PFAS Analysis by TOP Assay

PFAS and Total Oxidizable Precursor Assay

Perfluoroalkyl Substances (PFAS) are a family of fluorine containing chemicals used in heat, stain, and water resistant products. Due to their persistence, toxicity and bioaccumulative potential, these compounds are of increased concern to environment and health agencies.

Accredited laboratories typically determine approximately 30 of these specific chemicals. In many fire-fighting foams and other products containing PFAS, the bulk of these chemicals may be tied up in more complex molecules including polymeric compounds.

Traditional PFAS analysis targets only key analytes and therefore may greatly underestimate the presence of PFAS in the environment. However, a new method is being introduced early next year.

ALS will be offering PFAS analysis by Total Oxidizable Precursor Assay (TOP Assay) beginning January 2017. TOP Assay is a standardized pre-treatment of water samples or sample extracts designed to expose underlying PFAS not amenable to standard analysis. Perfluorinated carboxylates and sulfonates are stated to remain intact under the conditions of the assay.

Water samples, sample extracts (soil or water), or diluted foam products are incubated with potassium persulfate (60 mM) and sodium hydroxide (0.125 M) at 85°C for six hours. Samples are neutralized and then run for the full suite of PFAS compounds.

Note that this is an empirical test and comparable results can only be achieved by precisely following the conditions of the test.

Under the conditions of the assay, it is expected that fluortelomer sulfonates are broken down to shorter chain carboxylates by cleavage of the non-fluorinated portion of the molecule. Perfluorinated carboxylates and sulfonates are stated to remain intact under the conditions of the assay.
Oxidation of AFFF Products and Fabric Protectors

Over the last six months, ALS has performed numerous oxidation trials in order to obtain a deeper knowledge of the Total Oxidizable Precursor Assay. This includes the impact of concentration plus the differences between first generation and modern foams.

A number of foam products were subject to the TOP alkaline persulfate digest and analyzed by LC/MS/MS. Three products were examined: 3M Light Water™, Ansulite™, and Aer-o-Water™. The first of these products was the classic pre-2000 AFFF while the other two represent more recent short-chain foams. Note that only the Aer-O-Water™ product was in its original packaging while the other products had been supplied as subsamples of uncertain origin.

Figure 1 indicates significant growth in total PFAS following oxidation for Ansulite™ and Aer-O-Water™. Growth of perfluorocarboxylic acids in 3M Light Water™ may be attributable to unspecified “fluoroalkyl amide derivatives” described in a 1996 MSDS from 3M in Australia. The outcomes of these digests are consistent with results reported in the literature on this subject.

In figure 2, the concentration of the AFFF can affect both qualitative and quantitative outcome of the oxidation process. Oxidation at high dilutions leads to full conversion of the material to carboxylic acids. At higher concentrations, this conversion is less than complete which indicated exhaustion of the oxidant. At a 500-fold dilution, 6:2-FTS is a large component of the composition which is consistent with the presence of fluorotelomer sulfonamido betaines in some modern-day products.

Discussion

The TOP assay is capable of revealing the presence of PFAS that may, given time, weather to perfluorinated alkyl substances of concern, but is definitely not a predictor of the endpoint of abiotic and biotic breakdown in the field. Oxidation has been well considered as a treatment option. This includes both alkaline and heat activated persulfate, both of which are used in the TOP assay. Oxidation has been well considered as a treatment option. This includes both alkaline and heat activated persulfate, both of which are used in the TOP assay.

To some extent, this may explain the small loss of PFOS observed with oxidation of the 3M Light Water™. In experiments performed at ALS, a 13C-labeled PFOS surrogate was added pre-oxidation and regularly recovered around 80%. Oxidation of a full analytical standard (not under standard conditions) also yielded less than a mass balance when summed, which indicated some loss to shorter chain PFAS carboxylates not normally quantified. On the flip side, if the oxidant is exhausted either by competition from non-PFAS organic carbon or high concentrations of PFAS, both qualitative and quantitative conversion of AFFF PFAS precursors may be incomplete.

When comparing data between laboratories, it is essential that the oxidation conditions are absolutely standardized and that sample dilutions are reasonably equivalent. In conclusion, the TOP assay is a useful tool in exposing the potential for ongoing contamination by PFAS compounds through biotic and abiotic weathering processes. Results, however, should be treated with caution, especially where health or ecological risk assessment is required. There may also be a case to expand analytical suites to cover other PFAS that may arise from weathering that might include some oxidation and hydrolysis, and, ideally, to have better models for predicting environmental endpoints of AFFF degradation.

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