Adopted and Proposed ASTM Methods for the Analysis of Perfluorinated Compounds (PFCs), Select Pesticides and a Biocide Using Quick Sample Extraction/ Preparation Followed by UPLC/MS/MS Analysis

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Fracking Fire Intensifies Push to Change Ohio Chemical Disclosure Laws

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July 8, 2014

WOODSFIELD, Ohio - Environmentalists say the recent fire at a hydraulic fracturing well in southeastern Ohio highlights the flaws in state and federal disclosure laws for chemicals used in "fracking."

The fire at the Monroe County well site on June 28 spread to 20 nearby trucks on the drilling pad, and required additional firefighters from six counties to contain it. Melissa English, development director with Ohio Citizen Action, says first responders were probably unaware of the chemicals involved in the accident because the only ones listed were "condensate and produced water."

PHOTO: This fire at a fracking well site in Monroe County is intensifying efforts by some to update Ohio's chemical disclosure laws. Photo courtesy of the Monroe County Emergency Management Agency.

"There were more chemicals on-site at the time of the fire, because they had started fracking by that time," says English. "They had started actually stimulating the well to produce oil and gas, which they hadn't done at the time the hazardous chemical inventory was filed last year."

Under federal requirements, hazardous chemicals must be reported annually, and drillers must file reports for any additional chemicals brought on-site. For chemicals deemed "hazardous," drillers have 90 days to file. For chemicals termed "extremely hazardous," drillers have 30 days. English says it's possible during that 30- or 90-day window an accident could occur - and first responders would likely be unaware of the chemicals on-site.

Under Ohio law, oil and gas drillers are not required to disclose the chemicals they use. Teresa Mills with the Center for Health, Environment and Justice is among those who have worked to end Ohio's exemption for the fracking industry and bring the state in line with federal requirements.

"This antiquated way of presenting chemical hazards is unacceptable," says Mills. "All of this

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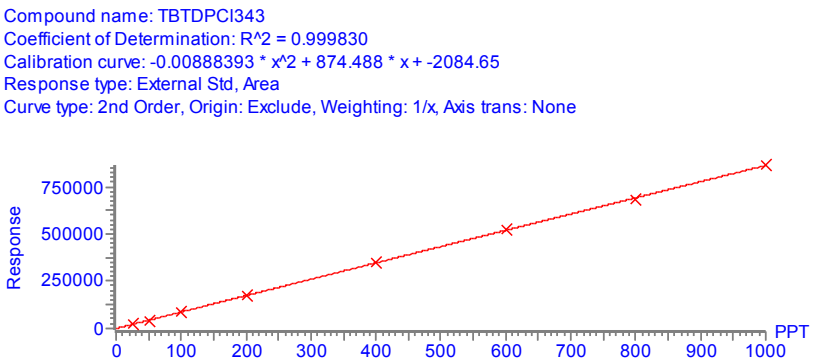
- (Tri-n-butyl)-n-tetradecylphosphonium chloride (TTPC), CAS: 81741-28-8

