Message

From: Washington, John [/O=EXCHANGELABS/OU=EXCHANGE ADMINISTRATIVE GROUP (FYDIBOHF23SPDLT)/CN=RECIPIENTS/CN=FDC3E8CE9F1D45C4894881FF420CA104-WASHINGTON, JOHN]
Sent: 7/15/2021 12:29:26 PM
To: Ryan, Jeff [Ryan.Jeff@epa.gov]
CC: Wickersham, Lindsay [wickersham.lindsay@epa.gov]; Jackson, Stephen [Jackson.Stephen@epa.gov]; Liberatore, Hannah [Liberatore.Hannah@epa.gov]; Davis, Mary J. [davis.maryj@epa.gov]
Subject: RE: PTFE Dispersion SOP?
Attachments: NHDES NTA Dispersion Report_5_FINAL05282019 (004).pdf; WashingtonEtAl2014ES&TSI.pdf

Hi Jeff,

Not sure if you all know this already, but we ran 13 St. Gobain dispersions and surfactants via: i) high-res nontargeted LC/MS; and ii) targeted GC/MS for compounds that we had detected previously in our commercial FTP research. These efforts led us to tentatively identify 40 PFAS in the St. Gobain dispersions/surfactants. I am attaching this report.

A general conceptual principle I have for commercial FTPs (at least historically) is that by far the dominant part of PFAS in commercial dispersions were GC/MS analytes, not LC/MS. For example, if you look at Table S1 in my attached supporting info, the concentration ratio of GC-able FTOHs to LC-able PFCAs was on the order of (100 to 1000) to 1. So if they are doing targeted LC/MS and finding very little, they might be omitting an important GC/MS universe of PFAS.

Moreover, if they are running LC/MS without proper dispersion with MTBE/THF, they run the risk of unknown amounts of LC/MS PFAS remaining sorbed to fluorinated polymer particulates. This exact flaw was what led DuPont to publish in ES&T the incorrect conclusion that their FTPs did not degrade – they saw no increases in PFAS with time, concluding no degradation, but instead their solvent extraction did not capture the ingrowing PFAS which remained sorbed to the FTP.

In my experience with dispersions (which is not anywhere near comprehensive), filtering can be a frustrating exercise. Instead, I would be inclined to centrifuge the hell out of them. From this perspective, I would consider trying two approaches in this order (this is just fast brainstorming and might be flawed or improved upon):

1) First see if PTFE particles dissolve in MTBE or THF (hoping that they do not for this purpose).
a. Starting with eyeball-visible PTFE granules, weigh the aliquot dry, then add MTBE (THF), sonicate for an hour or more, centrifuge, decant the liquid, dry the residual, and see if the solids weigh roughly the same as initially (or perhaps the granules are gone and you have your answer).
b. If the solids weigh roughly the same, take this as your MTBE extract does not contain confounding levels of PTFE in solution.
c. So use this approach and continue with your TOF on the liquid portion, perhaps requiring a blow-down to dryness but I don't know about this.
2) If the MTBE and THF decrease the mass of the granular PTFE, I would consider this:
a. To the aqueous dispersion, add ACN (with mass-labels as appropriate for your purposes) in amount necessary to achieve ACN:H2O 90:10 – this is roughly the best ratio for separating PFAS from fluorotelomer stationary phases but does not ensure that you recover PFAS internal to the PTFE micelles/granules.
b. Sonicate and rotisserie to extract.
c. Centrifuge the hell out of it. This is done after ACN addition for 2 reasons:
i. To do your best to separate sorbed PFAS from the exterior of PTFE particles, before dropping the particles out; and
ii. The ACN:H2O solution is lower density than pure water, fostering settling of the particulates.
d. Analyze the liquid phase via TOF.

We would be happy to talk with you all sometime if you want added confusion.

John

From: Ryan, Jeff <Ryan.Jeff@epa.gov>
Sent: Thursday, July 15, 2021 7:34 AM
To: Washington, John <Washington.John@epa.gov>
Cc: Wickersham, Lindsay <wickersham.lindsay@epa.gov>; Jackson, Stephen <Jackson.Stephen@epa.gov>; Liberatore, Hannah <Liberatore.Hannah@epa.gov>; Davis, Mary J. <davis.maryj@epa.gov>
Subject: Re: PTFE Dispersion SOP?

