US EPA 625 Method Validation Study for Automated SPE Disk Application

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Introduction

- Solid-phase extraction has been developing for more than 3 decades and is well characterized and used in both disk and cartridge formats
- Used extensively in environmental to capture analytes
- Although it provides significant benefit to laboratories, it is not clearly permitted to be used with some methods
- Laboratories are reluctant to move forward unless they are assured that
  - They are using technology that will be accepted by auditors
  - The technology is allowed for all samples, so implementation is cost effective

US EPA Methods – Drinking Water

Number	Title	Date	Compounds
508.1	Determination of Chlorinated Pesticides, Herbicides, and Organohalides by Liquid–Solid Extraction and Electron Capture Gas Chromatography	1995	Pesticides (45)
521	Determination of Nitrosamines in Drinking Water by SPE and GC with Large Volume Injection and Neg Chem Ionization MS/MS	Sept 2004	Nitrosamines (7)
522	Determination of 1,4–Dioxane in DW using SPE and GC/MS with SIM	Sept 2008	1,4–Dioxane (1)
523	Atrazine and Simazine by SPE and GC/MS	2011	Atrazine and Simazine (2)
525.3	SVOAs in DW by SPE and GC/MS	2012	Large suite
526	Selected SemiVOAs using SPE and GC/MS	June 2000	Acetochlor to nitrobenzene and 2,4,6–trichlorophenol (11)
527.0	Determination of Selected Pesticides and Flame Retardants in DW by SPE and GC/MS	Aug 2009	Atrazine to Malathion to Vinclozolin (26)
528	Determination of Phenols in DW with SPE and GC/MS	April 2000	12 phenols (12)

US EPA Methods – Drinking Water

Number	Title	Date	Compounds
529	Determination of Explosives and Related Compounds in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS).	Sept 2002	Explosives (14)
532	Determination of Phenylurea Compounds in DW with SPE and HPLC with UV Detection	June 2000	Diflubenzuron to Thidiazuron (8)
535.1	Measurement of Chloroacetanilide and Other Acetamide Herbicide Degradates in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry	2005	Degradates (12)
537	Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS).	Sept 2009	Perfluorinated compounds (14)
539	Determination of Hormones in DW by SPE and LC-ESI-MS/MS	Nov. 2010	Hormones (7)
549.2	Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection	June 1997	Diquat and paraquat (2)

Other Regulatory Methods

- Included in US EPA SW-846 sample prep method 3535A
- Can be coupled with methods 8270, 8081, 8082, 8061, 8141, 8330, 8095 and 8321 for the determinative step

- Currently, US EPA method 608 is the only wastewater method incorporating solid phase extraction (ATP for disk technology)