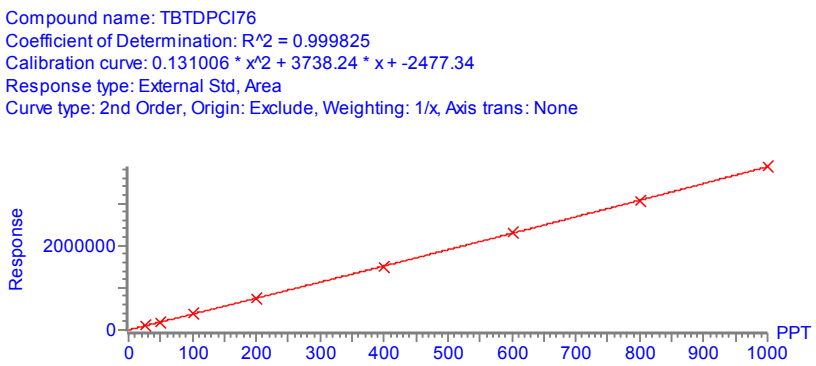
Sample Preparation

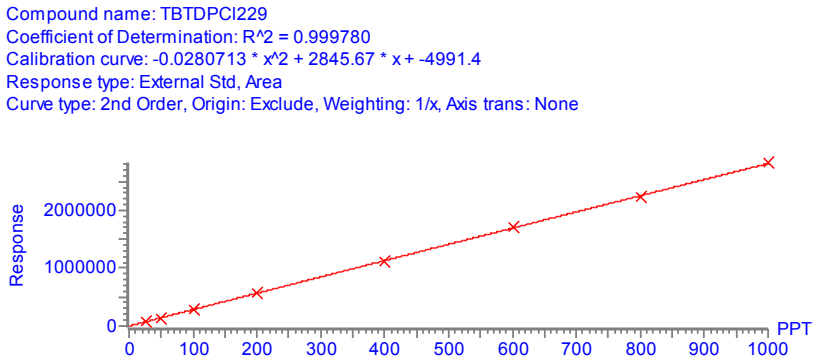
- Water
  - 2.5 mL Water Sample
  - 7.5 mL Acetone
  - Filter through 0.2 μm Nylon Filter Unit
  - Reporting Limit- 100 ppt
- Soil
  - 2 g Soil Sample
  - 15 mL Acetone and shake, 1 minute
  - Filter through 0.2 μm Nylon Filter Unit
  - Add 5 mL Water
  - Reporting Limit- 250 ppt

Three SRM transitions

- 399.5456734223 > 343.524689765432 Exactly
- 399.5 > 229.3
- 399.5 > 75.9







Acquity H-Class UPLC® and Waters Xevo® TQ-S

Matrices Tested

- DI Water
- Chicago River Water
- Sand
- Scotts Top Soil
- ASTM Soils
  - Sand
  - Fat Clay
  - Lean Clay
  - Silt

ASTM WK47926-Standard Test Method for Determination of (Tri-n-butyl)-n-tetradecylphosphonium chloride (TTPC) in Water by Multiple Reaction Monitoring Liquid Chromatography/Mass Spectrometry (LC/MS/MS)

Analyte	MDL (ng/L)	Reporting Ranges
		(ng/L)
TTPC	13.11	100 - 4000

ASTM WK47925-Standard Test Method for Determination of (Tri-n-butyl)-n-tetradecylphosphonium chloride (TTPC) in Soil by Multiple Reaction Monitoring Liquid Chromatography/Mass Spectrometry (LC/MS/MS)

Analyte	MDL (ng/Kg)	Reporting Range
		(ng/Kg)
TTPC	32.7	250 - 10000

PFCs Introduction

- Why involved?
  - Tailor the methods to our customers needs
    - Reporting limits- don't require drinking water reporting levels.
    - Broad matrices- influents, effluents, sludge, biosolids, soil….
    - Many samples
- Published methods on PFCs
  - Many methods have laborious extraction and clean-up procedures that limit sample throughput for a small operation.

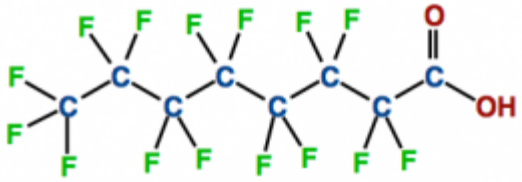
- Method development for the quicker extraction and analysis of fluorinated chemicals from waters, sludge, biosolids and soils

- To quantify and evaluate the levels of contaminants of emerging concern (CEC) based on biosolid/sludge/soil treatments