Hey John

This is indeed very helpful. Let me try and explain what we're trying to accomplish.

We're working with Cathy Beahm at NHDES to help her address the permitting of St Gobain's new thermal oxidizer. Short story is they do not want to install a HF scrubber and believe there's nothing to scrub as their targeted analysis of the dispersions only found a handful of compounds.

Of course there's more in the dispersions than that and we think a TOF analysis may be useful. But we don't want to include the PTFE in the measurement. So how do we isolate it?

Is simply filtering an option?

I do think this problem will get addressed either way as St Gobain will have to measure HF emissions during the TO commissioning tests which will occur in September and we will be a part of.

It would just be nice to have an idea ahead of time.

Any suggestions you have are most appreciated

Jeff

Sent from my iPhone

On Jul 15, 2021, at 7:16 AM, Washington, John <Washington.John@epa.gov> wrote:

Hi Lindsay,

I probably did make a strong distinction. I imagine my central message was I felt confident about the methods we developed for the commercial side-chain fluorotelomer-based polymers (FTPs) we tested, but had no experience with PTFE. I have no SOPs for PTFE but attached my SOP for FTP extraction.

A detail I consider essential for complete characterization of PFAS in fluorinated polymers of any type (e.g., FTPs or PTFE) is that you must 'dissolve' the polymer in one step or another. This was first proposed by Barb Larsen, then at DuPont, whose paper I reference, see below. The idea with polymer dissolution is that these solvents overcome the fluoro-felicity of the PFAS for the polymer. In absence of this, unknown amounts of PFAS may remain sorbed to the polymer and unaccounted for in the sample you inject . . . a black box.

The two solvents I know of that dissolve the commercial FTPs I worked with are THF (Larsen used this) and MTBE (I used this).

In my study of whether commercial FTPs biodegrade in soil (answer: they do), the MTBE dissolved the FTP and dispersed ionic PFAS, but these ionic PFAS in MTBE were ion-paired/complexed with unknown cations or positively charged soil dissolved OM. So the ionic PFAS fraction (i.e., the LC/MS analytes) were subjected to an ion pairing with concentrated TBAHS, then reconstituted in ACN/H2O for injection on LC/MS. But the non-ionic PFAS (e.g., FTOHs and FTAcs) in the MTBE could be shot directly on GC/MS. The extraction procedure we used for this is summarized in the outline below.

So bottom line suggestion I would check if working with PTFE: starting with PTFE particles in a tube, when you add the solvent, perhaps with some sonication, do the particles dissolve? If they remain settled on the bottom of your tube, you cannot be confident that any/all PFAS associated with them has dissolved into the solvent.

I am copying Mary Davis who works with us here in Athens and who is planning some research with a new-generation commercial FTP in the coming year.

Let me know of any other questions. Good luck. I will be interested to hear how your research develops.

Thanks,
John

Larsen ref:
<image003.png>

Commercial FTP extraction we used:
<image007.png>

From: Wickersham, Lindsay <wickersham.lindsay@epa.gov>
Sent: Wednesday, July 14, 2021 12:38 PM
To: Washington, John <Washington.John@epa.gov>
Cc: Jackson, Stephen <Jackson.Stephen@epa.gov>; Liberatore, Hannah <Liberatore.Hannah@epa.gov>; Ryan, Jeff <Ryan.Jeff@epa.gov>
Subject: PTFE Dispersion SOP?

Hi John,

I hope you are having a nice week so far! It's been a while since Stephen and I talked to you last and I wanted to reach out to see if I am remembering the details of our conversation on extraction of dispersions correctly.

When we talked back in February I remember you making a strong distinction between PTFE dispersions and Fluorotelomer dispersions, even suggesting that there was a different methodology for extracting PTFE based dispersions. Am I remembering this correctly? If so, do you happen to have an SOP or an outline of the methodology for extracting PTFE dispersions?

Thank you,
Lindsay

Lindsay Wickersham (she/her/hers)
BSPH, MSEE | Physical Scientist
US Environmental Protection Agency
Air Methods and Characterization Division
Research Triangle Park, NC | (919)-541-4340

<image001.png>

<D-EMMD-ECB-011-SOP-01_Exh_extr_soil_polymer_micro_FT_PF_Washington_11-15-17.pdf>