

# IMPORTANT CONSIDERATIONS IN SAMPLING, ANALYSIS, AND INTERPRETATION OF ANALYTICAL DATA FROM MEASUREMENTS OF HIGHLY FLUORINATED SUBSTANCES

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## Introduction

In the last eight years, many publications have appeared which reported the analytical determination of a wide variety of highly fluorinated compounds in environmental and commercial media<sup>1</sup>. Recently reports based on round-robin studies and literature reviews have shown the difficulty of measuring many of these compounds, especially in complex biological and environmental matrices<sup>2,3,4,5</sup>. Since highly fluorinated compounds have properties which are quite different from their hydrocarbon analogs<sup>6</sup>, often the assumptions the analyst makes in interpretation of the data impact the utility of the results. For example many colloid chemists have assumed that perfluorocarboxylic acids are completely dissociated in water<sup>7</sup>. Recent work demonstrated that perfluorocarboxylic acids can be transported from quiescent water<sup>8</sup>. This work also showed that fluorotelomer alcohols can escape readily from water, although they may be "soluble" at the ppb/ppm range. This mobility could lead to inaccuracies from sampling and sample preparation that may affect the interpretation of results.

In this paper, examples are given to show the effect of these unique physical properties on sampling, analyte determination, and data reduction. An example is also given of the effect of using the popular OSHA versatile sample (OVS) tubes to differentiate between particulate and vapor phases in sample collection, especially when the particulate mass is high.

## Materials and Methods

- OSHA versatile sampler (OVS) tubes, Supelco, Cat. # 20029U.
- Methanol, HPLC grade, EM Science Cat. # MS475-1 or B&J Cat. # 230-4.
- Perfluorooctanoic acid (PFOA), 97.99%, Sigma Aldrich, Cat. # 17,146-8.
- Carbon powder (generic)

## OVS tube sampling

Air sampling with OVS tubes and analytical determination via LC/MS/MS for perfluorooctanoate followed a previously published method<sup>9</sup>. The flow rate was set at 1-L per minute for eight hours. The three sections of the OVS tube (filter, first XAD sorbent, and backup XAD sorbent) were analyzed separately.

To check whether the material found on the first XAD sorbent was solid and not vapor (in cases where the quantity on the filter exceeded 50 ng), carbon black was used to represent the particulate trapped on the 0.3 $\mu$ m filter. Approximately 0.5 mg of carbon black was placed on the filter. The OVS tube was connected to an air sampling pump and the flow set at 1L/minute for 4 hours. After the tube was disconnected from the pump, the OVS tube was disassembled as usual into the three component parts used for analysis, the filter, the first XAD sorbent, and the backup sorbent. The usual procedure involves using a pair of stainless steel forceps to remove the holding ring (Figure 1). Then the forceps are used to remove the 0.3  $\mu$ m (pore size) glass (or quartz) filter. There is no polyurethane spacer between the filter and the first sorbent section. Then by gentle tapping, the first sorbent layer (XAD) is placed in a vial. The forceps are used to remove the polyurethane foam, and then the backup (smaller section of XAD) is placed in another vial.

## Effect of pH on sampling perfluorocarboxylic acids

PFOA is a weak acid. The pKa of PFOA is determined by titration with sodium hydroxide. The pH at the first derivative of the titration curve is the pKa.

## Results and Discussion

### OVS tube sampling

The results from the perfluorooctanoate determination varied from non-quantifiable to approximately 2  $\mu$ g on the filter. Often when the quantity of perfluorooctanoate on the filter was greater than 50 ng, there was often a

quantifiable amount measured on the first XAD sorbent. Data for a variety of particulate and air concentrations will be provided to demonstrate this effect..

In order to determine if the analyte on the first sorbent was truly a vapor and not an artifact of the preparation, an experiment with carbon black was performed. Figure 2 shows that the stainless steel forceps used to remove the filter and polyurethane spacers retained some of the carbon. Figure 3 illustrates the top view of the first sorbent section, demonstrating that some of the carbon black can fall off onto the top of the first section of sorbent.

#### **Effect of pH on sampling perfluorocarboxylic acids**

The pKa of PFOA was determined to be 2.8. According to the Henderson Hasselbach equation<sup>10, 11</sup>, fraction ionized =  $1 / \{1 + 10^{(pKa - pH)}\}$ . Table 1 shows the effect of pH on the percent of neutral (non-ionized) acid. Perfluoro groups are known to be quite hydrophobic as evidenced by the solvatochromic  $\pi$  scale<sup>12</sup> where perfluorooctane is -0.41, cyclohexane is 0, and water is 1.09. In the neutral form, the acid is hydrophobic. At room temperature its vapor pressure<sup>13</sup> is sufficient for it to remove itself from water to the vapor phase. For example at pH 4.0, the pH of acid rain, 6% of PFOA is in the neutral form. If some of it leaves the aqueous phase to go to the vapor phase, re-equilibration can occur and more neutral species may be freed to go into the vapor phase. In a closed container with zero headspace, this may not be an important loss mechanism. In an open environment pH is an important consideration in sampling and retention of sample integrity. Data show that keeping the pH above 4 and keeping the material wet reduce emissions..

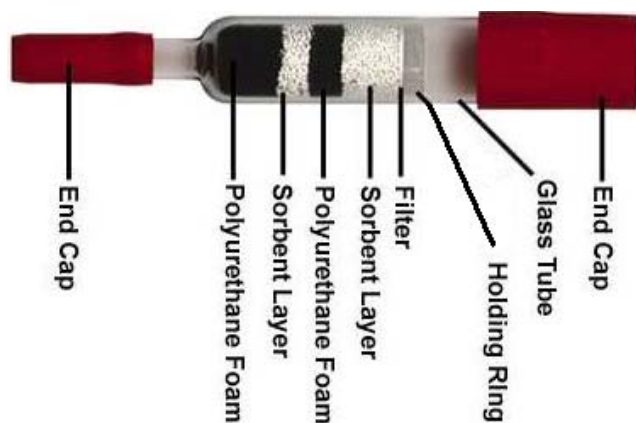
#### **Conclusions/Recommendations**

Due to their unique physical properties (hydrophobicity and pKa), highly fluorinated compounds can escape aqueous solutions used for sampling, storing, or preparing samples for analytical determination. Zero headspace containers should be used to avoid loss of these compounds from the aqueous phase during transport and sample preparation. Sampling protocol should include pH measurements in order to understand if pH may impact the analytical results. Adding a spacer (e.g., polyurethane foam) between the filter and the first XAD resin should help reduce false positives for vapor emission in OVS tube sampling.

#### **Acknowledgments**

The authors thank Michael J. Logue for his determination of the pKa for PFOA and Barbara S. Larsen, Stanley F. Bachmura, Jr., and Gilbert R. Wooler for their help with the LC/MS/MS determinations.

**Figure 1. OSHA Versatile Sampler Tube**



**Figure 2. Carbon black on the stainless steel forceps and 0.3µm filter.**



**Figure 3. Top view of the first sorbent section with the filter removed.**



**Table 1. Effect of pH on % neutral (non-ionized) acid**

pH	% neutral
1	98
3	39
4	6
5	0.006
7	0.00006

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