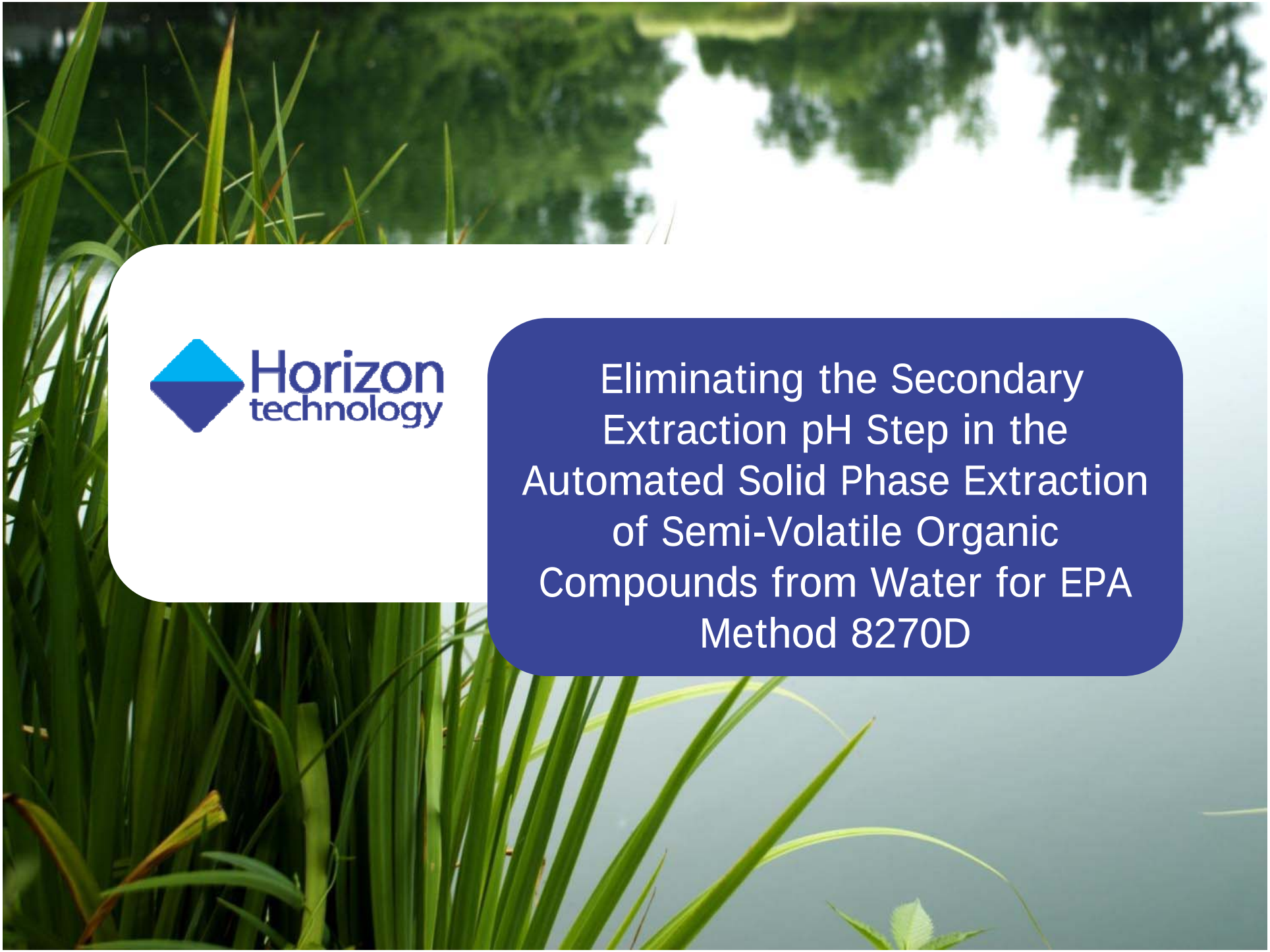


Horizon technology

Eliminating the Secondary Extraction pH Step in the Automated Solid Phase Extraction of Semi-Volatile Organic Compounds from Water for EPA Method 8270D

Outline

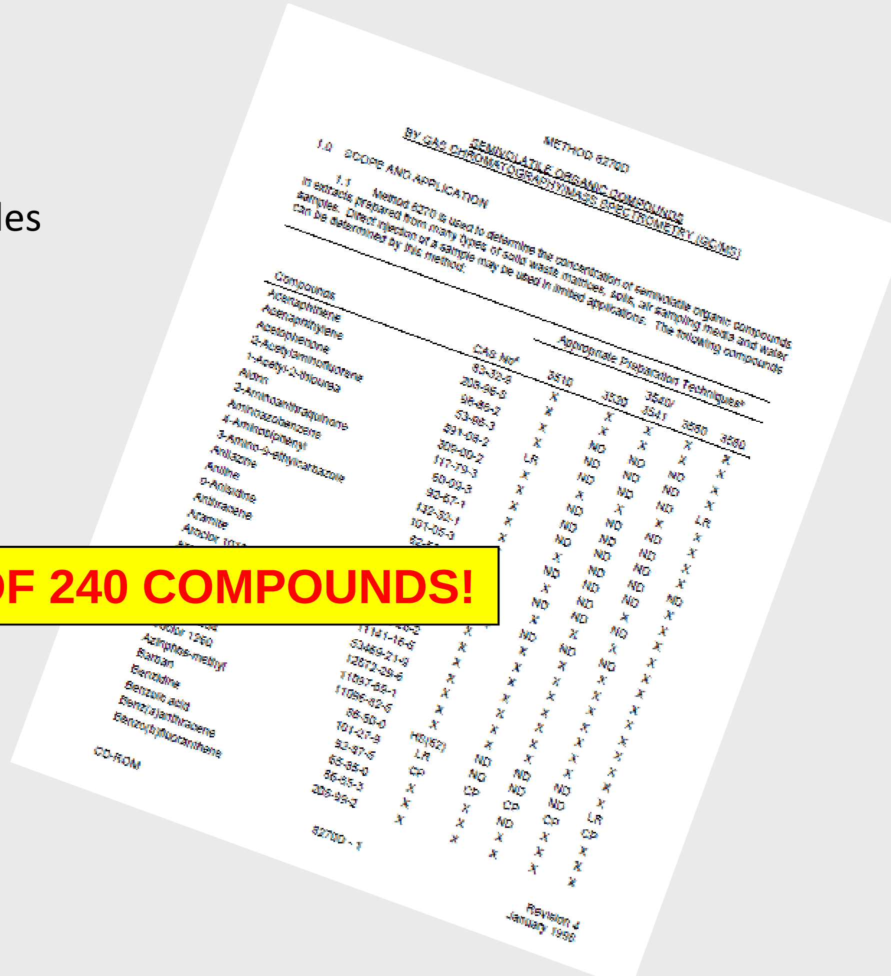
- **Discuss EPA Method 8270D.**
- **Brief Overview of Various Extraction Techniques.**
- **Review Chronology of SPE Technique Leading Up to Elimination of High pH Sample Adjustment Step.**
- **Show Examples and Performance.**

Method 8270D

EPA Method 8270D is used to determine neutral, acidic, and basic semi-volatile organic compounds that are soluble in methylene chloride.