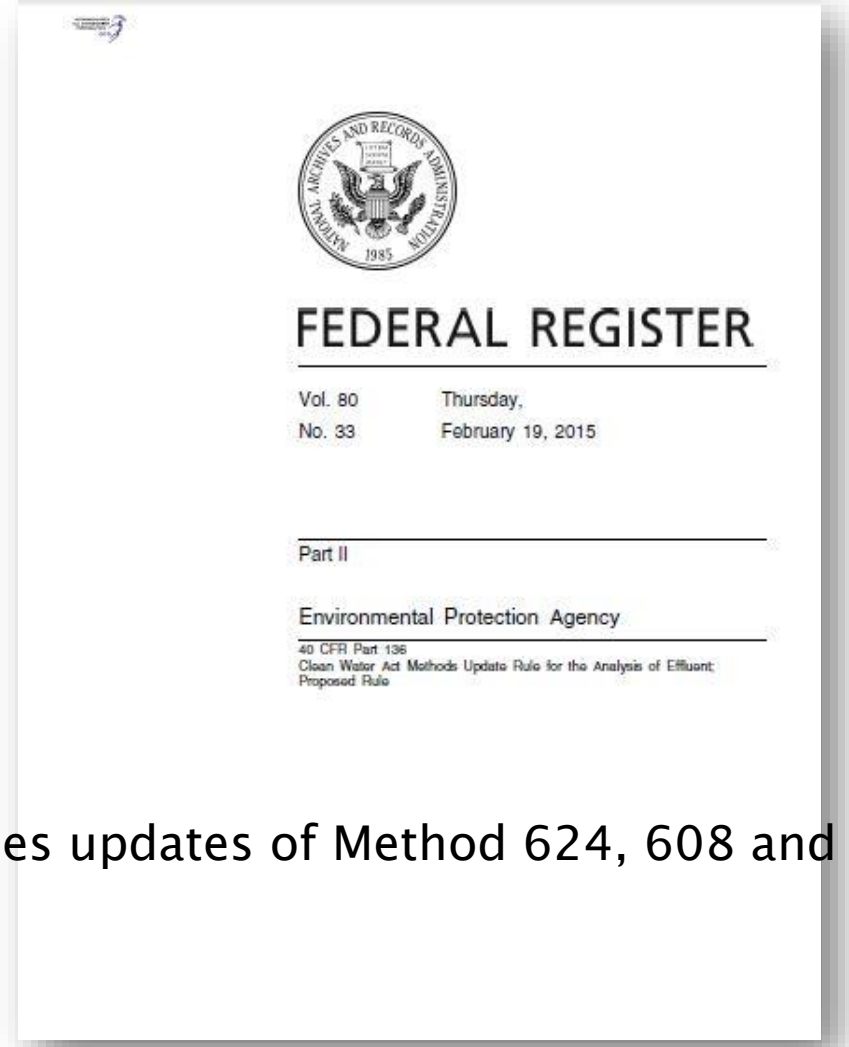
- Although many methods incorporate SPE, without a major wastewater method, such as 625, it is more difficult for laboratories to justify learning curve and the purchase of automation equipment

Problem

- Technology developers are unsure of how to proceed
  - Alternate technology procedure
  - New method

- Laboratories would like to consider new technology
  - More efficient
  - Less costly

Recent Method Update Rule (MUR) Clean Water Act



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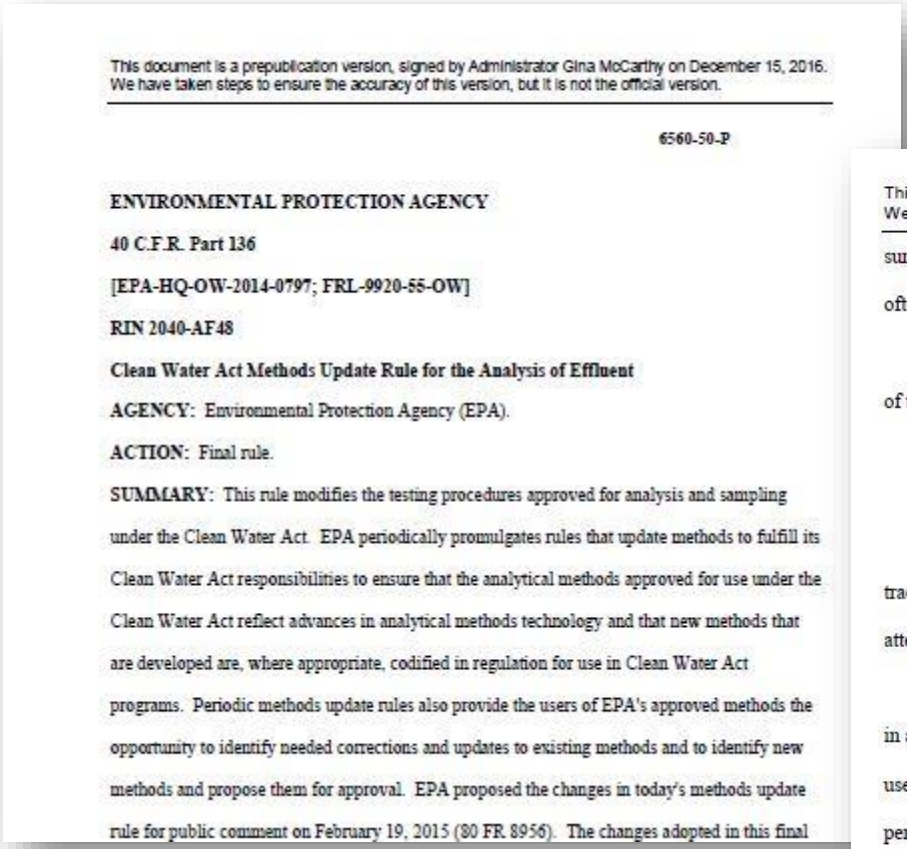
Part II