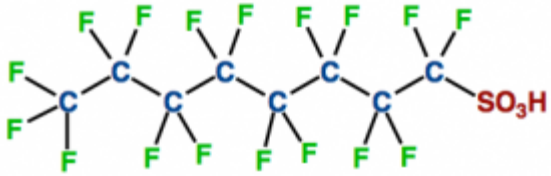
Dream Job

Target List

- **Perfluoroalkyl Sulfonates (PFAS) :**
- Perfluorobutyl Sulfonate (PFBS) - $C_4F_9\ SO_3^-$
- Perfluorohexyl Sulfonate (PFHxS) - $C_6F_{13}\ SO_3^-$
- Perfluorooctyl Sulfonate (PFOS) - $C_8F_{17}\ SO_3^-$
- Decafluoro - 4 - (pentafluoroethyl)cyclohexane Sulfonate (PFechS) - $C_8F_{14}\ SO_3^-$
- **Perfluoroalkyl Carboxylates (PFCA)**
- Perfluorobutonoate (PFBA) – $C_4F_7O_2^-$
- Perfluoropentonoate (PFPeA) – $C_5F_9O_2^-$
- Perfluorohexonoate (PFHxA) – $C_6F_{11}O_2^-$
- Perfluoroheptonoate (PFHpA) – $C_7F_{13}O_2^-$
- Perfluorooctonoate (PFOA) – $C_8F_{15}O_2^-$
- Perfluorononanoate (PFNA) – $C_9F_{17}O_2^-$
- Perfluorodecanoate (PFDA) – $C_{10}F_{19}O_2^-$
- Perfluoroundecanoate (PFUnA) – $C_{11}F_{21}O_2^-$
- Perfluorododecanoate (PFDoA) – $C_{12}F_{23}O_2^-$
- Perfluorotridecanoate (PFTriA) – $C_{13}F_{25}O_2^-$
- Perfluorotetradecanoate (PFTreA) – $C_{14}F_{27}O_2^-$



PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

A few more……

- 6:2FTCA – FHEA- 2-Perfluorohexyl ethanoic acid
- 8:2FTCA – F0EA- 2-Perfluorooctyl ethanoic acid
- 10:2 FTCA – FDEA- 2-Perfluorodecyl ethanoic acid
- 6:2 FTUCA – FHUEA- 2H-Perfluoro-2-octenoic acid
- 8:2 FTUCA – FOUEA- 2H-perfluoro-2-decenoic acid
- 7:3 Acid – FHpPA- 3-Perfluoroheptyl propanoic acid

Surrogates

- MPFAS- Isotopically labeled Perfluoroalkylsulfonates
  - MPFHxS- $^{18}O_2$-Perfluorohexylsulfonate
  - MPFOS- $^{13}C_4$-Perfluorooctylsulfonate
- MPFCA- Isotopically labeled Perfluoroalkylcarboxylates
  - MPFBA-$^{13}C_4$-Perfluorobutanoate
  - MPFHxA-$^{13}C_2$-Perfluorohexanoate
  - MPFOA-$^{13}C_4$-Perfluorooctanoate
  - MPFNA-$^{13}C_5$-Perfluorononanoate
  - MPFDA-$^{13}C_2$-Perfluorodecanoate
  - MPFUnA-$^{13}C_2$-Perfluoroundecanoate
  - MPFDoA-$^{13}C_2$-Perfluorododecanoate

Determine Chromatographic Parameters and Detection Levels

- Liquid Chromatography
  - Acquity UPLC® CSH™ Phenyl-Hexyl 1.7 μm, 2.1 x 100 mm column
  - Isolator Column- Acquity UPLC® BEH C18, 1.7 μm, 2.1 x 50 mm column
- Detector-MS/MS
  - Waters Xevo® TQ-S

PFAS/PFCA Gradient

Time (min)	Flow (mL/min)	95% Water: 5% Acetonitrile	Acetonitrile	95% Water: 5% Acetonitrile, 400 mM Ammonium Acetate
0	0.3	95	0	5
1	0.3	75	20	5
6	0.3	50	45	5
13	0.3	15	80	5
14	0.4	0	95	5
17	0.4	0	95	5
18	0.4	95	0	5
21	0.4	95	0	5

Calibration (PPT)

Analyte/Surrogate	LV1	LV2	LV3	LV4	LV5	LV6	LV7	LV8	LV9
PFPeA, PFBA	25	50	100	200	300	400	500	750	1000
PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFOS, PFNA, PFHxA, PFHpA, PFBS, PFechS, PFOA, PFHxS, FOUEA, FHUEA, FHpPA, MPFBS, MPFHxA, MPFUnA, MPFOA, MPFDA, MPFOS, MPFNA, MPFHxS, MPFBA	5	10	20	40	60	80	100	150	200
FHEA, FOEA, FDEA	100	200	400	800	1200	1600	2000	3000	4000

- Default 30 μL Injection Volume

MRM Transitions

Two Where Possible (All you have to see)!