Such compounds include:

- Polynuclear aromatic hydrocarbons
- Chlorinated hydrocarbons and pesticides
- Phthalate esters
- Organophosphate esters
- Nitrosamines
- Haloethers
- Aldehydes
- Ethers
- Ketones
- Anilines
- Pyridines
- Quinolines
- Aromatic nitro compounds
- Phenols (including nitrophenols)


METHOD 8270D

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

CD-ROM 8270D - 1 Revision 4 January 1998

A TOTAL OF 240 COMPOUNDS!

Method 8270D by Separatory Funnel

1. Acidify 1 Liter sample to **pH 2** place in separatory funnel.
2. Add 60 mL methylene chloride, shake 2 min., let stand for 10 min. collect solvent.
3. Repeat 2 more times.
4. Basify sample to **pH 12.**
5. Add 60 mL methylene chloride, shake 2 min., let stand for 10 min. collect solvent.
6. Repeat 2 more times.
7. A minimum of **360 mL of solvent is collected** and dried over sodium sulfate (**min 20 g).**
8. Amount of sodium sulfate is adjusted based on water in sample.
9. Concentrated to ~15 mL using KD or other large volume evaporation device.
9. Transferred to N-Evap to bring volume down to 1 mL
10. Add internal standard, transfer to GC vial for analysis.

Horizon technology

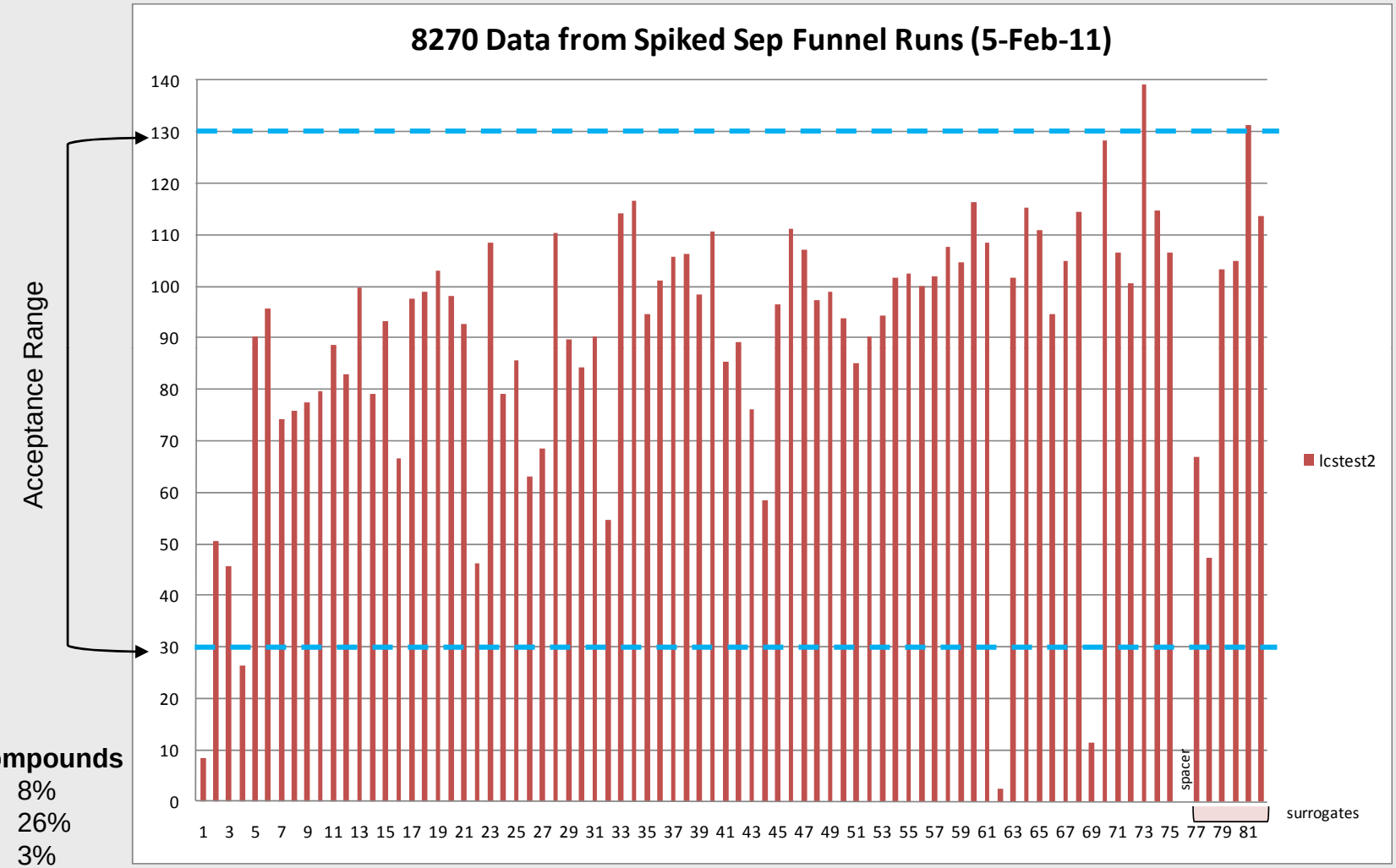
Continuous Liquid-Liquid Extraction

- Start with 1 liter of sample
- Spike with 1 mL surrogate spiking solution
- Adjust to pH 2.0 with 1:1 sulfuric acid
- Use 300 – 500 mL DCM
- **Extract for 18 – 24 hours**
- Adjust to pH 11.0 with 10N sodium hydroxide
- Use 300 – 500 mL DCM
- **Extract for 18 – 24 hours**
- **Total Processing time 36 – 48 hrs.**

Concentration Method – Impact on Recoveries.

- **The Final Recovery Result is a function of all the steps in the sample prep. process.**
- **Unless indicated, samples were dried using DryDisk® Separation Membrane instead if Na_2SO_4.**
- **Samples were concentrated using DryVap™ Concentrator System.**
  - **Evaporation temp. is BP of extract under vacuum (~28 deg C). Lower temp. minimizes imine formation.**
  - **KD runs at 75 deg C, the higher temp. reduces primary organic amine recoveries due to greater formation of imines (MW +40). A reaction from acetone from spike mixes in Sep. Funnel and or SPE.**

8270 Using Separatory Funnel Extraction



Problem compounds

Pyridine	8%
Aniline	26%
Benzidine	3%
Di-n-octyl phthalate	12%
Indeno (1,2,3,-cd)pyrene	140%
2,4,6,Tribromophenol (surr)	135%

Dried with Na_2SO_4,
Concentrated with KD & N-Evap

Horizon technology

Objective for 8270 by SPE

- **To develop a simple and optimized SPE method for the extraction of water samples using EPA Method 8270D**

- **While SPE offers many advantages over conventional LLE &CLLE techniques, several developments by Horizon Tech. have been made to deal with these limitations.**
  - **Improve recovery of light-end SVO**
  - **Handle High Particulates**
  - **Deal with High pH Precipitates**