Environmental Protection Agency

40 CFR Part 136
Clean Water Act Methods Update Rule for the Analysis of Effluent; Proposed Rule

Includes updates of Method 624, 608 and 625

Signed Dec 15, 2016



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ENVIRONMENTAL PROTECTION AGENCY

40 C.F.R. Part 136

[EPA-HQ-OW-2014-0797; FRL-9920-55-OW]

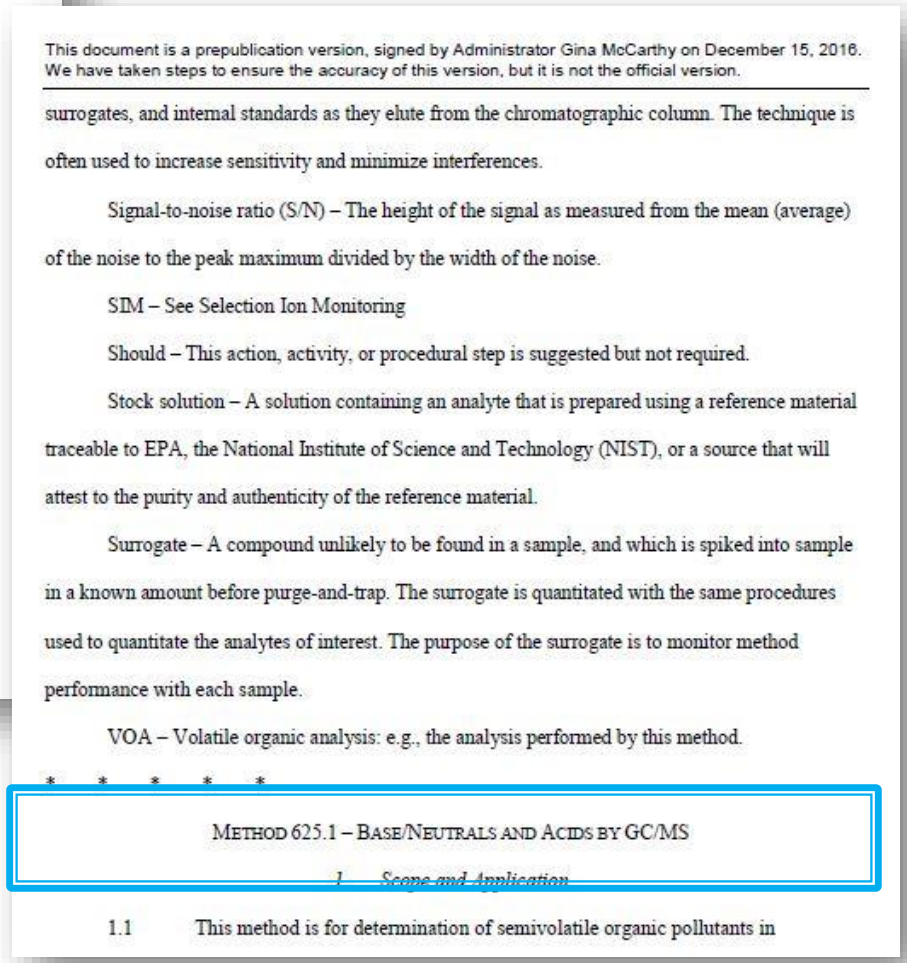
RIN 2040-AF48

Clean Water Act Methods Update Rule for the Analysis of Effluent

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This rule modifies the testing procedures approved for analysis and sampling under the Clean Water Act. EPA periodically promulgates rules that update methods to fulfill its Clean Water Act responsibilities to ensure that the analytical methods approved for use under the Clean Water Act reflect advances in analytical methods technology and that new methods that are developed are, where appropriate, codified in regulation for use in Clean Water Act programs. Periodic methods update rules also provide the users of EPA's approved methods the opportunity to identify needed corrections and updates to existing methods and to identify new methods and propose them for approval. EPA proposed the changes in today's methods update rule for public comment on February 19, 2015 (80 FR 8956). The changes adopted in this final



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surrogates, and internal standards as they elute from the chromatographic column. The technique is often used to increase sensitivity and minimize interferences.

