Teledyne ISCO ProPak™ Bags and LDPE HA-1000 Tubing for PFAS Sampling Applications

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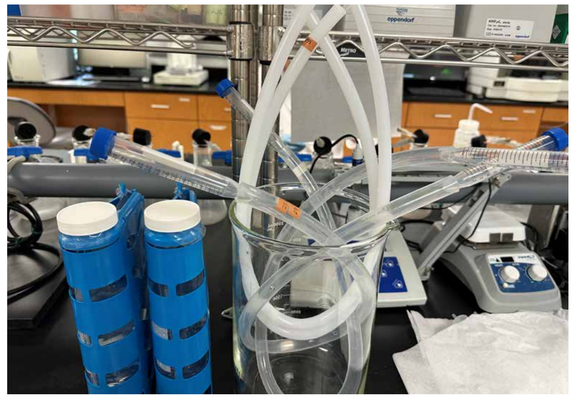
INTRODUCTION

Customer interest in using our Sampler products for PFAS sampling is rising. Earlier tests on our current vinyl suction line and silicone pump tubing shows cleanliness down below 2 ng/L of 18 PFAS species but a concerning degree of absorbance. With our pump tubing, contact time will be short, so absorbance should not be a significant issue. But the suction line tubing will be submerged continuously in the water being sampled during the entire sampling campaign. The Michigan EQ protocol recommends HDPE material for PFAS applications, but the tubing as suction line is awkward and frustrating (prone to kinking) to use. St. Gobain offers food-grade Tygon® HA-1000 LDPE tubing that appears promising as a suction line candidate. Samples of this tubing, along with HDPE tubing, ProPak bags and a control, are tested for cleanliness and absorbance of 18 PFAS species under EPA Method 537.1 (2018). This tubing is also tested for mechanical integrity for use at 28-foot head.

SETUP

Most of this work was done at the UNL Water Sciences Laboratory on East Campus, directed by Dr. Daniel Snow. The tubes tested are the St. Gobain Tygon® HA-1000 LDPE 5/8"OD x 3/8"ID (AVT00029) and St. Gobain HDPE 1/2"OD x 3/8"ID (TSEHD-0500-062), plus Teledyne ISCO ProPak sample bags (686700112). To test for cleanliness and absorbance during water contact, our traditional rinse and soak for 24 hours at 22 °C is used for the extraction step. Typical contact time with the samplers is usually a minute or less but 24 hours is a good benchmark. Only tubes with a 3/8" ID are tested for chemical appropriateness. Each tubing specimen is cut to the same length as the pump tubing, ca. 32.25". Using ultraclean water (e.g. Barnstead Nanopure II), each tubing specimen is rinsed inside with a liter of water and the water discarded. Each tube is formed in a U-shape and filled with water to soak for over 24 hours near 22 °C. Glass 10-mL beakers can serve as caps for both ends to reduce evaporation and possible contamination from dust. A glass 4-L beaker serves well in holding several tubing specimens in the U-shape. The beakers do not contact the water. See photograph on right. Tubes are run in duplicates. After 24 hours, all water from each tube is obtained and stored in PE/PP vials. Along with blanks and standards, these samples are assayed for 18 PFAS according to EPA Method 537.1. The absorbance test is very similar to the cleanliness, except fortified 80-ng/L each PFAS spiked blank water is used instead of ultrapure water during the 24-hour soak. Also, as a control, a PE/PP sample vial, routinely used in the EPA Method, is included, since it should have minimum absorbance issues. The 18 assayed PFAS are: PFOA, PFOS, PFTA, PFTrDA, PFUnA, PFBS, PFDA, PFDoA, PFHpA, PFHxA, PFHxS, PFNA, 11Cl-PF3OUds, 9 Cl-PF3ONS, ADONA, HFPO-DA, NEtFOSAA and MMeFOSAA.



PROCEDURE

EPA Method 537.1 uses SPE LC/MS/MS instrumentation. No fluorinated polymer tubing can be used anywhere on the instrument. Each water sample is concentrated on polySDVB SPE cartridge. Eluted from the cartridge by a small amount of Methanol which then is concentrated to dryness with a Nitrogen gas stream. The sample is adjusted to 1-mL Methanol:Water with internal standards. 10-uL is injected and separated on a C18 column using a Methanol:Water gradient. The separation is enhanced by tandem MS/MS with negative ion electrospray ionization. The analytes are identified according to LC retention times and MS mass units for corresponding analytes in the standards run under the same conditions.

