

Improving data quality on low level mercury wastewater analysis†

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In order to compare treatability test results evaluating low-level mercury (Hg) removal from oil refinery wastewater, improvements in Hg analytical methods were conducted at two US EPA certified analytical labs. The revisions in the analytical protocols improved Hg recoveries and hence enabled more reliable data interpretation and comparison for the specific wastewater tested. Nevertheless, significant differences between results from the two laboratories were identified in a split-sample experiment.

Introduction

The implementation of the Great Lakes Initiative (“a combined effort between the United States and Canada to help restore, maintain, and protect the ecosystem of the Great Lakes Basin”) (GLI) requires many point-source discharges within the Great Lakes basin to bring their final effluent Hg concentration to 1.3 ng L⁻¹ (parts per trillion).¹ Meeting the world’s most stringent surface water discharge limit represents a challenge because existing technologies either are not capable of removing mercury to such low levels, require adaptation to do so, or have not been tested at these low concentrations.

In our study, a broad range of technologies from the currently available wastewater treatment “toolbox” were tested at the bench scale using the same refinery wastewater effluent to determine if the Great Lakes Initiative’s (GLI) mercury discharge standard of 1.3 ng L⁻¹ could be met.² To minimize and understand experimental error and quality boundaries, the low Hg concentrations in the refinery effluent required the use of a Class 100 clean room (ISO class 5 clean room), specialized equipment cleaning methods, the use of “clean hands/dirty hands” procedures while conducting both the testing and the sample analysis, as well as analytical procedures with appropriate sensitivity.^{3,4} Two EPA certified analytical laboratories, namely Lab A and Lab B, were used for the analysis of the samples by EPA Method 1631E; however, during the course of the study, several difficulties in applying this method to refinery wastewater were found and overcome.

Method 1631E was developed by the EPA to determine Hg in the range of 0.5–100 ng L⁻¹ in ambient water and wastewater samples by oxidation, purge and trap and cold-vapor atomic fluorescence spectrometry.³ The lowest quantification limit of 0.5 ng L⁻¹ is below the GLI discharge standard of 1.3 ng Hg L⁻¹.¹ EPA Method 1631E is a performance-based method, which means that labs have a certain level of discretion in adjusting their procedures as long as all performance requirements specified within the method are met. The method’s detection limit (MDL) has been determined to be 0.2 ng L⁻¹ when there are no interferences present in the water samples. However, it is possible to obtain an MDL as low as 0.05 ng L⁻¹ when a large sample volume is used for analysis and extra steps are taken during sample handling.^{3,4} The acceptable matrix spike (MS) and matrix spike duplicate (MSD) recovery range for this method was 71–125%. MDLs and quantification are usually dependent on the level of interferences.³ Although there was no interference reported during the US EPA’s development of this method on marine and fresh water as well as on secondary effluent samples taken from a sewage treatment plant, the

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Environmental impact

The implementation of the Great Lakes Initiative (“a combined effort between the United States and Canada to help restore, maintain, and protect the ecosystem of the Great Lakes Basin”) requires many point-source discharges within the region to bring their final effluent Hg concentration to 1.3 ng L⁻¹ (parts per trillion) which is the world’s most stringent surface water discharge limit. To determine the best available technology alternatives for each discharger in this region, there is a need to improve data quality on low level mercury wastewater analysis by Method 1631. The improvements in Hg analytical methods were conducted at two US EPA certified analytical labs to compare treatability test results evaluating low-level Hg removal. The revisions in the analytical protocols improved Hg recoveries and hence enabled more reliable data interpretation and comparison for the specific wastewater tested.

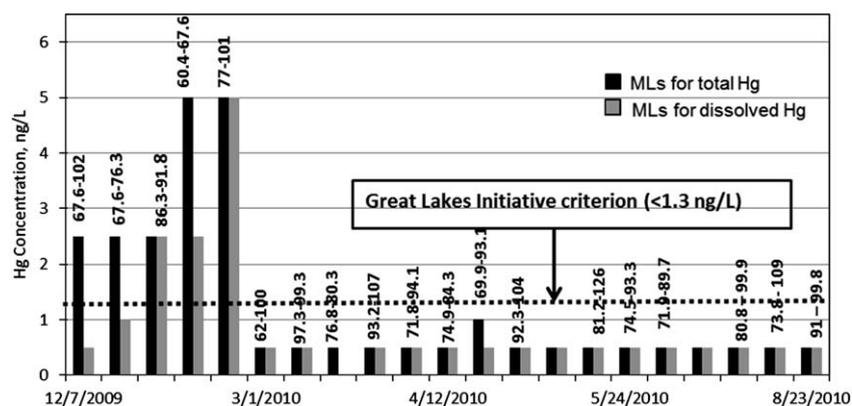


Fig. 1 MLs for Laboratory A over time. Black figures show recovery ranges. The first 5 sample dates were before method optimization.

matrix interferences might be challenging for the analysis of high strength industrial wastewater samples. As industrial dischargers begin to use this method to document compliance to new discharge limits, wastewater-specific matrix constituents, such as organics and solids, may influence the analytical method performance.

