. Peaks were measured with Guru™ basic integration and control software. Brook Rand Labs also packed the preconcentration traps used for this study.



Purge Vessels



Brooks Rand Model III AFS, Pyrolytic Coil and Temperature Controlled GC

24 Hour Hold Time

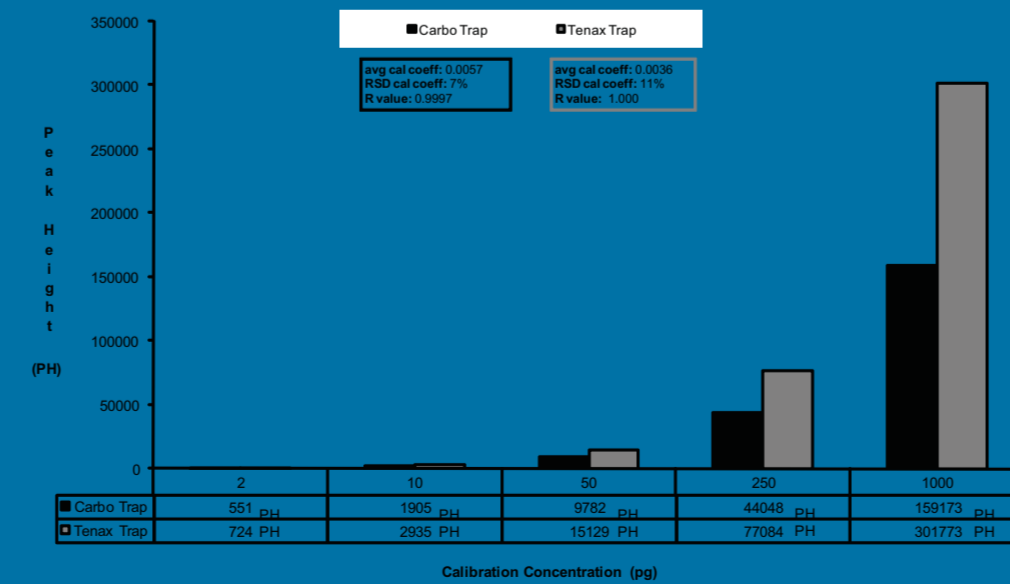


Figure 4a

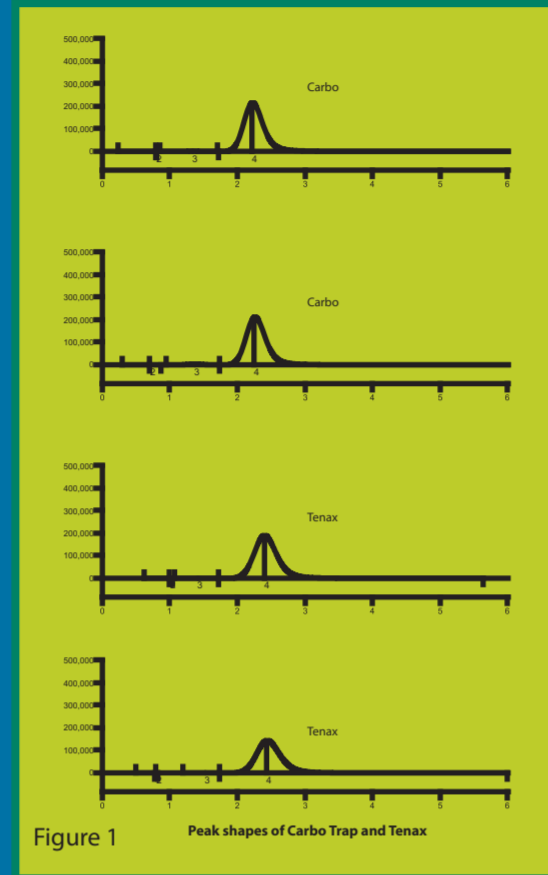


Figure 1 Peak shapes of Carbotrap and Tenax

Drying Time

Drying time testing was performed for zero, two, five, ten, fifteen, and thirty minutes in sets of four. Results were averaged in % recovery and are shown in figure 3a. Tenax™ showed abnormally bumpy Hg²⁺ peaks and yielded low recoveries around 60% at zero minutes of drying time (figure 3b). However, a drying time of two minutes made a significant difference in % recovery and peak shapes for Tenax™ trap material. Both traps recovered well for five, ten, and fifteen minutes of drying time. However, Carbotrap™ had poor recoveries when traps were dried for thirty minutes. Zero minute and two minute drying time was not performed for Carbotrap™.