Compound List for 8270

Target Compounds

2) NDMA
3) Pyridine
4) 2-Picoline
5) N-Nitrosomethylethylamine
6) Methyl methanesulfonate
7) 2-Fluorophenol
8) N-Nitroso-diethylamine
9) Ethyl methanesulfonate
10) Phenol-d6
11) Phenol
12) Aniline
13) Bis(2-chloroethyl)ether
14) Pentachloroethane
15) 2-Chlorophenol
16) 1,3-Dichlorobenzene
17) 1,4-Dichlorobenzene
18) 1,2-Dichlorobenzene
19) Benzyl alcohol
20) 2-Methyl phenol
21) Bis(2chloroisopropyl)ether
22) Acetophenone
23) 3+4 Methyl phenol
24) N-nitroso-di-n-propylamine
25) Hexachloroethane
26) o-Toluidine
27) Nitrobenzene-d5
28) Nitrobenzene
30) N-Nitrosopiperidine
31) Isophorone
32) 2-Nitrophenol
33) 2,4-Dimethylphenol
34) Bis(2-chlorethoxy)methane
35) Benzoic acid
36) 2,4-Dichlorophenol
37) 1,2,4-Trichlorobenzene
38) Naphthalene
39) 2,6-Dichlorophenol
40) 4-Chloroaniline
41) Hexachloropropene
42) Hexachlorobutadiene
43) N-Nitroso-di-n-butylamine
44) 4-Chloro-3-methylphenol
45) Isosafrole
46) 2-Methylnaphthalene
48) Hexachlorocyclopentadiene
49) 1,2,4,5-Tetrachlorobenzene
50) 2,4,6-Trichlorophenol
51) 2,4,5-Trichlorophenol
52) 2-Fluorobiphenol
53) Safrole
54) 2-Chloronaphthalene
55) 2-Nitroaniline
56) 1,4-Naphthoquinone
57) Dimethyl phthalate
58) 1,3-Dinitrobenzene
59) 2,6-Dinitrotoluene
60) Acenaphthylene
61) 3-Nitroaniline
62) Acenaphthene
63) 2,4-Dinitrophenol
64) Pentachlorobenzene
65) 4-Nitrophenol
66) Dibenzofuran
67) 2,4-Dinitrotoluene
68) 2,3,4,6-Tetrachlorophenol
69) 2-Naphthylamine
70) 1-Naphthylamine
71) Diethyl phthalate
72) Fluorene
73) 4-Chlorophenyl phenyl ethe
74) 4-Nitroaniline
75) 5-Nitro-o-toluidine
76) 4,6-Dinitro-2-methylphenol
77) Diphenylamine
78) Azobenzene
80) 2,4,6-Tribromophenol
81) 1,3,5-Trinitrobenzene
82) Phenacetin
83) 4-Bromophenyl phenyl ether
84) Hexachlorobenzene
85) Pentachlorophenol
86) Pentachloronitrobenzene
87) 4-Aminobiphenyl
88) Dinoseb
89) Phenanthrene
90) Anthracene
91) Carbazole
92) Di-n-butyl phthalate
93) 4-Nitroquinoline-1-oxide
94) Methapyriline
95) Fluoranthene
96) Benzidine
97) Pyrene
99) p-Terphenyl-d14
100) Dimethylaminoazobenzene
101) 3,3'-Dimethylbenzidine
102) Butyl benzyl phthalate
103) Acetylaminofluorene
104) 3,3'-Dichlorobenzidine
105) Benz(a)anthracene
106) Chrysene
107) Bis(2-ethylhexyl)phthalate
108) Di-n-octyl phthalate
110) 7,12-Dimethylbenz(a)anthra
111) Benzo(b)fluoranthene
112) Benzo(k)fluoranthene
113) Benzo(a)pyrene
114) 3-Methylcholanthrene
115) Indeno(1,2,3-cd)pyrene
116) Dibenz(ah)anthracene
117) Benzo(ghi)perylene

50 ug of each analyte is spiked into the DI water sample.

6 Surrogates are also included in this mix.

Horizon technology

SPE Chronology

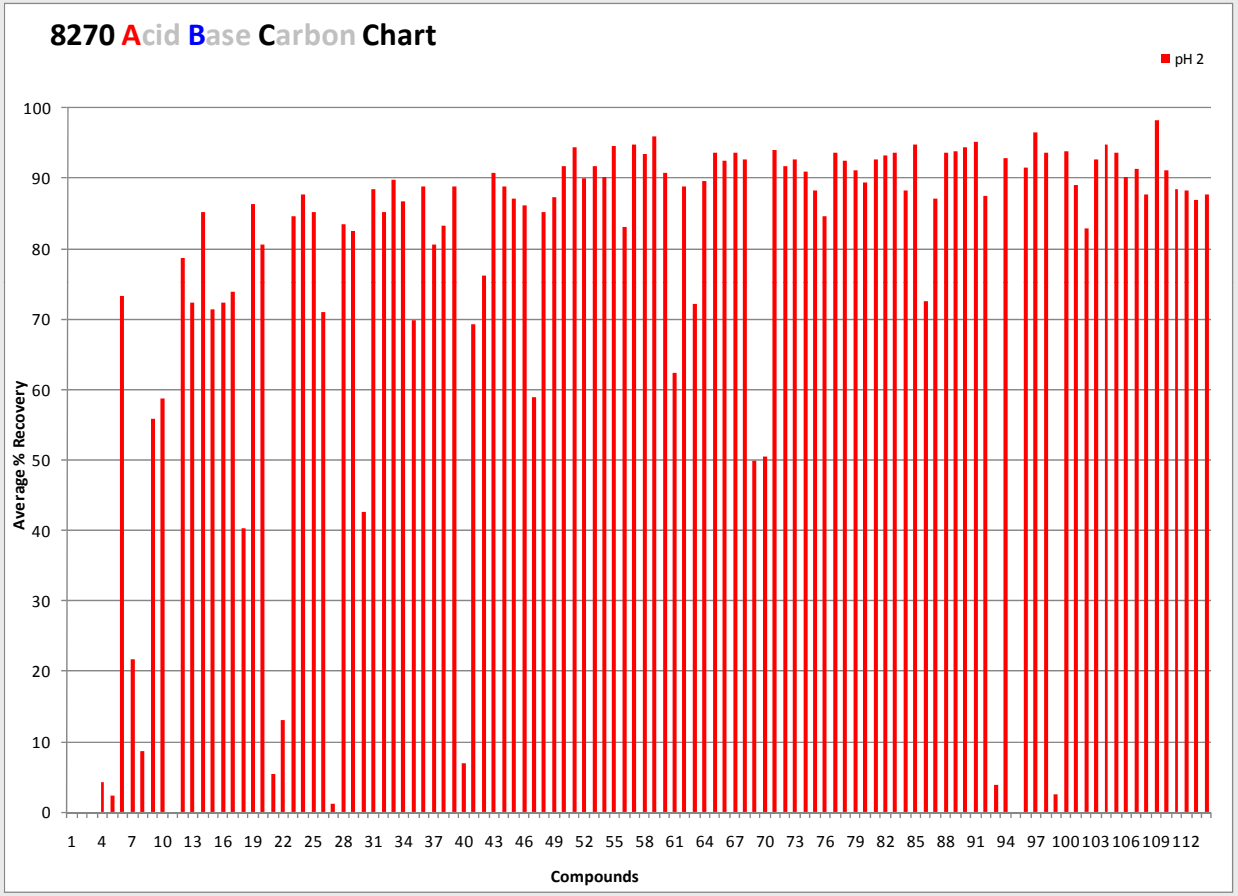
2008 | 2009 | 2010 | 2011

Introduced SPE Disks with Two Mechanisms for Analyte Retention.