Additionally, the HA-1000 tubing is tested for mechanical integrity for use at 28-foot head. A 30-foot length of HA-1000 tubing is installed with a strainer on a Teledyne ISCO 6712 sampler pump controller. The strainer-end of the tubing is lowered down Deep Well. The water level in Deep Well is adjusted to give a 28-foot head, i.e., the sampler pump needs to draw water out of the well over a 28-foot height, which is maximum lift height. The criterion is based on a water line velocity of over 1.5 ft/s, according to Title 40 CFR Part 136 EPA guidelines for automatic samplers. The pump is activated and a water sample from the well is collected directly into a plastic 1-L graduate cylinder. Over 700 mL of water need to be collected within 20 seconds of pumping time. Five samples are attempted. Water volume is determined gravimetrically. The tubing needs enough physical integrity so that it does not collapse under vacuum during maximum water lift. Any constriction of the tubing should reduce the line velocity. See photograph of the testing fixture on the left. This test is performed by Keith Belt at Teledyne ISCO Flow Lab in the Deep Well.

ANALYSIS

All samples showed no detection of any of the 18 PFAS analytes down to the 2 ng/L minimum detection limit. The absorbance test used fortified blanks spiked with the 18 PFAS near 80 ng/L each for the tubes. Results are in the table below. As a control for comparison, a PE/PP sample vial, routinely used in the EPA Method, is included, and performed slightly worse than the tubing and bag samples. Recoveries over 100% should not be too alarming since the fortified spike blank concentrations are quite low, think measurement noise. Also, for the silicone pump tubing contact time with the water sample is not over 24 hours but typically a minute for our samplers, i.e. (25 ft suction line + 3 ft pump + 3 ft distributor tube) / (2 ft/s flow line velocity) = 75 s sample grab time. As noted earlier, 24 hours is a good benchmark for comparisons, though.

A table of results for the absorbance can be seen below. The red-highlighted results are based on recovery limits between 130% to 50%. Using Normal statistics at the 99% confidence level in the table, the average recovery is near 85%, even with the control PE/PP sample vial. The average is based on 18 values and the standard deviation has a degree of freedom at 17. With such a high degree of freedom, t-Student statistics approach Normal statistics. The Standard Error limits are calculated as: 3 (Standard Deviation)/√17, where 3 standard deviations have a confidence level near 99% for Normal statistics and 17 is the degrees of freedom, for this case: 18 data point – 1 average value. These results give error limits between 101% to 69% recovery. These test results are tighter than last year results from the Water Sciences Lab, indicating better performance with the PFAS analysis. The control performed slightly worse than the other test samples. Poor recoveries are consistently seen with PFTA.

During testing of the mechanical integrity of the HA-1000 tubing, Teledyne ISCO standard vinyl suction line tubing is included as a control. Both 30-foot tubing samples delivered nearly 830 mL (average n=5) water within 20 seconds of pumping time, indicating a line velocity nearly 1.9 feet/second. No evidence is seen for collapse of the tubing at 28-foot lifting head.

CONCLUSION

Since the cleanliness test cannot predict the future, it should be routinely repeated on future lots by us or our customers. Also, only 18 PFAS species are tested here. The new EPA Method 1633 covers 40 PFAS species. The goal of this project is to check the performance of LDPE materials for use in the PFAS sampling and compare to HDPE materials which appear to be given carte blanche approval. Both the LDPE ProPak bags and HA-1000 tubing performed slightly better under absorbance than the PE/PP sample vial that is used routinely in the EPA Methods. HA-1000 tubing also has the mechanical integrity to lift water to nearly the maximum lift height. It performed as well as our standard vinyl suction line. ProPak bags and the HA-1000 tubing as suction line should be good for the PFAS sampling application. The HDPE tubing is also good but awkward to use. The silicone pump tubing does suffer from absorbance issues, but hopefully short contact time will render this insignificant. These new materials should be applicable to our proposed PFAS sampling kit.

	11Cl-PF3OUsD	9Cl-PF3ONS	ADONA	HFPO-DA	NEtFOSAA	NMeFOSAA	PFBS	PFDA	PFDoA	PFHpA	PFHxA	PFHxS	PFNA	PFOA	PFOS	PFTA	PFTrDA	PFUnA
	Average % Recovery																	
LDPE HA1000 Tubing	66%	99%	86%	83%	73%	84%	91%	97%	73%	93%	92%	97%	94%	92%	98%	14%	49%	101%
HDPE St. Gobain Tubing	68%	103%	78%	72%	70%	71%	93%	105%	83%	85%	83%	98%	92%	86%	99%	28%	59%	106%
ProPak Bag	76%	104%	78%	76%	47%	75%	93%	112%	90%	83%	82%	99%	94%	86%	101%	39%	64%	116%
Control	40%	95%	81%	89%	60%	78%	105%	89%	50%	90%	88%	106%	91%	84%	94%	11%	40%	79%

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*The **5800** Stationary (left) and*
***3700, 6712, and GLS Series** Portable Samplers (right).*