

Extraction Of Phosphorus Flame Retardants from Drinking Water Using the FMS TurboTrace® Solid Phase Extraction System

Introduction

Brominated Flame Retardants (BFRs) have become standard analytes of interest in environmental labs. Their persistent nature and possible links to various health effects have led to the banning of PBDEs and PBBs. Initially introduced as replacements for BFRs, Phosphorus Flame Retardants have also come under scrutiny over potential health concerns. As a result, testing procedures and regulation guidelines have begun to emerge for monitoring of many of these compounds.

Solid Phase extraction is an ideal fit for monitoring these analytes in water sources designated for human consumption. The following employs automated SPE paired with GC Triple Quad analysis to deliver low level of analysis for a selection of PFR commercially available from standard manufacturers.

Instrumentation

- FMS, Inc. TurboTrace® SPE system
- FMS, Inc. SuperVap®12 Concentrator
- FMS, Inc. 50 ml concentration vessels with direct to GC vial termination
- SuperVap® Vial Concentrator
- Thermo Trace GC with Split/Splitless injection port
- Thermo TriPlus Autosampler
- Thermo Quantum XLS Triple Quad Mass Spec

Consumables

- 1 gram HLB SPE cartridges
- Hexane, pesticide grade or equivalent
- Methylene Chloride, pesticide grade or equivalent
- Methanol, pesticide grade or equivalent
- Toluene, pesticide grade or equivalent
- Ultrapure DI water
- 6N HCl
- Anhydrous Sodium Sulfate, ACS grade or equivalent

- Native and deuterated PFR standards

Sample/Reagent Prep

1. 5 grams NaSO₄ to empty SPE cartridges and attached to fraction lines before collection vials.
2. Affix HLB cartridge to TurboTrace system
3. Bring samples to pH 2 adding HC drop wise
4. Add add methanol to samples (5mls per 1 Liter)
5. Add respective surrogate and spiking solutions to samples
6. Attach sample bottles to SPE system

SPE Procedure

1. Condition HLB cartridges with 10mls Hexane:Methylene Chloride (50:50)
2. Condition HLB cartridge with 10mls Methanol
3. Condition HLB cartridges with 20mls H₂O
4. Load Samples across HLB SPE cartridges via vacuum
5. Dry HLB Cartridge with N₂ for 10 minutes
6. Automatic solvent rinse of sample bottles with 50% hexane/DCM
7. Bottle rinse loaded across HLB cartridges and collected in SuperVap Vials through NaSO₄ tubes.
8. Additional 10 mls elution solvent passed HLB cartridges
Remaining elution solvent N₂ purged to collection vials.

Total elution solvent: ~30mls



SuperVap

1. Preheat temperature: 60 °C
2. Evap mode: 10PSI Nitrogen with sensor

SuperVap Vial Evaporator

At 1ml, GC vials removed from SuperVap tubes and transferred to Vial Evaporator. 5 µl CIL EDF-5999 added as a recovery standard and 2 µl dodecane added to extract.

Extracts reduced to <10 µl at ambient temperature at 1-2 PSI N2.

Extracts reconstituted to 100 µl Toluene for GC analysis.

Analytical Conditions

2µl injections were performed on a splitless injection.

GC column specifications used were a 30m, .25mm, .25µm (DB-5 or equivalent)

Analysis on the Quantum XLS were conducted in the SRM mode.

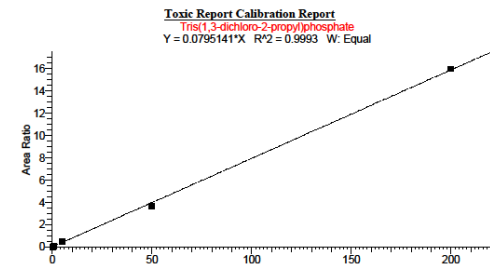
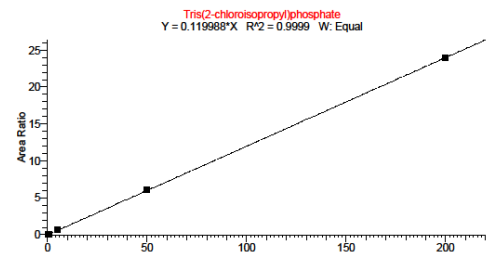
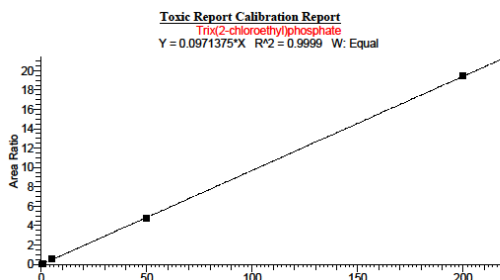
A 5 point calibration was run with concentrations ranging from 1 ng/ml to 2000 ng/ml.

All results were calculated by isotope dilution.

Results

Analyte	Mean		RSD	
	Native	Surr	Native	Surr
Tris(2-chloroethyl)phosphate	9.87	76.6%	1.8%	15.0%
Tris(2-chloroisopropyl)phosphate	12.54	74.7%	7.6%	14.8%
Tris(1,3-dichloro-2-propyl)phosphate	11.89	87.4%	0.2%	10.9%

Results of IPR study performed on TurboTrace system



Linearity of calibration for native PFRs

Conclusions

Extraction of the water spiked with PFRs yielded recoveries of deuterated surrogates within 70%-130% acceptance criteria with RSDs below 20%. Native PFR concentrations from spiked runs also resulted in 70%-130% recoveries from actual spiked concentrations. For native PFRs, RSDs between spiked replicates were all less than 10%. Method blanks in clean matrices yielded very clean extracts with no detected background levels >.1ng/L.

Conclusions from the study demonstrate that the subset of PFR standards measured all have a strong affinity for SPE sorbents and were an good fit for automated SPE. Utilizing the TurboTrace SPE system and SuperVap concentrator, a complete turnkey solution was delivered enabling rapid extraction process. Paired with GC/QQQ instrumentation, low level sample analysis was achieved while achieving high levels of precision and accuracy.

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FMS TurboTrace and SuperVap systems