- Introduce a 47 mm disk with resin based media containing both Hydrophobic and Hydrophilic sites called the **Atlantic™ HLB disk**.

- Being resin based, there are no pH limitations as with silica based media.

- The inclusion of hydrophilic groups improves general recoveries for polar groups on the analytes.



SPE Chronology

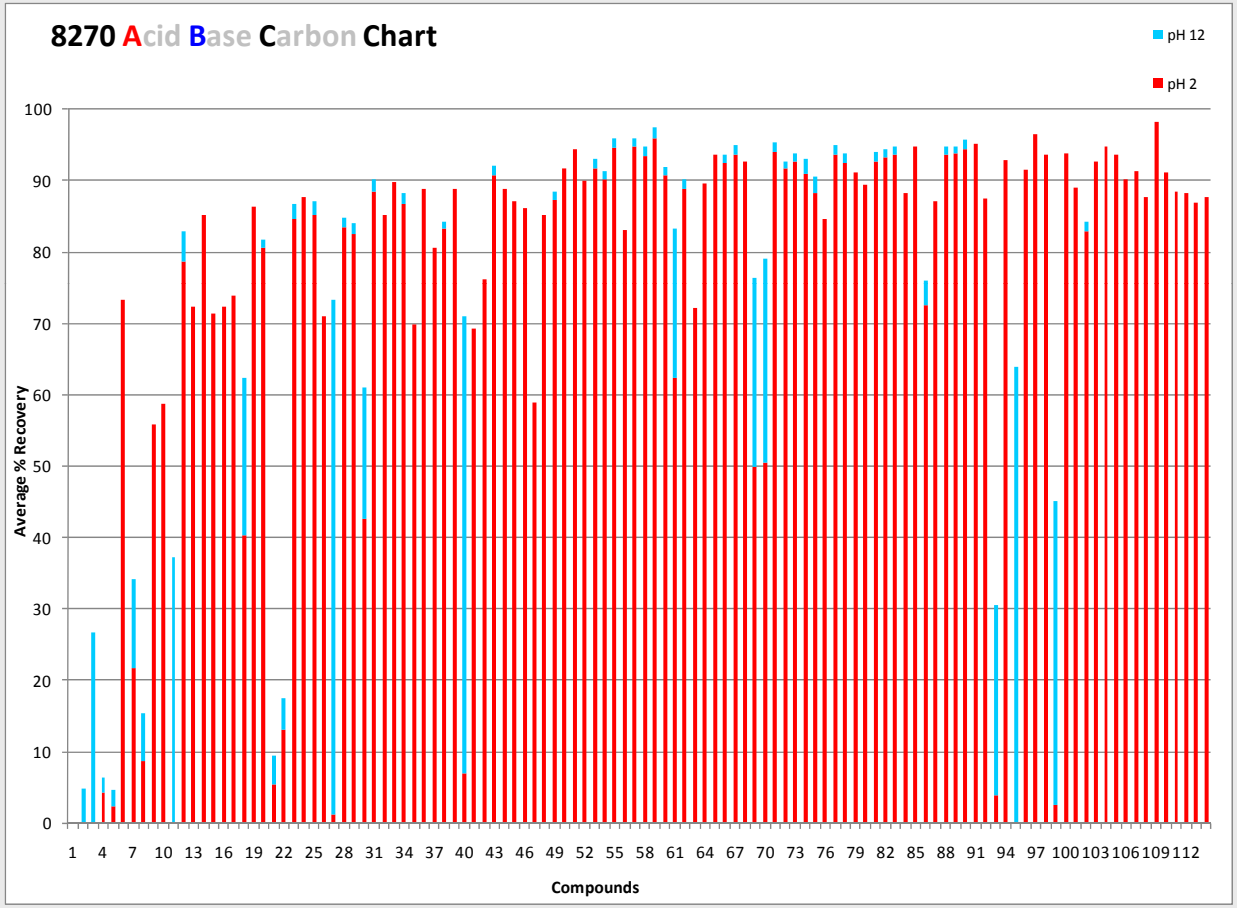
2008 2009 2010 2011

Use Atlantic HLB-H in Combination with Dual pH Kit.

Now include a sample bottle kit with line connections that enables the automatic extractor to collect the effluent from the first passing of the sample through the disk instead of going to aq. waste.

The acidic effluent is adjusted to pH 12 and passed through the same disk a second time to capture organic bases.

The blue columns are the bases such as aniline, 4-chloroaniline and benzidine that are now being captured and added to the extract.