Chemical	Primary/ Confirmatory	Retention Times (min)	Cone (V)	Collision (eV)	MRM Transition	Primary/ Confirmatory SRM Area Ratio
PFTreA	Primary	10.63	20	13	712.9→668.9	7.4
	Confirmatory		20	30	712.9→169	
PFTriA	Primary	10.17	25	12	662.9→618.9	7.4
	Confirmatory		25	28	662.9→169	
PFDoA	Primary	9.61	10	12	612.9→568.9	8.2
	Confirmatory		10	25	612.9→169	
PFUnA	Primary	9.05	15	10	562.9→519	7.2
	Confirmatory		15	18	562.9→269	
PFDA	Primary	8.45	20	10	512.9→468.9	6.5
	Confirmatory		20	16	512.9→219	
PFOS	Primary	8.78	10	42	498.9→80.1	1.3
	Confirmatory		10	40	498.9→99.1	
PFNA	Primary	7.78	20	10	462.9→418.9	4.9
	Confirmatory		20	16	462.9→219	
PFecHS	Primary	8.1	10	25	460.9→381	2.2
	Confirmatory		10	25	460.9→99.1	
PFOA	Primary	7.11	20	10	412.9→369	3.6
	Confirmatory		20	16	412.9→169	
PFHxS	Primary	7.39	15	32	398.9→80.1	1
	Confirmatory		15	32	398.9→99.1	
PFHpA	Primary	6.35	15	10	362.9→319	4.1
	Confirmatory		15	15	362.9→169	
PFHxA	Primary	5.54	15	8	312.9→269	24.1
	Confirmatory		15	18	312.9→119.1	
PFBS	Primary	5.66	10	30	298.9→80.1	1.6
	Confirmatory		10	25	298.9→99.1	
PFPeA	Primary	4.68	10	8	263→219	NA
PFBA	Primary	3.67	10	8	212.9→169	NA
FHEA	Primary	6.14	15	20	376.9→293	3.6
	Confirmatory		15	6	376.9→313	
FOEA	Primary	7.54	15	18	476.9→393	4.3
	Confirmatory		15	12	476.9→413	
FDEA	Primary	8.83	15	8	576.8→493	3.2
	Confirmatory		15	15	576.8→513	
FOUEA	Primary	7.54	20	12	456.9→392.9	NA
FHpPA	Primary	7.54	15	12	440.9→337	1.1
	Confirmatory		15	20	440.9→317	
FHUEA	Primary	6.08	10	12	357→293	NA
MPFBA	Primary	3.67	10	7	217→172.1	NA
MPFHxA	Primary	5.54	15	8	315→270	NA
MPFHxS	Primary	7.39	15	34	402.9→84.1	NA
MPFOA	Primary	7.11	15	10	417→372	NA
MPFNA	Primary	7.81	15	9	467.9→423	NA
MPFOS	Primary	8.78	15	40	502.9→80.1	NA
MPFDA	Primary	8.45	15	10	514.9→470	NA
MPFUnA	Primary	9.05	15	10	564.9→519.9	NA
MPFDoA	Primary	9.61	15	12	614.9→569.9	NA

PFAS/PFCA Water Sample Preparation

- 5 mL water sample
- Add “Spikes”
  - Wellington MPFAC-MXA- 40 μL of 20 μg/L
    - Labeled PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS and PFOS
- Add 5 mL MeOH
- Shake
- Filter through Polypropylene Filter Unit
  - Pall Acrodisc® 25 mm Syringe Filter, with GxF/0.2μm GHP Membrane
- Add 10 μL acetic acid
- Analyze