Signal-to-noise ratio (S/N) – The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

SIM – See Selection Ion Monitoring

Should – This action, activity, or procedural step is suggested but not required.

Stock solution – A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Surrogate – A compound unlikely to be found in a sample, and which is spiked into sample in a known amount before purge-and-trap. The surrogate is quantitated with the same procedures used to quantitate the analytes of interest. The purpose of the surrogate is to monitor method performance with each sample.

VOA – Volatile organic analysis: e.g., the analysis performed by this method.

* * * * *

METHOD 625.1 – BASE/NEUTRALS AND ACIDS BY GC/MS

1 Scope and Application

1.1 This method is for determination of semivolatile organic pollutants in

Language in MUR

8.1.2.1.1 If SPE, or another allowed method modification, is to be applied to a specific discharge, the laboratory must prepare and analyze matrix spike/matrix spike duplicate (MS/MSD) samples (Section 8.3) and LCS samples (Section 8.4). The laboratory must include surrogates (Section 8.7) in each of the samples. The MS/MSD and LCS samples must be fortified with the analytes of interest (Section 1.3). If the modification is for nationwide use, MS/MSD samples must be prepared from a minimum of nine different discharges (See Section 8.1.2.1.2), and all QC acceptance criteria in this method must be met. This evaluation only needs to be performed once other than for the routine QC required by this method (for example it could be performed by the

vendor of the SPE materials) but any laboratory using that specific SPE material must have the results of the study available. This includes a full data package with the raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory (see Section 8.1.2.2.5, items a–q).

8.1.2.1.2 Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification:

(a) Effluent from a POTW.

(b) ASTM D5905 Standard Specification for Substitute Wastewater.

(c) Sewage sludge, if sewage sludge will be in the permit.

(d) ASTM D1141 Standard Specification for Substitute Ocean Water, if ocean water will be in the permit.

(e) Untreated and treated wastewaters up to a total of nine matrix types (see *http://water.epa.gov/scitech/wastetech/guide/industry.cfm*) for a list of industrial categories with existing effluent guidelines).

At least one of the above wastewater matrix types must have at least one of the following characteristics:

(i) Total suspended solids greater than 40 mg/L.

(ii) Total dissolved solids greater than 100 mg/L.

(iii) Oil and grease greater than 20 mg/L.

(iv) NaCl greater than 120 mg/L.

(v) $CaCO_3$ greater than 140 mg/L.

Clarification Document

Validation of SPE Products and Associated Procedures with Method 625.1

This document summarizes the requirements that EPA has developed in order for laboratories to utilize solid-phase extraction (SPE) as an extraction technique in EPA Method 625.1. It also provides the requirements that vendors of SPE products and equipment would have to meet in order to minimize the effort required of each individual laboratory customer. The document is divided into two sections, based on whether the product is to be applied to analytes in Method 625.1 that have existing QC acceptance criteria, or if it is to be applied to analytes in Method 625.1 without existing QC acceptance criteria.

Requirements for an SPE Vendor

Alternatively, a vendor may test their SPE product and associated procedures by performing a DOC and analyzing a background sample, and MS/MSD pairs on nine different matrix types as specified above. They must also analyze a PT sample fortified with all analytes that they are claiming that their product and associated procedures may be used to measure when performing Method 625.1.

Table A - Summary of Validation Approaches for SPE Products and Associated Procedures with EPA Method 625.1 for Measurement of the Analytes in Tables 1 & 2[1]

	Number of		Number of Analyses					
Method Application	**Labs**	**Matrix types**	**Back-ground Analysis**	**IPR-Reagent Water[2]**	**PT Sample[3]**	**MS/MSD[4]**	**MDL[5]**	**Total**
Tier 1 - Single-lab First matrix type	1	1	1	4	1	2	7	15
Each additional matrix type (8 max.)	1	1-8	1-8	0[5]	0	2[7] (16 max)	0[5]	3 (24 max)
Vendor-performed Study – All labs, all matrix types	1	9	9	4	1	18[7]	7	39

Horizon Technology Study

- Prepare samples at Horizon Technology Laboratory, Salem, NH
- Analysis and generation of data package at an accredited lab Concentrate on Table 1 and 2 compounds
- Use one liter samples

- ESC Lab Sciences, a subsidiary of Pace, Mount Juliet, TN
  - Fully accredited to ISO 17025 and other accreditations

Solid Phase Extraction and Drying Consumables

Atlantic® 8270 One Pass Disk (47 mm)

- Multi-modal media disk.
- Extracts BNA (bases, neutrals and acids) at pH 2.
- Eliminates sample basification step and extraction.
  - Saves time
  - Avoids metal hydroxide precipitation.