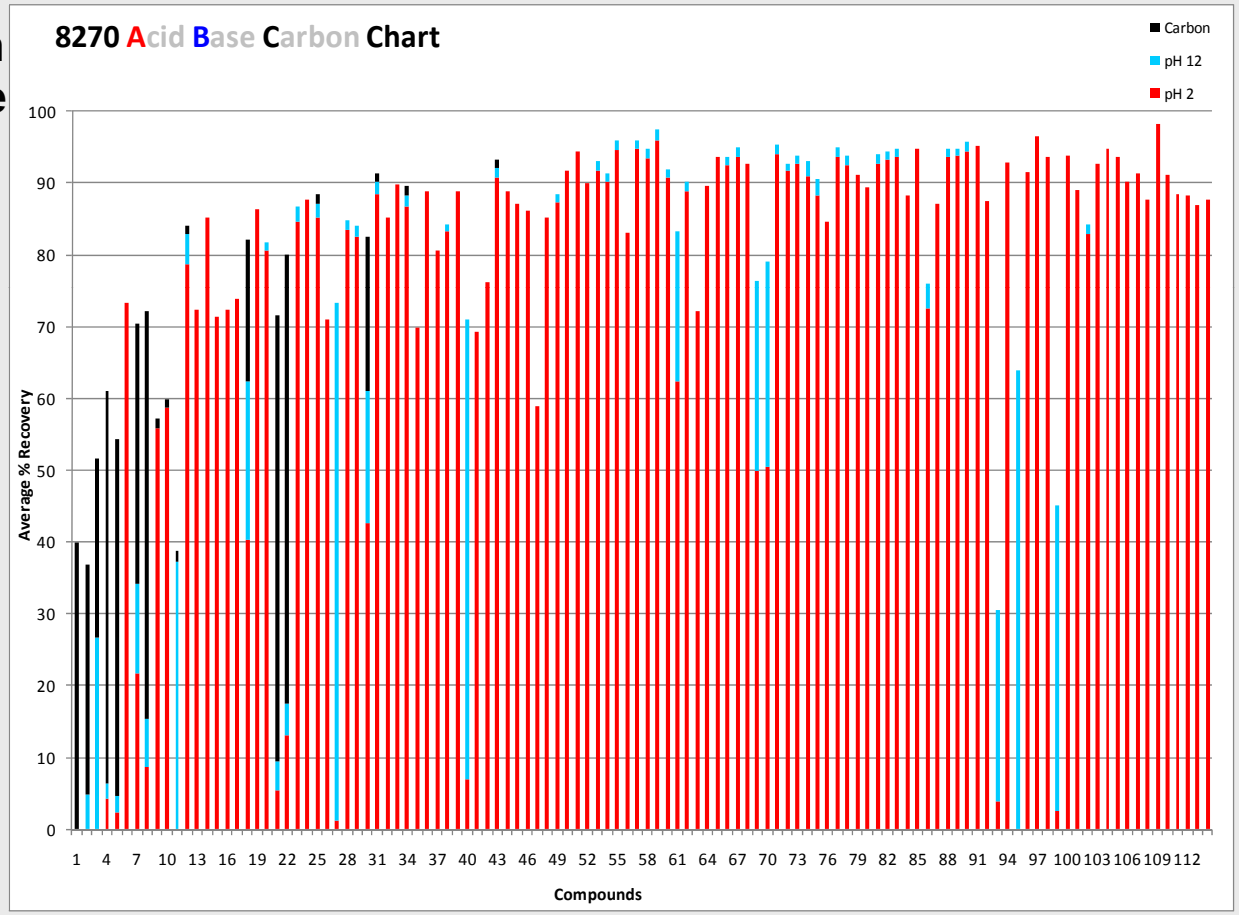
Horizon technology

SPE Chronology

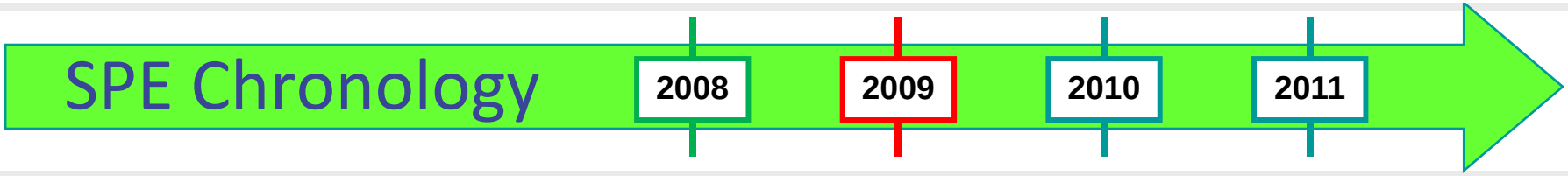
2008 | 2009 | 2010 | 2011

Enhance Dual pH Kit with Carbon Cartridge and Interface.

Include the **8270 Carbon Cartridge** with effluent collection kit. The **8270 Carbon Cartridge** scavenges the pH 12 effluent for light-end semi-volatiles such as n-nitrosodimethylamine (**NDMA**), **pyridine** and **short-chain sulfonates.**



Horizon technology



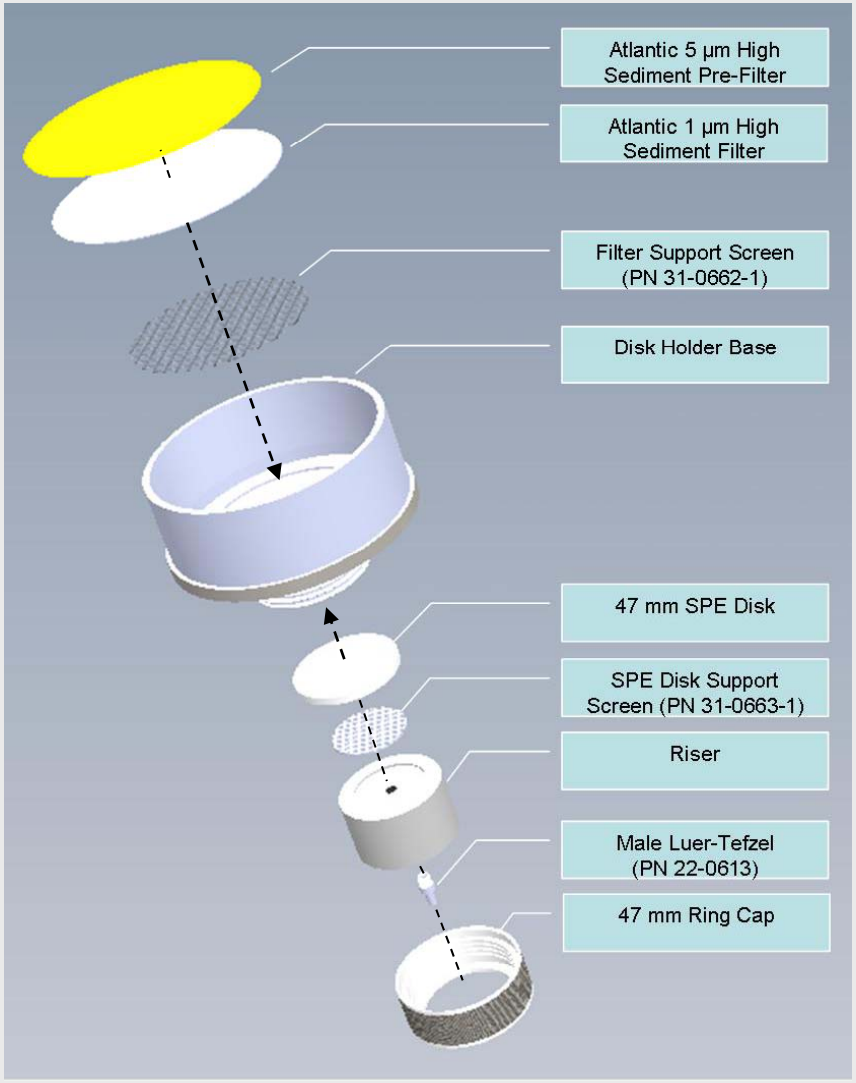
Extend Atlantic HLB Disk Line with Different Media Capacities.

- Disks offered in High, Medium, and Low media capacity.
- Choose disk that meets analytical needs.
- Disk formulation refined – reduced glass fiber .
  - Improves efficiency for GC based extractions.
  - Reduces water remaining in the extract.
    - Reduces concentration time for LC based extractions.

SPE Chronology

2008 | 2009 | 2010 | 2011

Provide a 47 mm Disk Holder with 6x More Filtering Surface Area.