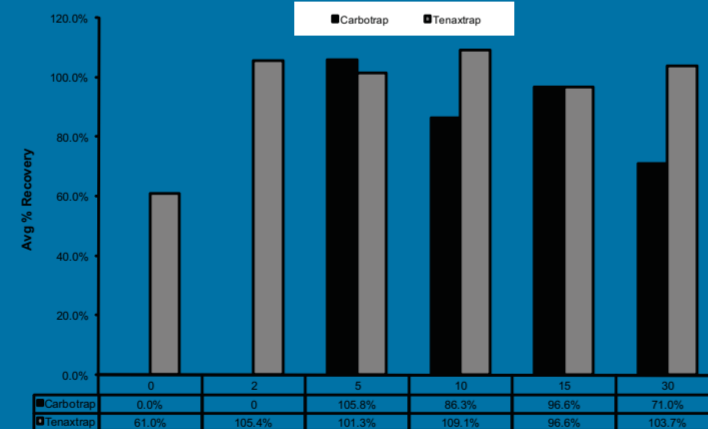


Figure 3a

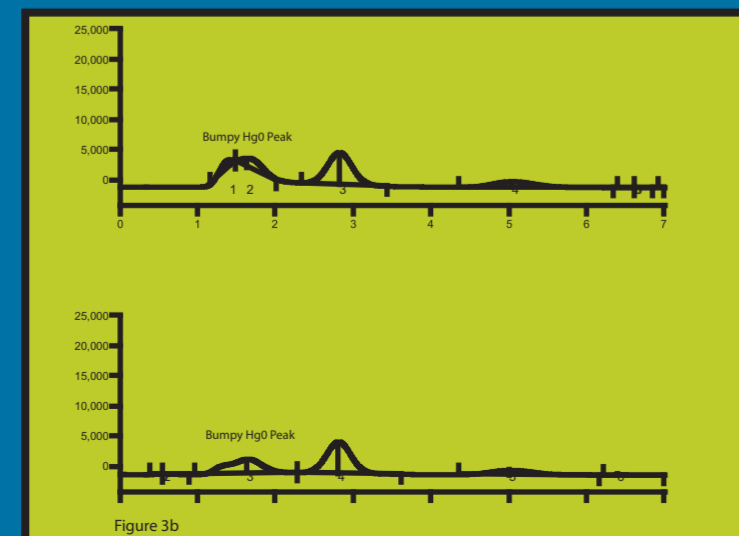


Figure 3b Peak shapes of Tenax when it was not dried with mercury-free nitrogen

48 Hour Hold Time

Traps were purged with known concentrations of methyl mercury standard of 2, 10, 50, 250, and 1000 pg (Brooks Rand Labs usual calibration concentration). Traps were then plugged and stored in a dark place for twenty-four hours and forty-eight hours before they were analyzed. Although, after forty-eight hours, Tenax™ lacked Hg²⁺ peak at the 1000pg level and Carbotrap™ lacked Hg²⁺ peaks at the 10, 50, 250, and 1000 pg level, the methyl peak was not affected. Calibrations for both twenty-four hours and forty-eight hours displayed r value greater than 0.9995. Results are shown on figure 4a and 4b.

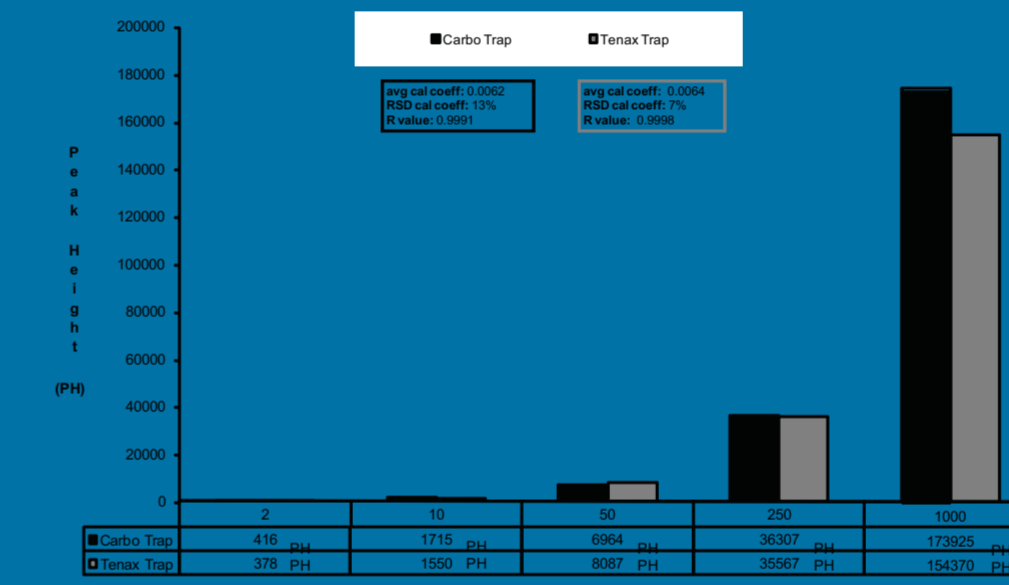


Figure 4b

Carryover

Carryover testing was performed by purging high concentration of methyl mercury standard, analyzing the trap and reanalyzing the same trap again to determine if any residual methyl mercury was on the traps. Testing was done at 500, 1000, 2000, 3000, and 4000 pg levels. Neither type of trap showed a significant amount of carryover. Carbotrap™ did show bit more carryover at 3000, and 4000pg level than Tenax™. Results were averaged and compared in figure 5 along with average percent recoveries of the concentration.

