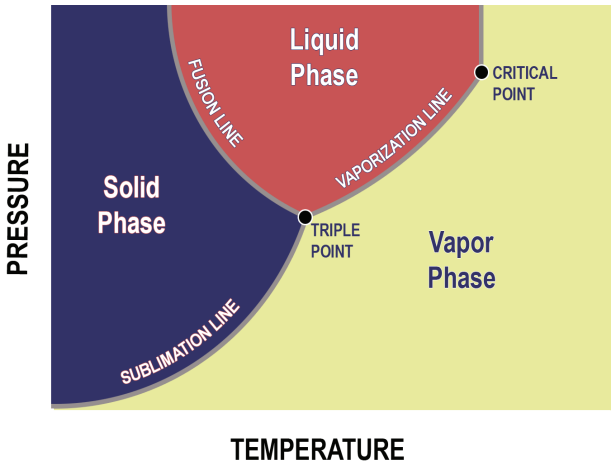
Increasing Extraction Efficiency of Organic Contaminants from Solid Substrates using Freeze Drying: A Case Study

By Gregory Salata, Ph.D., Todd Poyfair, Jeff Coronado, Carl Degner, and Lance Jording;
gsalata@caslab.com, jcoronado@caslab.com, 360.577.7222

Abstract

The accurate identification of organic contamination in any environmental matrix is dependent on the ability to efficiently extract contaminants from a particular substrate. In many cases, the most efficient extraction solvents for organic contaminants are non-polar. The extraction efficiency of organic contaminants from a variety of environmental matrices, including soil, sediment, sludge, and tissue, is therefore directly dependent on the removal of water from the sample matrix prior to extraction. Traditional drying techniques such as mixing the substrate with sodium sulfate can generate excess heat, potentially degrading and/or volatilizing low molecular weight target analytes. Alternatively, the use of diatomaceous earth (Celite®, Hydromatrix®, etc.) to bind water in a matrix eliminates problems associated with heat generation. However, this can significantly increase the volume of a sample with low solids, limiting the amount of substrate that can be placed in a single extraction vessel. An alternative to these methods is water removal by freeze drying which, when properly used, has been shown to efficiently remove water from frozen sample matrices by sublimation without significant loss of target analytes.



The study presented here compares the extraction efficiency of freeze drying with that of sodium sulfate drying for analysis of Chlorinated Pesticides, PCBs, Organotins, Semivolatile Organics, and Polycyclic Aromatic Hydrocarbons. The study shows that extraction of freeze dried samples consistently yields higher recoveries of analytes when compared with analytical results for chemically dried sediments. Because freeze drying also allows for larger amounts of a given substrate to be extracted without increasing the size of the extraction vessel, the higher extraction efficiency may allow for lower detection limits for these analytes to be achieved using traditional laboratory extraction techniques.

Introduction

Freeze drying, or Lyophilization, is the process of removing water from a product by sublimation and desorption. A sediment, soil, or tissue sample is frozen thoroughly and placed in a vacuum chamber, where the frozen water sublimes at low pressure (Figure 1). Analytes with higher vapor pressures, i.e. the environmental contaminants of interest, are left behind. The sample must be completely frozen to prevent removal of the contaminants of interest during freeze drying.

Columbia Analytical Services™

Materials & Methods

Bulk sediment was collected from a contaminated area near Palos Verdes, CA, air dried, and homogenized to ensure uniformity. For each experiment listed in Table 1, deionized water was added to 100 g of the dried sediment to produce samples of either 50% or 80% solids by weight. Eight replicate samples were prepared for each analytical method. To ensure complete water removal prior to extraction, four aliquots were individually freeze dried per the instrument manufacturers instructions. Additionally, four aliquots were mixed thoroughly with Sodium Sulfate until the sample was free flowing, indicating complete water removal from the sediment. The samples were then processed as outlined in Table 1.

Table 1.

Analysis	Method	Detector	% Solids
Pesticides	EPA 3545/8081	GC/ECD	80%
Pesticides*	EPA 3545/8081	GC/ECD	50%
PCB Congeners	EPA 3540/8082	GC/ECD	80%
PAHs	EPA 3541/8270	GC/MS	80%
PAHs	EPA 3541/8270	GC/MS	50%
Butyltins	Krone et al, 1988	GC/FPD	80%

*Pesticide spike was added prior to water removal due to low native concentrations.

Results and Discussion

Average recoveries for the freeze dried replicates were plotted against the average recoveries for the chemically dried replicates (Figures 2-7). A best fit linear regression for each data set yielded slopes <1 for all but one of the analytical sets, with the sixth yielding a linear slope slightly above 1. Also, the %RSDs for the replicate data in each instance were consistently below 20%, with few exceptions, indicating that no adverse affect was noted in the freeze dried samples based on molecular weight or compound class, regardless of the percent solids.