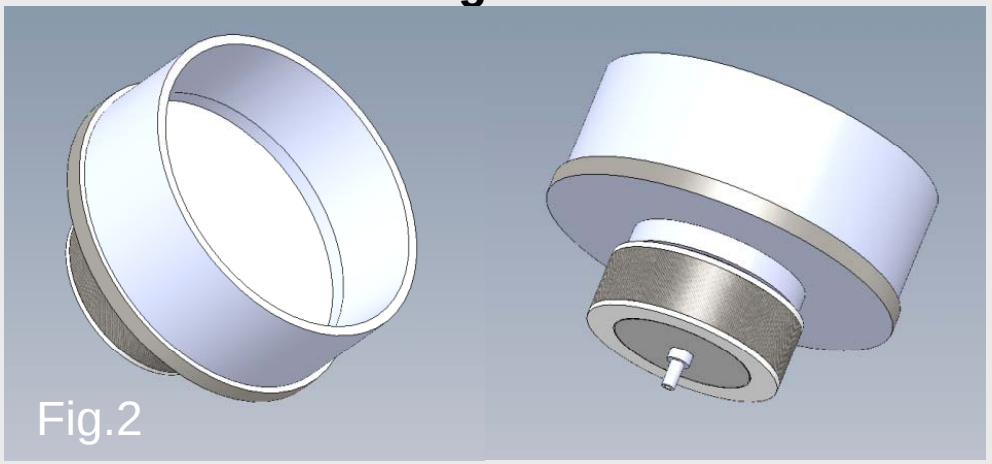


Fig.2

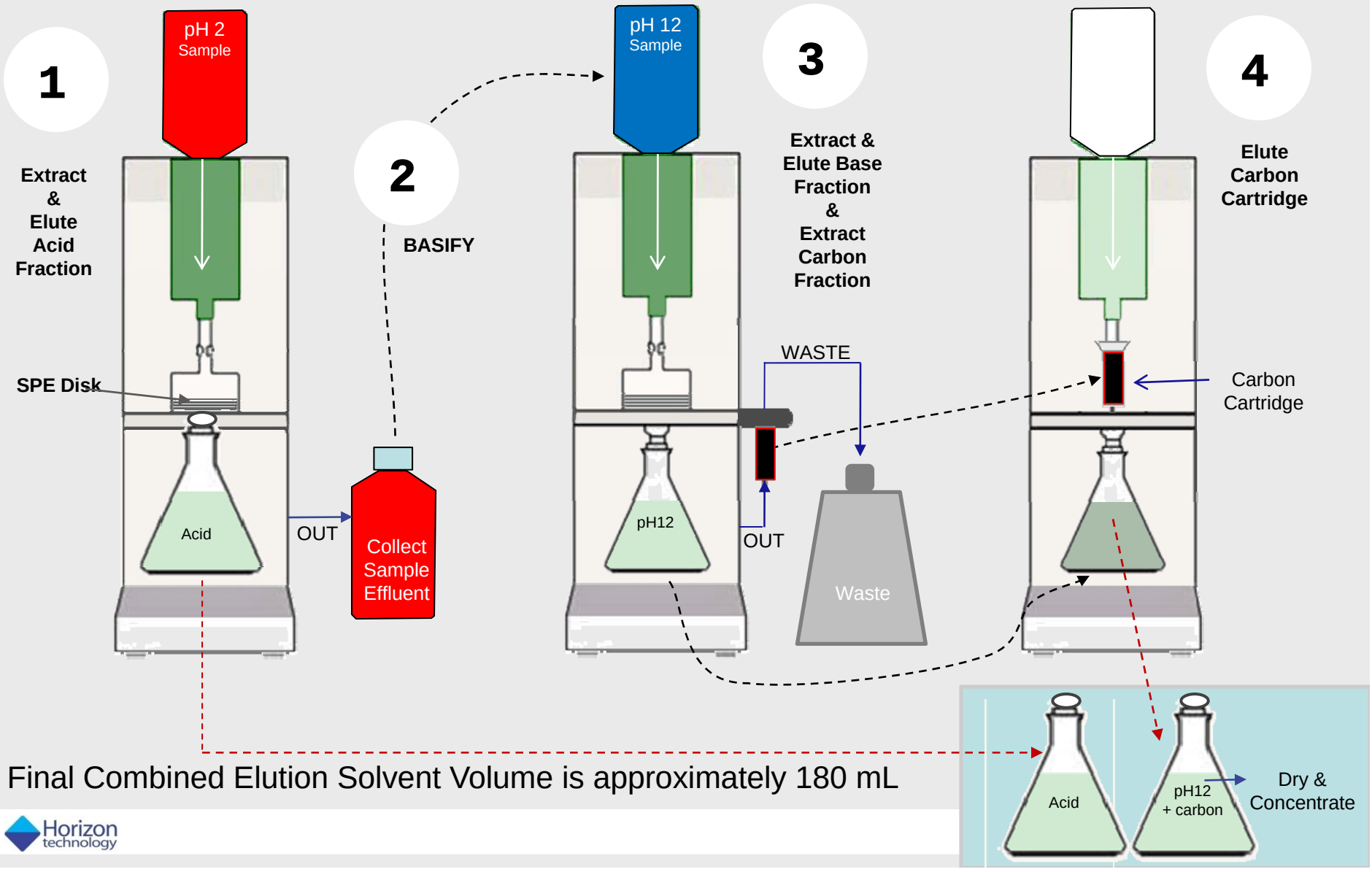
Fast Flow Sediment Disk Holder (FFSDH)

- Uses 1 and 5 um prefilters.
- 230 mL sample reservoir.
- Additional accessories available for stratifying highly sedimentatious samples.
- Greatly expands the range of particulate and solid laden samples. (e.g. waste water treatment samples.)

Horizon technology

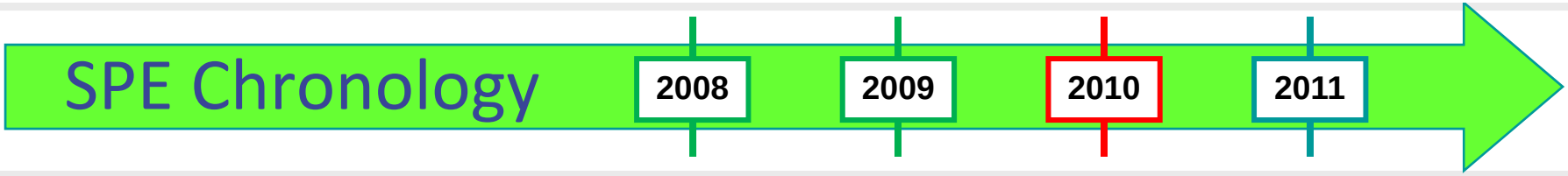
8270 Two Pass – Three Elutions (Method Summary)

One Automated Extractor Used Throughout



Final Combined Elution Solvent Volume is approximately 180 mL

Horizon technology

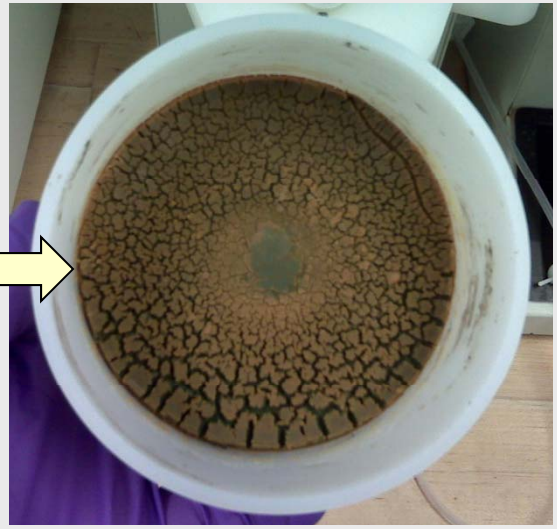


The FFSDH Layering Effect for an 8270 Run

500 mL of an actual customer wastewater sample

Run using FFSDH with 1 Atlantic Fine Prefilter and 2 Atlantic Coarse Prefilters.

Process Time: 22 min



Process Time (w/ Carbon): 25 min

Horizon technology

SPE Chronology

2008 | 2009 | 2010 | 2011

Effect of High pH with Hard Water and Transition Metals.