One Pass Carbon Cartridge

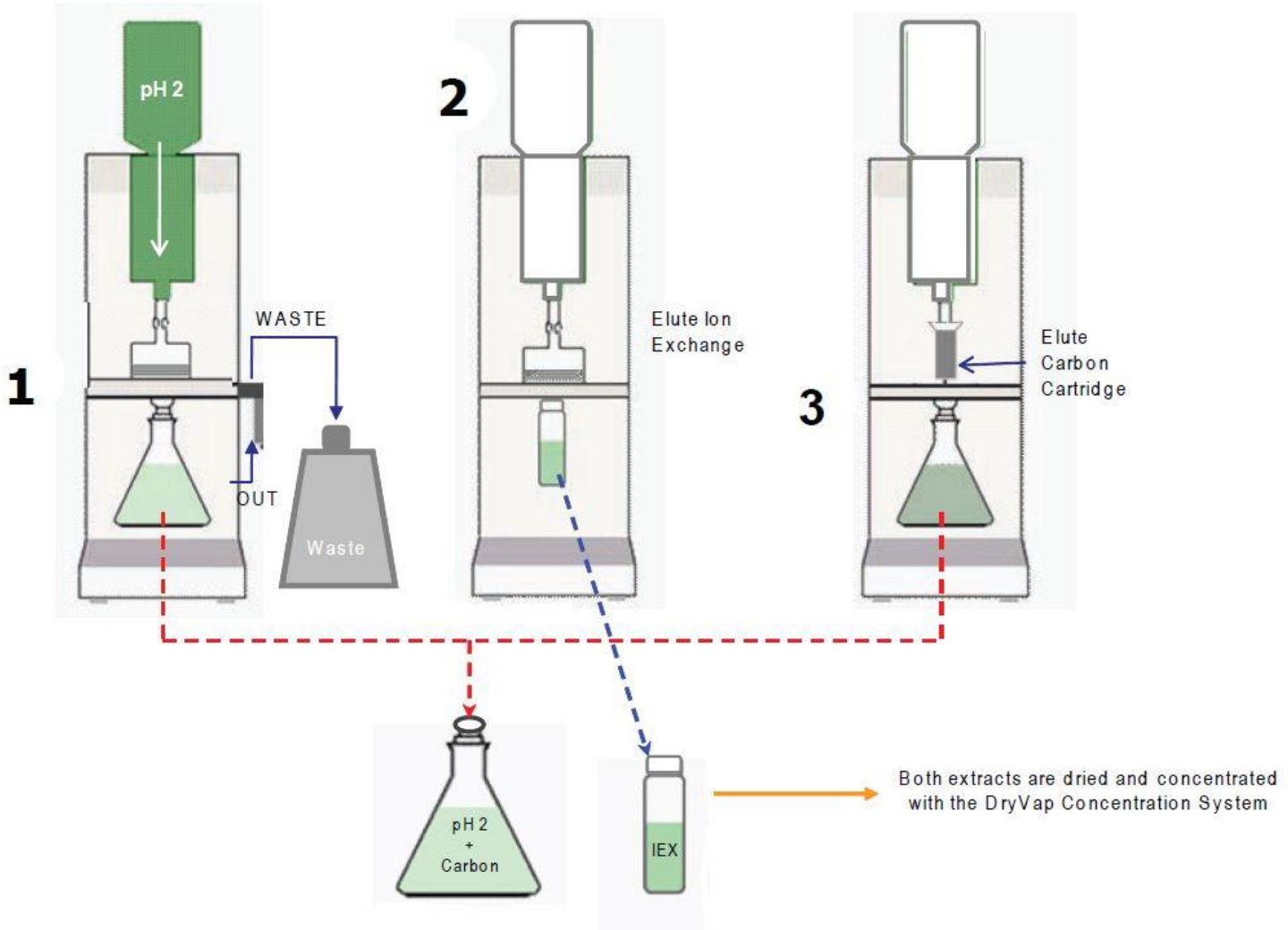
- Recovers light-end organics from post-disk sample effluent.
- e.g., NDMA, benzyl alcohol, & methyl methanesulfonate.