PFAS/PFCA Sludge Sample Preparation

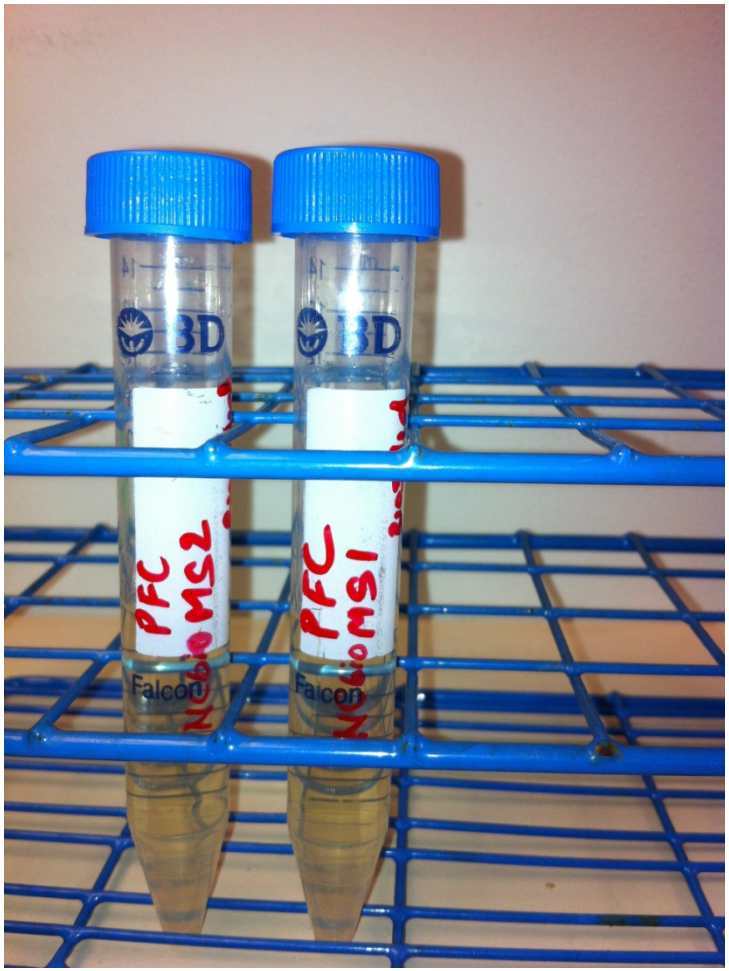
- 5 mL Sludge sample
- Add "Spikes"
  - Wellington MPFAC-MXA
    - Labeled PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS and PFOS
- Add 5 mL MeOH
- Add 20 μL NH_4OH, Shake, check if basic, pH 9-10.
- Mix for 2 minutes
- Decant the liquid and filter through Polypropylene Filter Unit
  - Pall Acrodisc® 25 mm Syringe Filter, with GxF/0.2μm GHP Membrane
- Add 50 μL acetic acid
- Analyze

PFAS/PFCA Soil/Biosolid Sample Preparation

- 2 gram sample
- Add “Spikes”
  - Wellington MPFAC-MXA
    - Labeled PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS and PFOS
- 10 ml of methanol:water (50:50) -shake/vortex for ~ 2 minutes.
- Add 20 μL NH_4OH, shake/vortex for ~ 2 minutes, check if basic, pH 9-10.
- Tumble for 1 hr
- Centrifuge
- Decant the liquid and Filter through Polypropylene Filter Unit
- Add 50 μL acetic acid
- Analyze

