Determining Elemental Mercury in Soils by Selective Volatilization

Group 2

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Introduction

Remediation of mercury contaminated soils is an important area of research. One difficult aspect of planning remediation efforts is determining the speciation of the mercury present in the soil. Specifically, being able to selectively measure the amount of elemental mercury (Hg^0) present is crucial. Currently it is difficult to separate different mercury species when evaluating a contaminated site, as most extraction protocols alter the speciation of the mercury present. However, volatilization of Hg^0 has shown promise in this regard.[1]

Our selective volatilization method was developed to solve the problem of separating Hg^0 from non-volatile species. Carefully controlling the temperature while purging, allows for selective volatilization of elemental mercury from solid matrices. The mercury vapors are trapped and analyzed using cold vapor atomic fluorescence spectroscopy. Volatilizing mercury in this way provides a more accurate understanding of the elemental mercury content in contaminated soils.

The method was validated showing that elemental mercury can reproducibly be removed from a solid matrix and that this process is also selective against other common mercury species found in soils and sediments. The validation study included reference materials and soil samples from a remediation site with high levels of mercury present. Contaminated soils examined by selective volatization had comparable results with 5-step sequential extractions, which were historically used to characterize them.[2]

Common mercury species in soils

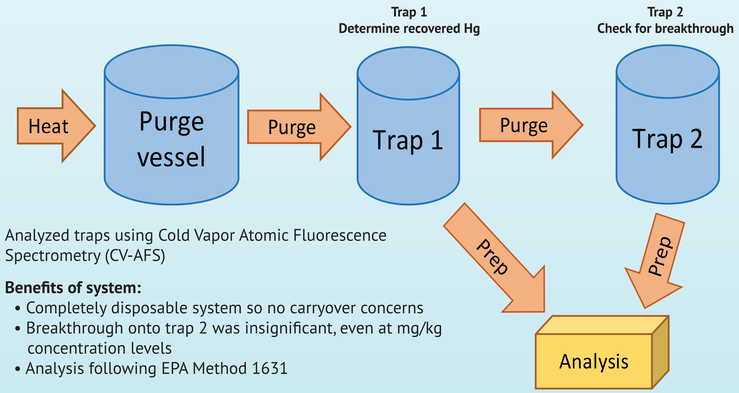
Organo-mercury complexes
- *eg* CH_3Hg^+

Ionic mercury
- *eg* $HgCl_2$
- Includes chelated ions

Elemental Mercury
- Main target for remediation

Mineral (Cinnabar HgS)
- Naturally occurring
- Mercury is sequestered

Procedure and Basic Apparatus



Analyzed traps using Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS)

Benefits of system:
- Completely disposable system so no carryover concerns
- Breakthrough onto trap 2 was insignificant, even at mg/kg concentration levels
- Analysis following EPA Method 1631

Reference Material Characterization

Reference material used for validation study

Reference materials for HgS, $HgCl_2$, and Hg^0 were produced by diluting the appropriate species into Kaolin and the mercury values were validated by a round robin study.[3]

These reference materials were used to determine selectivity of elemental Hg over other common Hg species found in soils.

Certified reference materials DOLT-5 and TORT-3 were used to test for specificity against methylmercury.

Concentrations of reference materials

TORT-3 (certified)
MeHg = 0.1370 mg/kg
Hg_{total} = 0.2920 mg/kg

DOLT-5 (certified)
MeHg = 0.1190 mg/kg
Hg_{total} = 0.4400 mg/kg

HgS (reference)
Hg_{total} = 2150 mg/Kg

$HgCl_2$ (reference)
Hg_{total} = 1900 mg/Kg

Hg^0 (reference)
Hg_{total} = 5861 mg/Kg

Further characterization of the Hg^0 reference material

Rep	Recovery Hg mg/kg	Hg % Recovery
1	4295	73.1
2	4483	76.7
3	4424	75.4
4	4406	75.2
Avg = 4399 ± 82.8 mg/kg		

Table 1 - Elemental mercury recovery by selective volatilization

Reference Hg concentration
Hg_{total} = 5861 mg/kg

The recovery of Hg^0 by selective volatilization was low compared to expected total concentration from the round robin study. To further explore why the Hg^0 was also analyzed by IP-CV-ICP-MS.

Rep	Recovery Hg(II) mg/kg	Hg(II) % Recovery
1	1752	29.9
2	1679	28.6
3	1742	29.7
Avg = 1724 ± 39.7 mg/kg		

Table 2 - Hg(II) recovery by IP-CV-ICP-MS

Refence Hg^0 concentration
Hg^0_{calc} = 4137 mg/kg

Based on the IP-CV-ICP-MS results the elemental mercury reference material contains approximately 30% Hg(II) accounting for the lower than expected recovery compared to the certified total concentration. Methyl mercury was also tested for but was present at negligible concentrations.