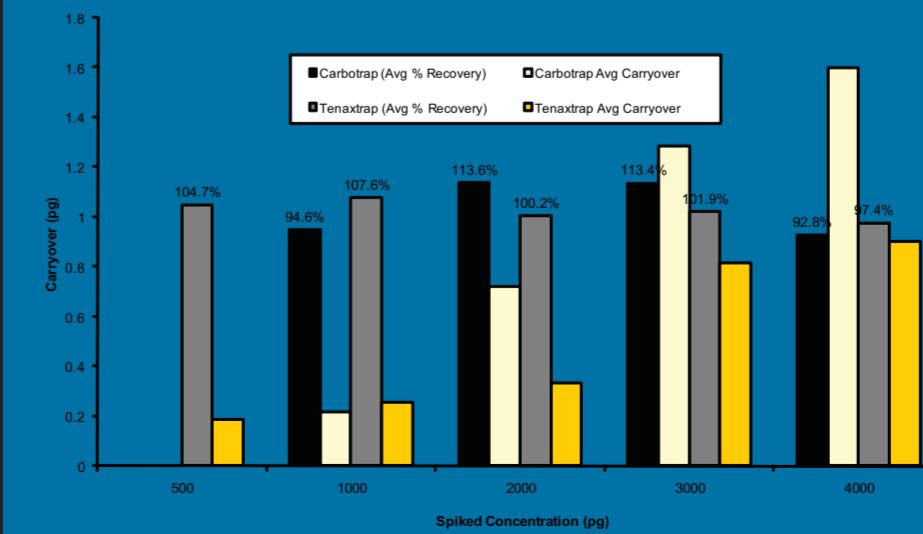


Figure 5

Tenax™



Carbotrap™



Breakthrough

Concentration (pg)	Carbotrap Recovery (%)	Carbotrap Breakthrough (%)	Tenaxtrap Recovery (%)	Tenaxtrap Breakthrough (%)
2	100%	4%	98%	0%
10	113%	0%	98%	0%
50	126%	0%	95%	2%
250	73%	0%	100%	8%
1000	105%	-	95%	4%

Concentration (pg)	Recovery (%)	Breakthrough (%)	Average Breakthrough (%)
1000	105%	0.00%	0.00%
1000	44%	0.00%	0.00%
1000	103%	0.00%	0.00%
1000	99%	0.00%	0%
2000	103%	1.01%	0.26%
2000	102%	0.62%	0.26%
2000	89%	0.28%	0.26%
4000	83%	1.25%	1%
4000	97%	0.00%	0.00%
4000	91%	0.56%	0%

Concentration (pg)	Recovery (%)	Breakthrough (%)	Average Breakthrough (%)
1000	92%	0.15%	0.15%
1000	70%	0.88%	0.40%
1000	97%	0.27%	0.40%
1000	89%	1.40%	1%
2000	88%	0.81%	0.81%
2000	91%	0.98%	0.98%
2000	93%	0.54%	0.54%
2000	94%	0.30%	1%
4000	93%	0.25%	0.25%
4000	92%	0.05%	0%

Conclusion

Parameters	Carbotrap™	Tenax™
Purging time	Optimum average % recovery at ten min. Worst at three min. Recoveries vary from 84% to 100% after six min.	Optimum average % recovery at eight min. Worst at three min. Fairly consistent after seven min.
Drying time	Poor recovery when dried for thirty min. Optimum recovery at 5 min.	Excellent recoveries as long as it is dried.
24 hour holding time	RSD= 7% R value= 0.9997	RSD= 11% R value= 1.000
48 hour holding time	RSD= 13% R value= 0.9991	RSD= 7% R value= 0.9998
Carryover testing	High carryover (about 1.6 pg) with 92.8% recovery of at 4000 pg level.	Lower carryover (about 0.9 pg) with 97.4% recovery at 4000 pg level.
Breakthrough	Average of 1% or less breakthrough.	Average of 1% or less breakthrough.

The purpose of this study was to observe the difference between Carbotrap™ and Tenax™. Both trapping materials are intended to measure various organic compounds; however, this study was focused on methyl mercury. Visible peak shapes were compared and various tests were performed based on EPA method 1630. During purging time and carryover testing phase, Tenax™ showed more consistency and less carryover was observed at the 4000 pg level. Carbotrap™ yielded sharper peaks throughout the tests and less breakthrough. Both trap materials absorbed and desorbed methyl mercury efficiently and they reacted similarly to different drying time and purging time. There was much more variability within Carbotrap™ than Tenax™. For example, during the forty-eight hour holding time, Carbotrap™ yielded 13% relative standard deviation (RSD) and Tenax™, 7%. Although EPA method 1630 mentions the use of Carbotrap™, observations from this study show that Tenax™ is a suitable substitution.

References

1. L. R. Goldman, M.W. Shannon and the Committee of Environmental Health, *Technical Report: Mercury in the Environment: Implications for Pediatricians*, 2001.
2. A. A. Saulo, *Methylmercury in Fish*, 2004
3. N. S. Bloom, *Speciation of Mercury*, class notes (available upon request), 2004