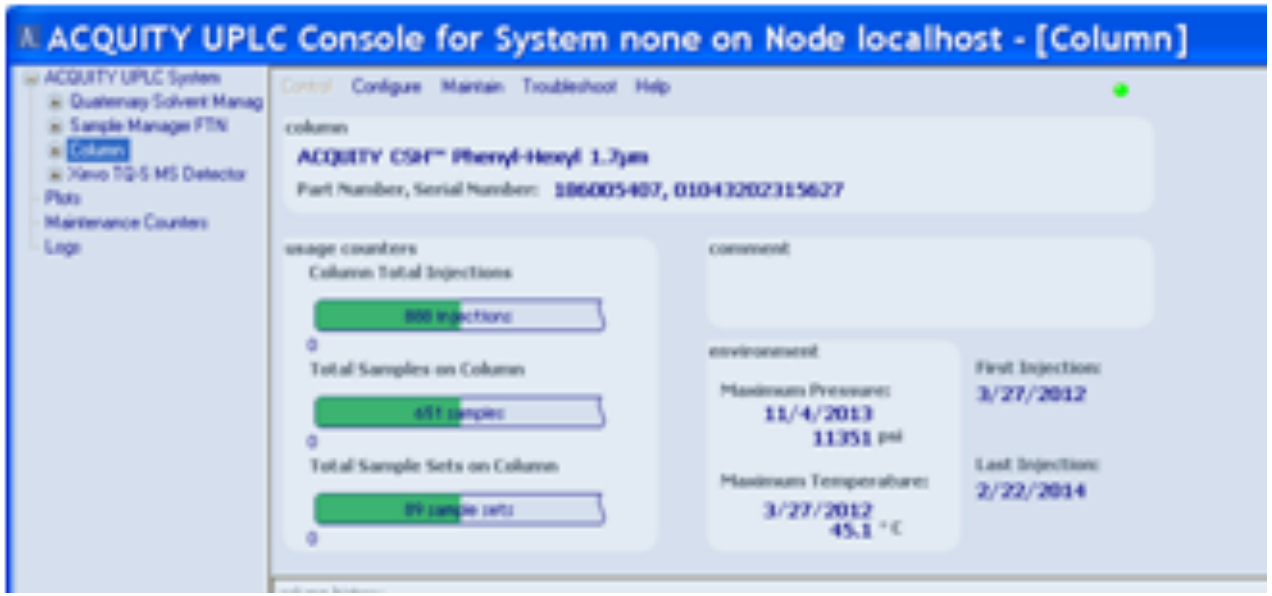
Sludge samples

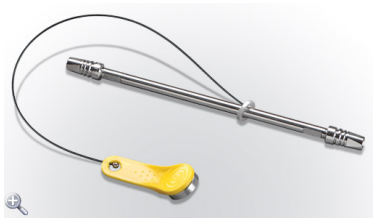
NC Sludge Sample
Before Extraction



NC Sludge Sample
After Extraction

Column Life with the “dirty” Samples





- Column performing well even with simple sample preparation.

Water Reporting Ranges

Analyte	MDL (ng/L)	Reporting Ranges (ng/L)
PFTreA	1.74	10 - 400
PFTriA	2.65	10 - 400
PFDoA	2.42	10 - 400
PFUnA	1.08	10 - 400
PFDA	3.03	10 - 400
PFOS	4.19	15 - 400
PFNA	1.76	10 - 400
PFecHS	1.93	10 - 400
PFOA	3.04	10 - 400
PFHxS	2.51	10 - 400
PFHpA	2.32	10 - 400
PFHxA	1.31	10 - 400
PFBS	7.60	30 - 400
PFPeA	11.59	50 - 2000
PFBA	13.85	50 - 2000
FHEA	92.93	300 - 8000
FOEA	106.75	300 - 8000
FDEA	47.17	200- 8000
FOUEA	2.31	10 - 400
FHpPA	3.25	10 - 400
FHUEA	1.53	10 - 400

Soil Reporting Ranges

Analyte	MDL (ng/Kg)	Reporting Limit (ng/Kg)
PFTreA	6.76	25 – 1000
PFTriA	5.26	25 – 1000
PFDoA	3.56	25 - 1000
PFUnA	2.45	25 - 1000
PFDA	5.54	25 - 1000
PFOS	18.83	50 - 1000
PFNA	2.82	25 - 1000
PFecHS	2.41	25 - 1000
PFOA	6.24	25 - 1000
PFHxS	7.75	25 - 1000
PFHpA	5.80	25 - 1000
PFHxA	15.44	50 - 1000
PFBS	6.49	25 - 1000
PFPeA	20.93	125 – 5000
PFBA	22.01	125 – 5000
FHEA	199.04	600 – 20,000
FOEA	258.37	750 – 20,000
FDEA	137.46	500 – 20,000
FOUEA	4.85	25 – 1000
FHpPA	5.09	25 – 1000
FHUEA	3.50	25 – 1000

Matrices Used to Validate ASTM D7979-15 Standard Test Method for Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

- Reagent Water
- Chicago River Water
- Sewage Treatment Plant I (STP) Effluent
- STP I Influent
- STP II (Effluent with supplemental sewage)
- STP III (Effluent with supplemental sewage)

Matrices Used to Validate ASTM D7968-14 Standard Test Method for Determination of Perfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

- Ottawa Sand
- Four ASTM Soils
  - Sand
  - Lean Clay
  - Fat Clay
  - Silt

ASTM Work Item WK50058- Standard Test Method for Determination of Select Pesticides in Water by Multiple Reaction Monitoring Liquid Chromatography Tandem Mass Spectrometry

Analyte	Reporting Ranges (ng/L)	Analyte	Reporting Ranges (ng/L)
2,4-D	250- 10,000	Dicamba	12,500- 500,000
Acetochlor	250- 10,000	Fipronil	250- 10,000
Alachlor	250- 10,000	Imidacloprid	62.5- 2,500
Aldicarb	250- 10,000	Malathion	125- 5,000
Atrazine	62.5- 2,500	Methomyl	250- 10,000
Desethylatrazine	62.5- 2,500	Metolachlor	62.5- 2,500
Desisopropylatrazine	125- 5,000	Metribuzin	125- 5,000
Azoxystrobin	31.25- 1,250	Picloram	6,250- 250,000
Bentazon	250- 10,000	Propiconazole	62.5- 2,500
Carbaryl	250- 10,000	Simazine	62.5- 2,500
Chlorpyrifos	250- 10,000	Tebuconazole	62.5- 2,500
Clopyralid	25,000- 1,000,000	Thiamethoxam	62.5- 2,500
Clothianidin	62.5- 2,500	Triclopyr	1,250- 5,000
Diazinon	62.5- 2,500		