Average Hg concentrations in the wastewater samples for this study were between <0.5 and 10 ng L^{-1} .² Early in the study it was found that sample dilutions to increase the recovery and decrease matrix interferences in the refinery wastewater samples in several cases increased the minimum level of quantitation (MLs) to as high as 5 ng L^{-1} (Fig. 1). These higher MLs, even though the MS recoveries were within the EPA acceptance criteria, meant that the initial test results obtained from Lab A could not be used to evaluate and compare the effectiveness of each treatment technology in achieving the target Hg concentration.

Another difficulty encountered was the wide range of MS recovery allowed by the 1631E method. Recoveries in the lower end of this range were not sufficient to ensure that all detectable concentrations reported as lower than 1.3 ng L^{-1} would in fact be truly below this limit. Several residual Hg concentrations in the filtered wastewater were in the range of 0.5 to 1 ng L^{-1} , which, depending on the analytical recovery, might be above 1.3 ng L^{-1} when the percentage recoveries are at the lower end of the acceptable range, $\geq 70\%$.

Results and discussion

In order to address these issues, the authors worked with both commercial analytical labs to improve the method for the specific purposes of this study. The method suggests that an increase in the volume of BrCl from 0.5 mL to 5 mL per 100 mL of water sample and the digestion at elevated temperatures ($50 \text{ }^\circ\text{C}$ for 6 h) in sealed bottles instead of room temperature might be necessary to overcome the matrix interferences in the water samples containing organics and solids.

In this study, the 1631E method was modified with higher BrCl concentrations, longer oxidation times and elevated temperatures. Lab A digested wastewater samples in a series of steps. First, each 100 mL of water sample was digested with 5 mL of BrCl at $60 \text{ }^\circ\text{C}$ for 24 hours . After completion of 24 hours of oxidation, digested samples were further digested with the addition of a second 5 mL of BrCl at $60 \text{ }^\circ\text{C}$ for 6 hours . Lab A mixed the BrCl after each addition by hand shaking several times. Lab B digested wastewater samples with $2\text{--}5 \text{ mL}$ BrCl per 100 mL of water sample at $50 \text{ }^\circ\text{C}$ for 8 hours , mixing by inverting the sample by hand a few times. The tested digestion conditions are much harsher than the Method 1631 guidelines.

The modifications in the analysis method resulted in the release of particle bound Hg within wastewater samples, and hence higher Hg

Table 1 Comparison of Lab A and Lab B split samples after method improvement^d

Lab	Data summary	Sample "as is" (duplicate) ^a	Sample after $0.45 \mu\text{m}$ filtration	Filtered sample with 10 ng/L Hg^{+2} spike (duplicate)	Filtered sample with $5 \text{ ng L}^{-1} \text{ Hg}^{+2}$ spike	MilliQ ($18 \text{ M}\Omega \text{ cm}$ resistivity) with $5 \text{ ng L}^{-1} \text{ Hg}^{+2}$ spike	Trip blank
Lab A ^b		3.35	<0.5	7.26	3.06	3.9	<0.5
		3.43	<0.5	6.13	3.57		
		3.50	<0.5	6.32	3.88		
	Average	3.43		6.57	3.50		
	Std. Dev.	0.08		0.61	0.41		
	Deviation%	2.2		9.2	11.8		
Lab B ^c		4.0 (4.19)	0.52	9.35	4.76	4.67	<0.5
		2.19	0.55	9.26 (9.73)	4.67		
		4.57	0.74	9.35	4.57		
	Average	3.59	0.60	9.32	4.67		
	Std. Dev.	1.24	0.12	0.05	0.10		
	Deviation%	34.6	19.8	0.6	2.0		

^a Analytical duplicates: analytical duplicates were not provided by Lab A on samples from this project. ^b Commercial lab reported MS/MSD recovery for this set of samples was $74.2\text{--}88.8\%$. ^c Commercial lab reported MS/MSD recovery for this set of samples was $95.6\text{--}104\%$. ^d Sample filtration and Hg^{+2} spiking done by authors. Analysis done by commercial EPA certified labs.