Eluate from
pH 2 pass.
Nice and Clear.

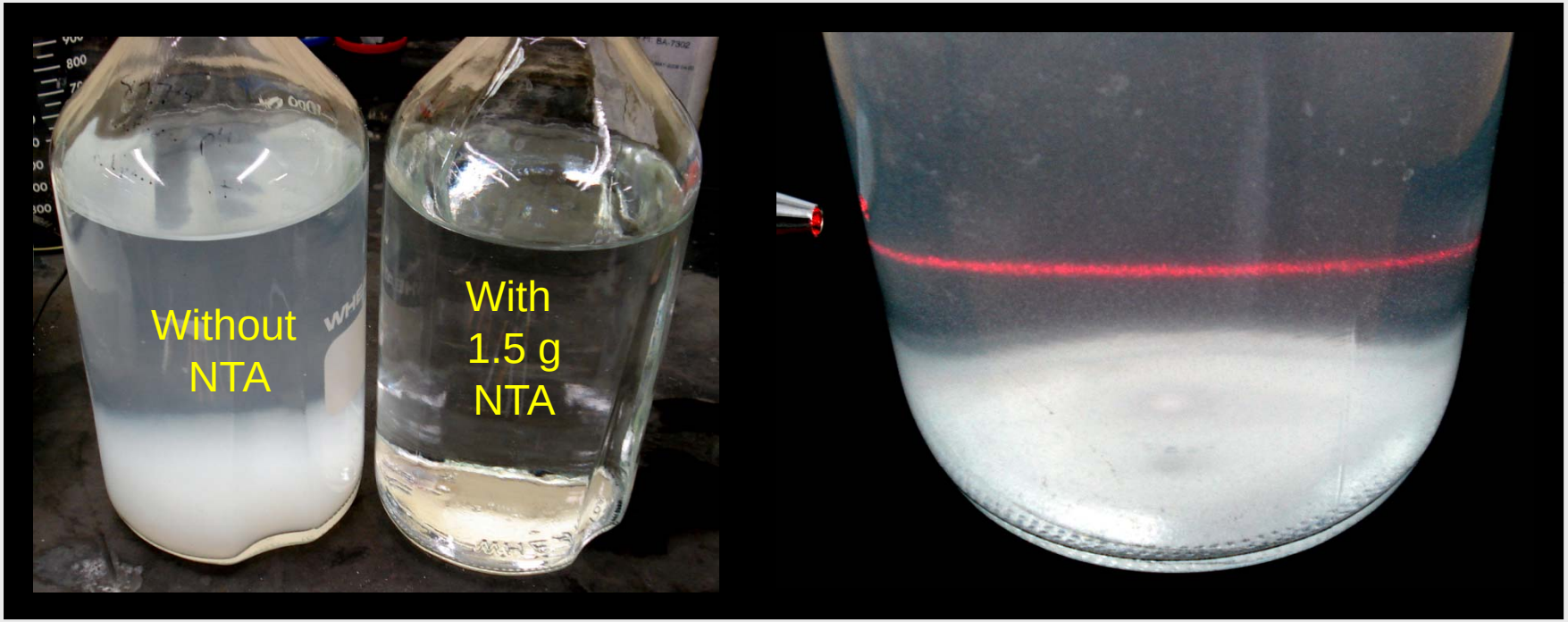
pH 12 adjusted Pond Water turned yellow. Particulates (precipitate) forming as evident by the visible laser pointer beam reflecting light as it passes through bottle.

Horizon technology

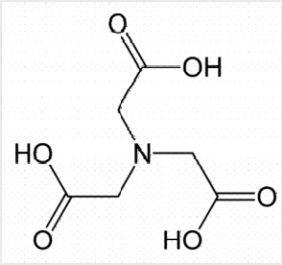
SPE Chronology

2008 | 2009 | 2010 | 2011

Using Biodegradable Chelating Agent to Negate Precipitate



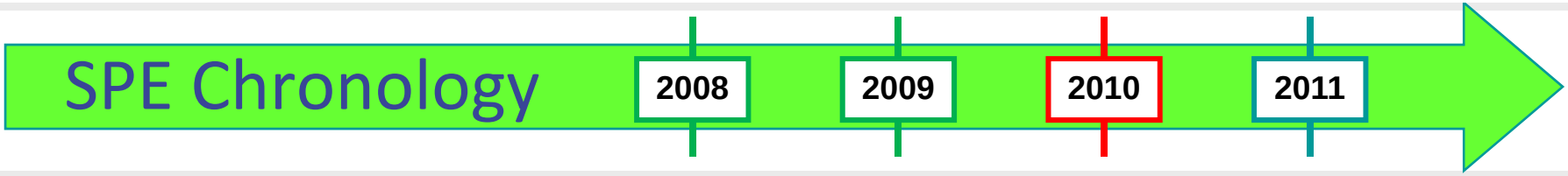
Synthetic Hard Water (400 ppm) @ pH 12



NTA (Nitrilo triacetic acid)
Chelates with Mg and Ca Ions.
I

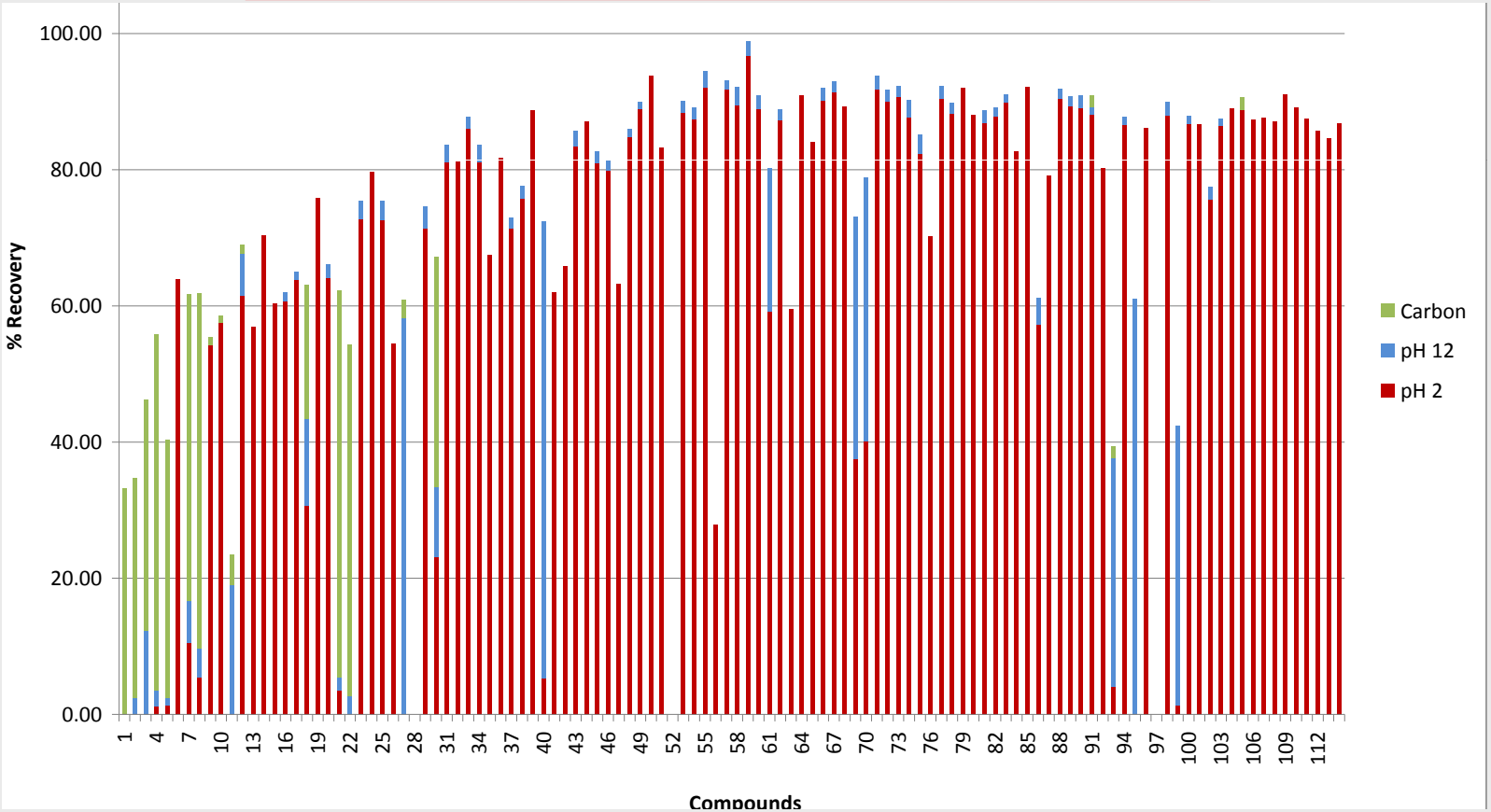
Excessive water hardness
can challenge even the FFSDH.