DryDisk® Separation Membrane

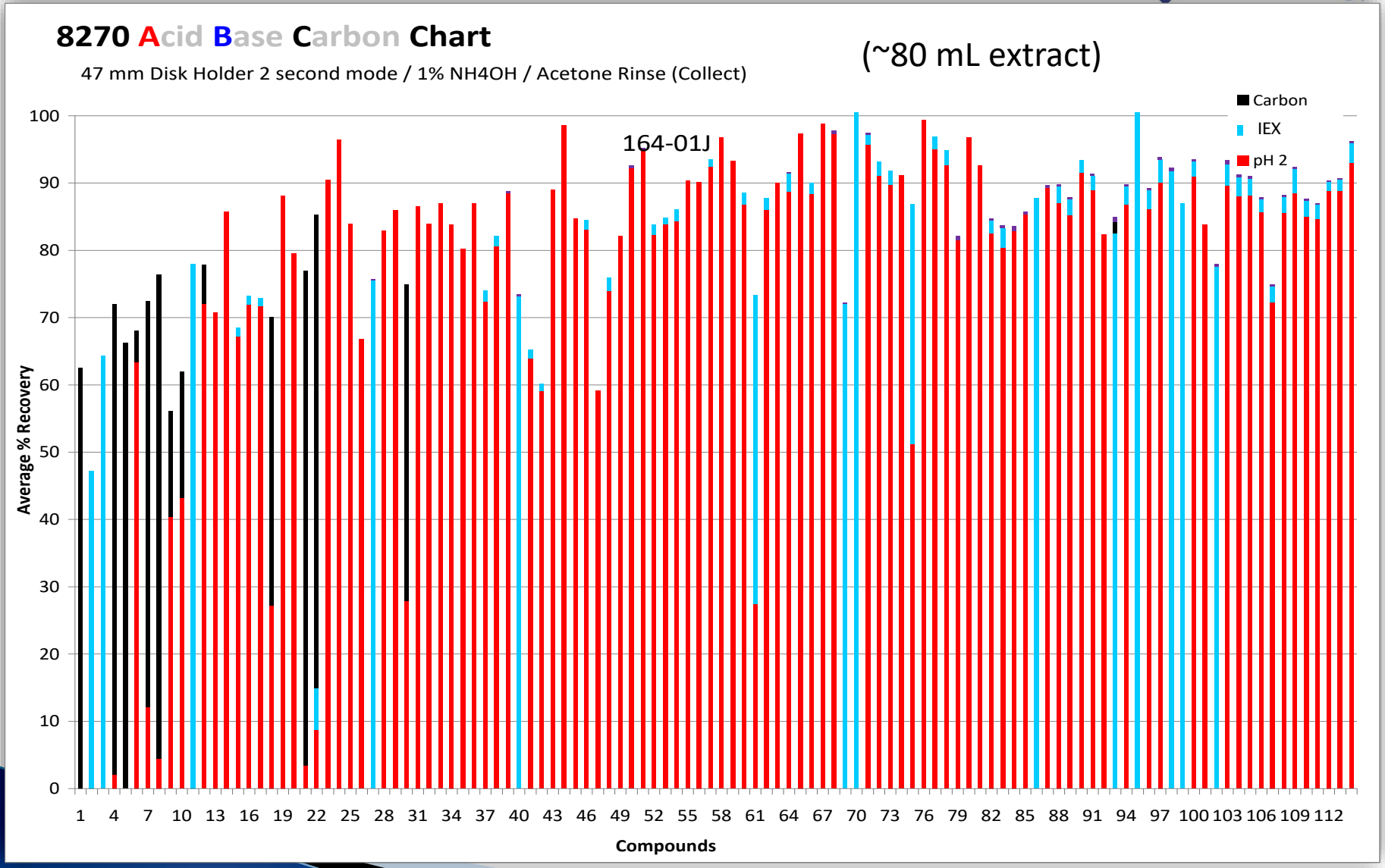
- Efficiently removes water from extract.
- Unlimited capacity for water.
- Eliminates sodium sulfate.