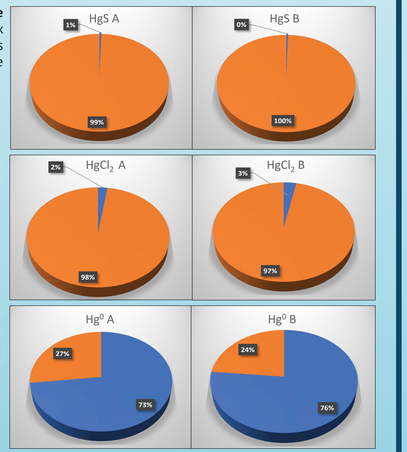
Selectivity Studies

Recovery for different reference materials by selective volatilization

Fig 1. Recovery of HgS reference material: Hg^0 recovers at blank level, indicating that no HgS is recovered by the selective volatilization method.

Fig 2. Recovery of $HgCl_2$ reference material: Approximately 2-3% recovery as Hg^0 indicating a small false positive effect when high levels of Hg(II) ionic compounds are present.

Fig 3. Recovery of Hg^0 reference material: Approximately 75% recovery, which correlates with the calculated amount of elemental mercury in the reference material.

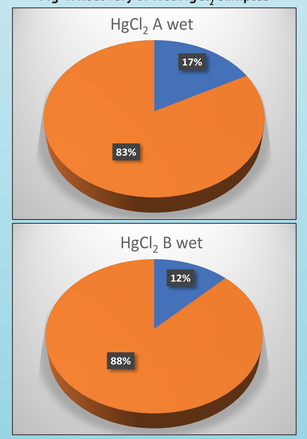


Recovery in the presence of moisture

Most samples analyzed will have some amount of moisture present. Therefore, a key consideration is the effect of moisture on Hg^0 recovery while using the selective volatilization method. To determine the effect of moisture on recovery of Hg^0, 250 µL of H_20 was added to 100 mg of reference material.

- The recovery of the Hg^0 reference material was not affected by the presence of moisture. The same average recovery and similar RSD's for both wet and dry reference materials were achieved.
- The recovery of Hg^0 from the $HgCl_2$ reference material was approximately 10-fold higher when the reference material was wet compared to the recovery when dry. Indicating an increase in the false positive result for $HgCl_2$ when the sample is wet.
- Further research is underway to lower the recovery of $HgCl_2$ in wet samples without affecting the recovery of Hg^0.

Fig 4. Recovery of wet $HgCl_2$ samples



Evaluation of Remediation Site Soil Samples

Selective volatilization appears to separate Hg^0 from other species in reference materials but what about from actual soil samples?

To answer this question, soil samples from a contaminated site that had previously undergone Hg speciation characterization by the 5-step sequential extraction method were also analyzed by selective volatilization. If selective volatilization is more selective for Hg^0 then it is expected that recoveries would be the same or lower than the corresponding step's recovery (step 4).

The 5-step process separates mercury species through different extraction conditions into potentially environmentally impactful groups.[4] While the selective volatilization method separates species based on their volatility at specific temperatures.

Things to keep in mind about the 5-step sequential extraction:
- It is semi quantitative
- Each step corresponds to several different mercury species
- Step 4 is associated with elemental mercury but not selectively

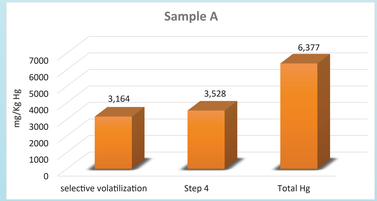


Fig 5. 90% selective volatilization recovery compared to step 4 so 50% of mercury species are likely elemental compared to the total Hg present.

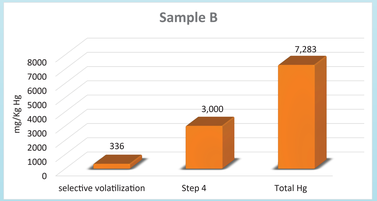


Fig 6. 11% selective volatilization recovery compared to step 4 so only 4.6% of mercury species are likely elemental compared to the total Hg present.

Reproducibility and robustness of selective volatilization

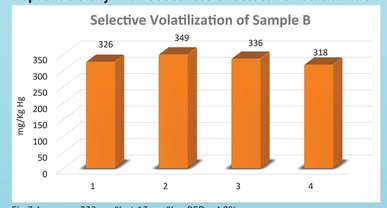


Fig 7. Average = 332 mg/Kg ± 13 mg/K RSD = 4.0%

Fig 5 and 6. The results are consistent with selective volatilization being more specific for elemental mercury. Shown by the fact that the selective volatilization recoveries are similar or significantly less than the step 4 recoveries. This also indicates that there are minimal interferences from the other mercury species present. Sample B (Fig 6) shows that the selective volatilization method has greater specificity towards Hg^0 than the 5-step sequential extraction method.

Fig 7. Results obtained from the selective volatilization method have good reproducibility. Similar results were seen for sample B over multiple preparations and analytical runs, with an RSD comparable to those obtained for the reference materials.

Conclusion

Good reproducibility: As seen in soil samples from actual remediation sites.

Low risk of cross contamination: Apparatus is fully disposable and self-contained, drastically reducing cross contamination risks.

Highly selective: Using selective volatilization, we can fully separate elemental mercury selectively from HgS and MeHg+ and achieve good separation from Hg(II) species in dry samples.

Further research underway: To reduce the observed high bias to Hg^0 results when samples are wet and contain significant concentrations of Hg(II).

Another tool for Hg characterization: The selective volatilization method compliments the 5-step sequential extraction. Giving a more accurate determination of the Hg^0 content in soils.

References

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