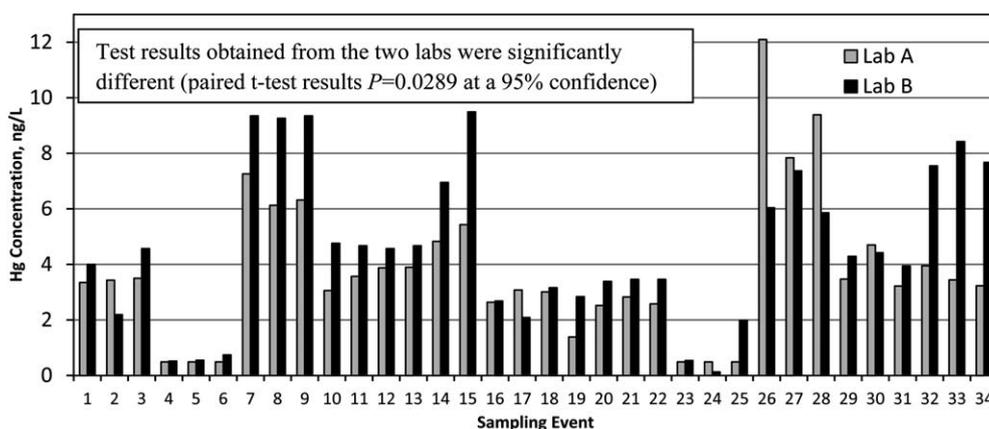


Fig. 2 Comparison of Lab A and Lab B Hg split sample test results.

recoveries. This is consistent with what has been reported by Lytle *et al.* (2008), namely that heated BrCl digestion yields better recoveries than room temperature BrCl digestion.⁵

After the method improvements, the authors spiked wastewater samples and compared analyses done by both labs, as shown in Table 1. Lab B reported consistently higher concentrations than Lab A, even after method improvement. Although both labs are using increased amounts of BrCl, heated digestion and similar mixing, Lab A is using approximately twice the amount of BrCl and heating at a slightly higher temperature for nearly four times longer than Lab B. It is unlikely that the difference in results can be attributed to a loss of BrCl from Lab A's increased heating time and temperature since the bottles are sealed as per the method. It may be that the difference is due to the relatively high level of BrCl used by Lab A and insufficient reduction of the BrCl after digestion. After digestion, hydroxylamine is added to the sample to reduce the BrCl—a color change from yellow to clear is used to indicate if the BrCl has been reduced. The visual observation of when this color change occurs may vary from analyst to analyst. The reduced sample is then poured into the bubbler, a SnCl₂ solution is added, and the sample is purged onto a gold trap with nitrogen. As per the method's guidance, high concentrations of BrCl in the bubbler can adversely affect the downstream gold traps, and show up as a matrix interference itself.⁶ It should be noted that both Lab A and Lab B reported MS/MSD recovery ranges (74.2–88.8% and 95.6–104%, respectively) within the limits mandated by Method 1631E.

To understand the differences between the two EPA certified labs, split samples from each wastewater batch were therefore routinely collected and sent to both Lab A and Lab B for side-by-side comparison. A total of 34 split samples were collected from March 11 to August 30, 2010, and analyzed by the two labs, as shown in Fig. 2. The results obtained from Lab B were usually higher because of the higher recoveries. The test results were also analyzed by a paired *t*-test at a 95% confidence interval, since the analyzed samples were from the same original batch. Statistical analysis showed that test results obtained from the two labs were significantly different ($P = 0.0289$ at a 95% confidence interval).

Conclusions

Method adjustment to address specific matrix issues such as high organic and solids concentrations in the refinery wastewater samples

was critical to increase the data quality and allow the determination of success or failure in meeting the GLI for the treatability tests. Increases in recoveries, even incremental, may be crucial for comparative studies and perhaps also for compliance monitoring. The revisions in the test protocols improved the expertise of the laboratories and hence enabled more reliable data generation for this specific wastewater type. An increase in the accuracy of the analytical results was necessary not only to strengthen the experimental data at near-detection limit concentrations but also to ultimately increase our understanding of the performance of the wastewater treatment technologies we tested. In spite of similar and significant work to optimize the extraction method, differences in quality of results between the two labs still persisted, highlighting the importance of benchmarking when operating under low level analyte concentrations.

Acknowledgements

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Notes and references

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