Figure 2

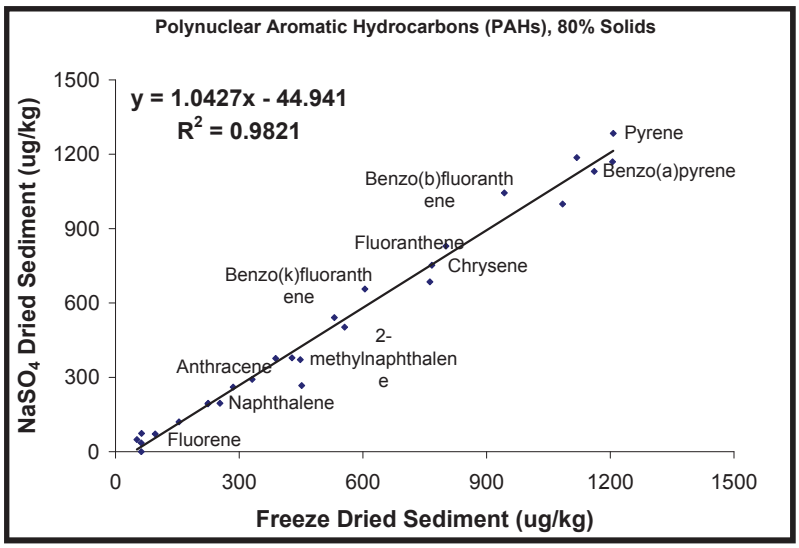


Figure 3

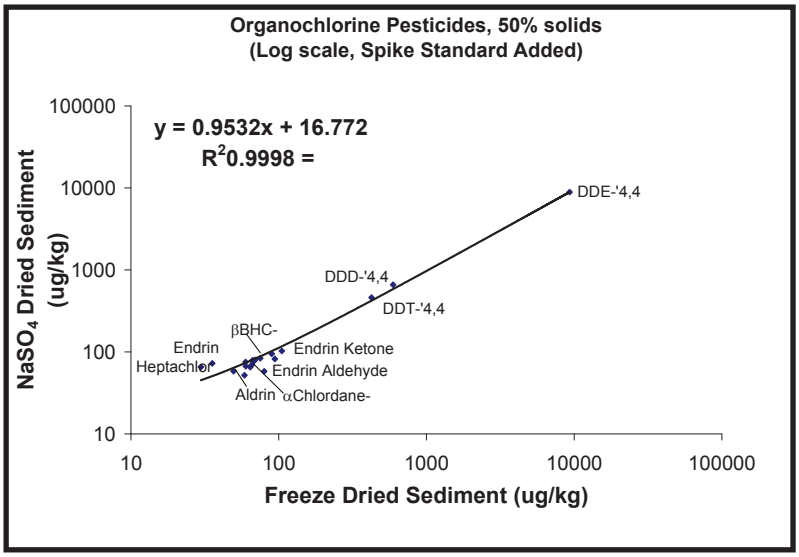


Figure 4

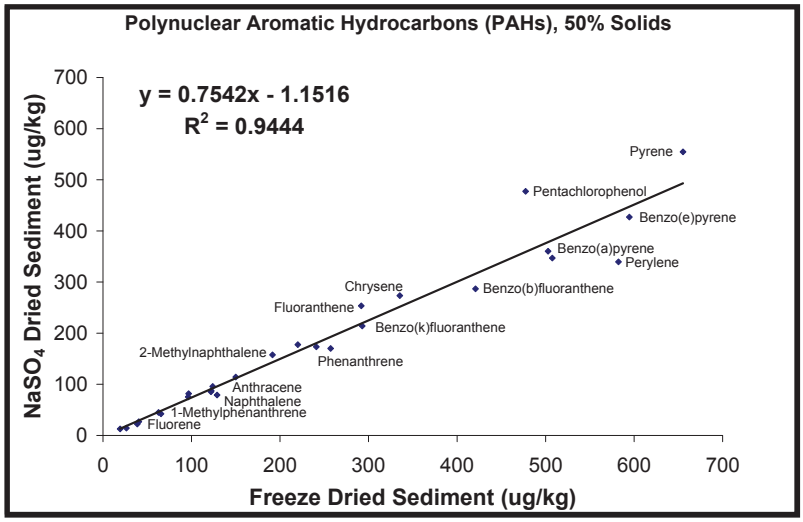
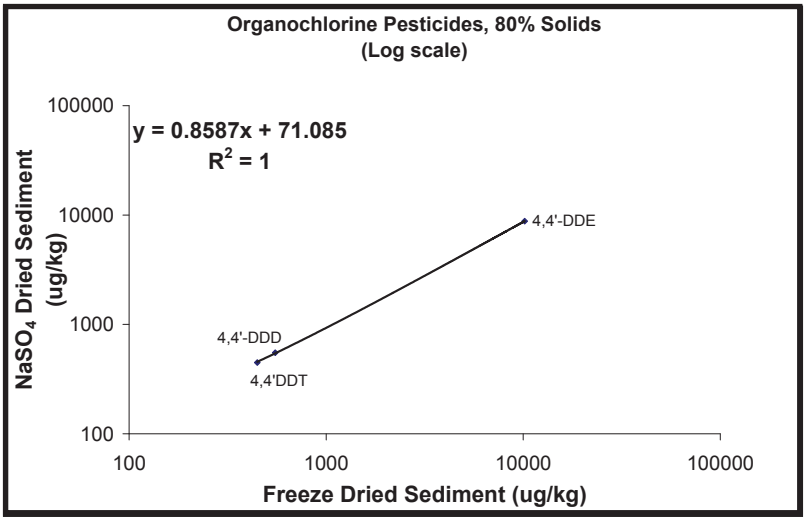