Sample Preparation

- Water Samples
  - 8 mL Water Sample
  - 2 mL Methanol
  - Filter through 0.2 μm PTFE Filter Unit
  - Analyze

Surrogates
2,4-D (Ring-D3)
Atrazine (ethyl-D5)
Desethylatrazine (iso-propyl-D7)
Desisopropylatrazine (ethyl-D5)
Bentazon -D7
Carbofuran (Ring-13C6)
Clothianidin-D3
Diazinon-(diethyl-D10)
Dicamba-D3
Imidacloprid-D4
Methomyl (Acetohydroxamate-13C2, 15N)
Simazine (diethyl-D10)
Tebuconazole (tert-Butyl-D9)
Thiamethoxam-D3

Primary/Confirmatory SRM Ratios

Chemical	Primary/Confirmatory	MRM Transition	Retention Time Minutes	Primary/ Confirmatory SRM Area Ratio
2,4-D*	Primary	218.9®160.9	7.6	1.5
	Confirmatory	220.9®162.9		
Acetochlor	Primary	270.1® 224.1	10.3	2.5
	Confirmatory	270.1® 148		
Alachlor	Primary	270.1®238.1	10.3	2.6
	Confirmatory	270.1® 162		
Aldicarb	Primary	213® 88.9	8	2.1
	Confirmatory	213® 116		
Atrazine	Primary	216.1® 174	9.2	3.6
	Confirmatory	216.1® 95.9		
Desethylatrazine	Primary	188®146	7.6	5.4
	Confirmatory	188®78.8		
Desisopropylatrazine	Primary	174®96	6.6	1.3
	Confirmatory	174®78.8		
Azoxystrobin	Primary	404.2® 372.2	9.6	3.7
	Confirmatory	404.2® 344.2		
Bentazon	Primary	239®197	6.4	1.1
	Confirmatory	239®175		
Carbaryl	Primary	202.1®145	8.8	3.6
	Confirmatory	202.1®127		
Chlorpyrifos	Primary	350®197.9	11.4	1.8
	Confirmatory	350®322		
Clopyralid*	Primary	189.9®145.9	5.2	1.5
	Confirmatory	191.9®147.9		
Clothianidin	Primary	250®169	6.9	1.6
	Confirmatory	250®131.9		
Diazinon	Primary	305.1® 169	10.6	1.6
	Confirmatory	305.1® 153		
Dicamba*	Primary	218.9®174.9	7.1	1.5
	Confirmatory	220.9®176.9		
Fipronil	Primary	435®330	10.3	5.7
	Confirmatory	435®318		
Imidacloprid	Primary	256.1®209.1	6.9	1.1
	Confirmatory	256.1®175		
Malathion	Primary	331.1®127	9.9	1.2
	Confirmatory	331.1®285		
Methomyl	Primary	163® 87.9	6.1	1.8
	Confirmatory	163®105.9		
Metolachlor	Primary	284.1®252.1	10.3	2.4
	Confirmatory	284.1®176.1		
Metribuzin	Primary	215.1®187.1	8.5	NA
Picloram*	Primary	240.9®196.9	5.9	1
	Confirmatory	238.9®194.9		
Propiconazole	Primary	342.1®158.9	10.6	7.2
	Confirmatory	342.1®205		
Simazine	Primary	202® 132	7.6	5.4
	Confirmatory	202® 124		
Tebuconazole	Primary	308.2®70	10.5	11.2
	Confirmatory	308.2®125		
Thiamethoxam	Primary	292.1®211.1	6.3	4
	Confirmatory	292.1®131.9		
Triclopyr*	Primary	253.9® 195.9	7.8	2.9
	Confirmatory	253.9® 217.9		

Conclusion

- http://portal.astm.org
- http://intranet.epa.gov/desktop/astm.html.
- Quick, pretty robust analyses
- Meet Customer Needs
- More Boring Details: Contact me.
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