Horizon technology

One-Pass process



50 µg Spike into 1L DI Water, conc. to 1 mL
Standard 47 mm Disk Holder



Wastewater Descriptions

	Wastewater	Description
1	Synthetic wastewater	Prepared following ASTM D 5905 - 98
2	Synthetic seawater	Prepared from Instant Ocean, a commercially available product closely matching the composition of seawater
3	POTW Influent 1	Geographical coverage of the southern section including residential and treated industrial waste
4	POTW Effluent	Effluent from a large treatment plant
5	POTW Effluent plus O&G > 20 mg/L	To ensure the criterion is met, the effluent was spiked with 24 mg/L of Oil & Grease Standard
6	Industrial Effluent 1-RC1	PART 446—PAINT FORMULATING POINT SOURCE CATEGORY
7	Industrial Effluent 2-RC2	PART 437—THE CENTRALIZED WASTE TREATMENT POINT SOURCE CATEGORY
8	Industrial Effluent 3-ES	PART 432—MEAT AND POULTRY PRODUCTS POINT SOURCE CATEGORY
9	Industrial Effluent 4-Alpha	Part 414 - Organic Chemicals. Plastics and Synthetic fibers (OCPSF)

- A variety of wastewater types from different NPDES categories were processed

Analysis

- GC/MS with additional surrogates specified in the latest revision of method 625.1
- Additional deuterated surrogates were added to method 625.1 to better monitor performance of the method, since the previous set was shown to be inadequate

Table 8 – Suggested Internal and Surrogate Standards

	Range for Surrogate Recovery (%) [1]	
Base/neutral fraction	Calibration verification	Recovery from samples
Acenaphthalene-d_8	66 - 152	33 - 168
Acenaphthene-d_{10}	71 - 141	30 - 180
Aniline-d_5		
Anthracene-d_{10}	58 - 171	23 - 142
Benzo(a)anthracene-d_{12}	28 - 357	22 - 329
Benzo(a)pyrene-d_{12}	32 - 194	32 - 194
4-Chloroaniline-d_4	1 - 145	1 - 145
bis(2-Chloroethyl) ether-d_8	52 - 194	25 - 222
Chrysene-d_{12}	23 - 290	23 - 290
Decafluorobiphenyl		
4,4'-Dibromobiphenyl		
4,4'-Dibromooctafluorobiphenyl		
1,4-Dichlorobenzene-d_4	65 - 153	11 - 245
2,2'-Difluorobiphenyl		
Dimethyl phthalate-d_6	47 - 211	1 - 500
Fluoranthene-d_{10}	47 - 215	30 - 187
Fluorene-d_{10}	61 - 164	38 - 172
4-Fluoroaniline		
1-Fluoronaphthalene		
2-Fluoronaphthalene		
2-Methylnaphthalene-d_{10}	50 - 150	50 - 150
Naphthalene-d_8	71 - 141	22 - 192
Nitrobenzene-d_5	46 - 219	15 - 314
2,3,4,5,6-Pentafluorobiphenyl		
Perylene-d_{12}		
Phenanthrene-d_{10}	67 - 149	34 - 168
Pyrene-d_{10}	48 - 210	28 - 196
Pyridine-d_5		
Acid fraction		
2-Chlorophenol-d_4	55 - 180	33 - 180
2,4-Dichlorophenol-d_3	64 - 157	34 - 182
4,6-Dinitro-2-methylphenol-d_2	56 - 177	22 - 307
2-Fluorophenol		
4-Methylphenol-d_8	25 - 111	25 - 111
2-Nitrophenol-d_4	61 - 163	37 - 163
4-Nitrophenol-d_4	35 - 287	6 - 500
Pentafluorophenol		
2-Perfluoromethylphenol		
Phenol-d_5	48 - 208	8 - 424