Figure 5



Columbia Analytical Services

Advantages of Freeze Drying:

- Higher recoveries of organic analytes regardless of water content.
- Complete removal of water, preventing possible interference during extraction of water/drying agent mixture.
- No increase in sample volume due to addition of chemical drying agent, allowing for extraction of larger sample aliquot.
- No heat generation, preventing breakdown/ volatilization of temperature sensitive analytes.

Freeze Drying Drawbacks:

- Drying of large aliquots or high water content samples may require 2-3 days.
- Specialized equipment required, but readily available.

Figure 6

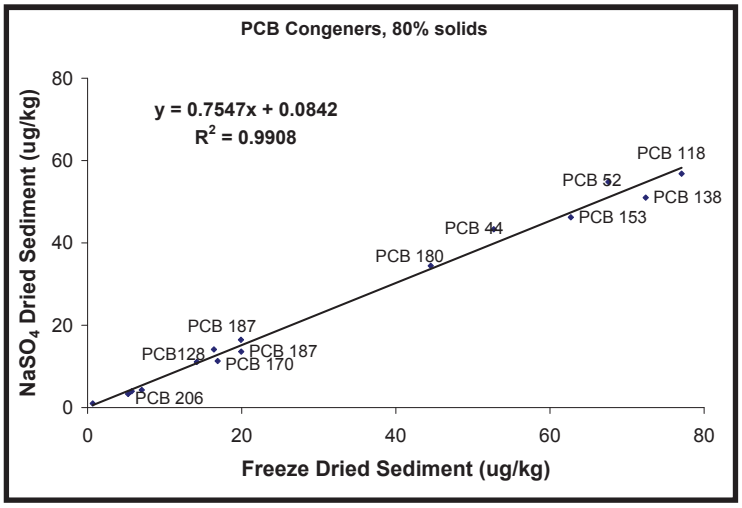
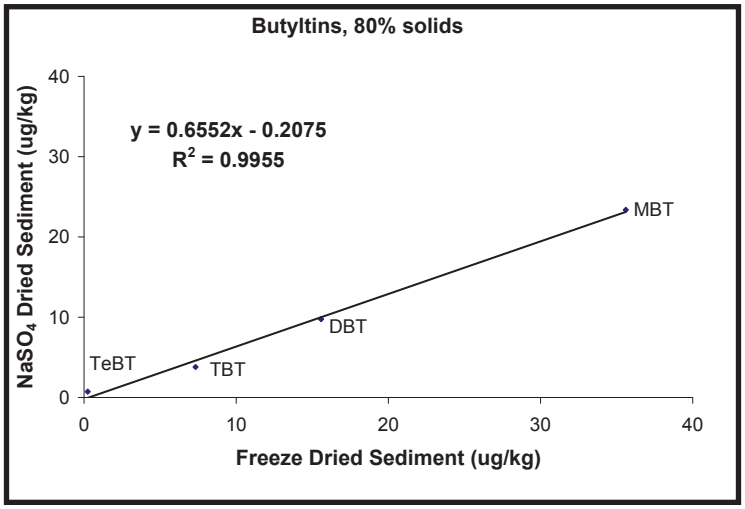


Figure 7



Conclusion

The extraction of a variety of organic analytes can be enhanced by using freeze drying as an alternative to chemical drying. The results of this study indicate that organic analytes can be extracted more efficiently from sediment that has been freeze dried than from sediment that has been chemically dried. Freeze drying also allows for larger amounts of a given substrate to be extracted without increasing the size of the extraction vessel, the higher extraction efficiency may allow for lower detection limits for these analytes to be achieved using traditional laboratory extraction techniques.

References

1. Krone C.A.; Brown, D.W.; Burrows, D.G.; Bogar, R.G.; Chan, S.; and Varanasi, U. A Method for Analysis of Butyltin Species and Measurement of Butyltins in Sediment and English Sole Livers from Puget Sound, Environmental Conservation Division, Northwest and Alaska Fisheries Center, National Marine Fisheries Service, NOAA, November 1988.
2. Test Methods for Evaluating Solid Waste, Automated Soxhlet Extraction, EPA SW-846, Third Edition, Update II, September 1994, Method 3541, Revision 1.
3. Test Methods for Evaluating Solid Waste, Soxhlet Extraction, EPA SW-846, Third Edition, Update II, September 1996, Method 3540C, Revision 2
4. Test Methods for Evaluating Solid Waste, Pressurized Fluid Extraction (PFE), EPA SW-846, Final Update III, December 1996, Method 3545, Revision 0.