Complex Wastewater

Industrial Wastewater, PART 437 THE CENTRALIZED WASTE TREATMENT POINT SOURCE CATEGORY	RC2 EFF-B L880935-27 10x	RC2 EFF-B L880935-27 20x	RC2 EFF-MS L880935-28 10x	RC2 EFF-MS L880935-28 20x	RC2 EFF-MSD L880935-29 10x	RC2 EFF-MSD L880935-29 20x	Spike Recovery 10x	Spike Recovery 20x	Range P,Ps(%)		RPD (%)	RPD Limit %	
Compound	0105_37	0110_13	0105_38	0110_14	0105_39	0110_15							
Acenaphthene	N.D.	N.D.	74.76	101.83	81.82	104.23	74.8	102	47-145	Pass	2.34	48	Pass
Acenaphthylene	N.D.	N.D.	71.35	90.43	76.68	99.24	71.4	90.4	33-145	Pass	9.29	74	Pass
Anthracene	N.D.	N.D.	77.15	105.57	85.58	111.01	77.2	105.6	27-133	Pass	5.02	66	Pass
Benzo(a)anthracene	N.D.	N.D.	76.44	98.75	84.84	102.58	76.4	98.7	33-143	Pass	3.80	53	Pass
Benzo(a)pyrene	N.D.	N.D.	81.11	99.57	86.36	105.39	81.1	99.6	17-163	Pass	5.68	72	Pass
Benzo(b)fluoranthene	N.D.	N.D.	105.47	105.21	115.58	114.39	105	105	24-159	Pass	8.36	71	Pass
Benzo(k)fluoranthene	N.D.	N.D.	110.77	115.23	122.76	115.64	111	115	11-162	Pass	0.35	63	Pass
Benzo(g,h,i)perylene	N.D.	N.D.	28.41	67.53	33.71	72.10	28.4	67.5	D-219	Pass	6.55	97	Pass
Benzylbutyl phthalate	N.D.	N.D.	109.23	103.84	124.08	106.44	109	104	D-152	Pass	2.47	60	Pass
bis(2-Chlorethoxy)methane	N.D.	N.D.	74.17	97.05	81.50	100.92	74.2	97.1	33-184	Pass	3.91	54	Pass
bis(2-Ethylhexyl)phthalate	3.681	3.841	109.80	106.11	121.25	110.08	110	106	36-166	Pass	3.67	76	Pass
bis(2-Chloroisopropyl)ether	N.D.	N.D.	65.69	86.18	72.76	96.40	65.7	86.2	8-158	Pass	11.2	82	Pass
4-Bromophenyl-phenylether	N.D.	N.D.	77.59	104.00	88.09	114.43	77.6	104	53-127	Pass	9.55	43	Pass
2-Chloronaphthalene	N.D.	N.D.	67.43	87.06	73.73	95.08	67.4	87.1	60-120	Pass	8.81	24	Pass

Red = Failing ISTD

Performance Samples

- Normal PT samples have only 60% of compounds in any one set to meet NELAC criteria

- How do we comply with requirement to include all compounds in performance testing?
  - Phenova looked through their PT samples to see how many we would have to measure to cover the full suite and it was 7 sets!
  - We worked with them to provide one PT sample with varying concentrations of 60% of the compounds of interest and also
  - A certified material with all the compounds at one concentration
  - We believe that between the two we will provide adequate support for our package

Conclusions

- Automated SPE using a one-pass disk met all the criteria specified in the new validation requirements in method 625, included in the MUR
- It was a challenge interpreting the requirements, especially when it comes to the performance materials section, although the guidance document created was very helpful
- The process was less intense that a full ATP since only one laboratory was involved rather than nine
- This also makes the cost more reasonable
- The entire study could be completed in a more timely fashion since there was less coordination required
- We are waiting for the MUR to be released

Acknowlegements

- Thank you for a wonderful variety of wastewater samples!
  - Rogers and Callcott Environmental
  - Enersolv Analytical Laboratory
  - Alpha Analytical
  - MWRA, Deer Island, MA Treatment Plant
  - City of Lawrence, MA Wastewater Treatment Plant

  - Shimadzu, Braham Prakesh and William Lipps
  - Phenova, Ty Garber

Horizon technology