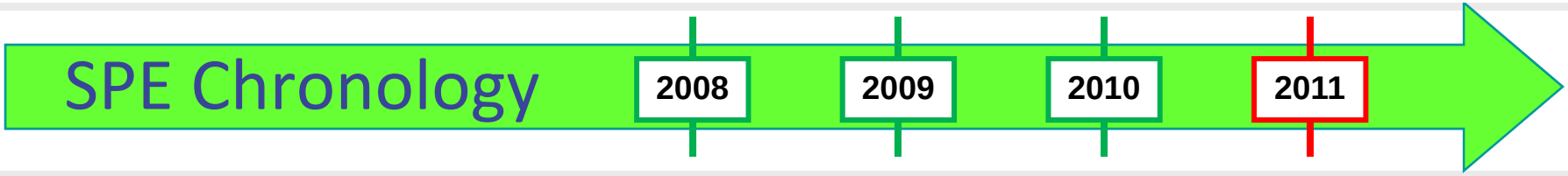
Horizon technology



8270 Analysis of 400 ppm Hard Water using 1.5 g NTA

Chemistry shows compatibility with GC-MS analysis.
Can this basification step be eliminated?.





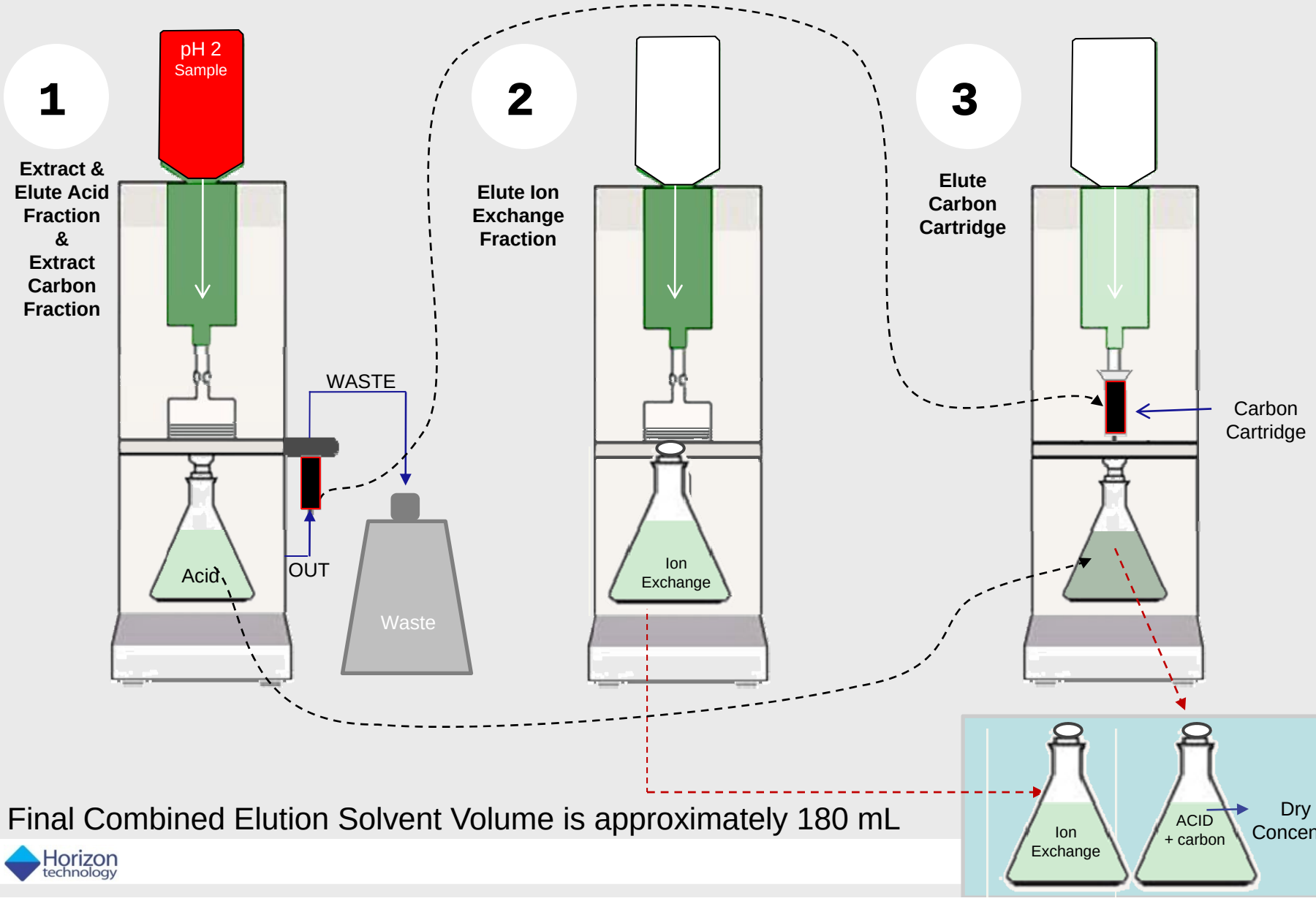
Introduce a SPE Disk with Three Mechanisms for Analyte Retention.

Atlantic™ 8270 One Pass Disk

- Incorporate Ion Exchange with Hydrophilic and Lipophilic character to the disk.
- Formulated to handle high levels of inorganic cations, hard water, brackish and near sea water levels of sodium.

8270 One Pass – Three Elutions (Method Summary)

One Automated Extractor Used Throughout



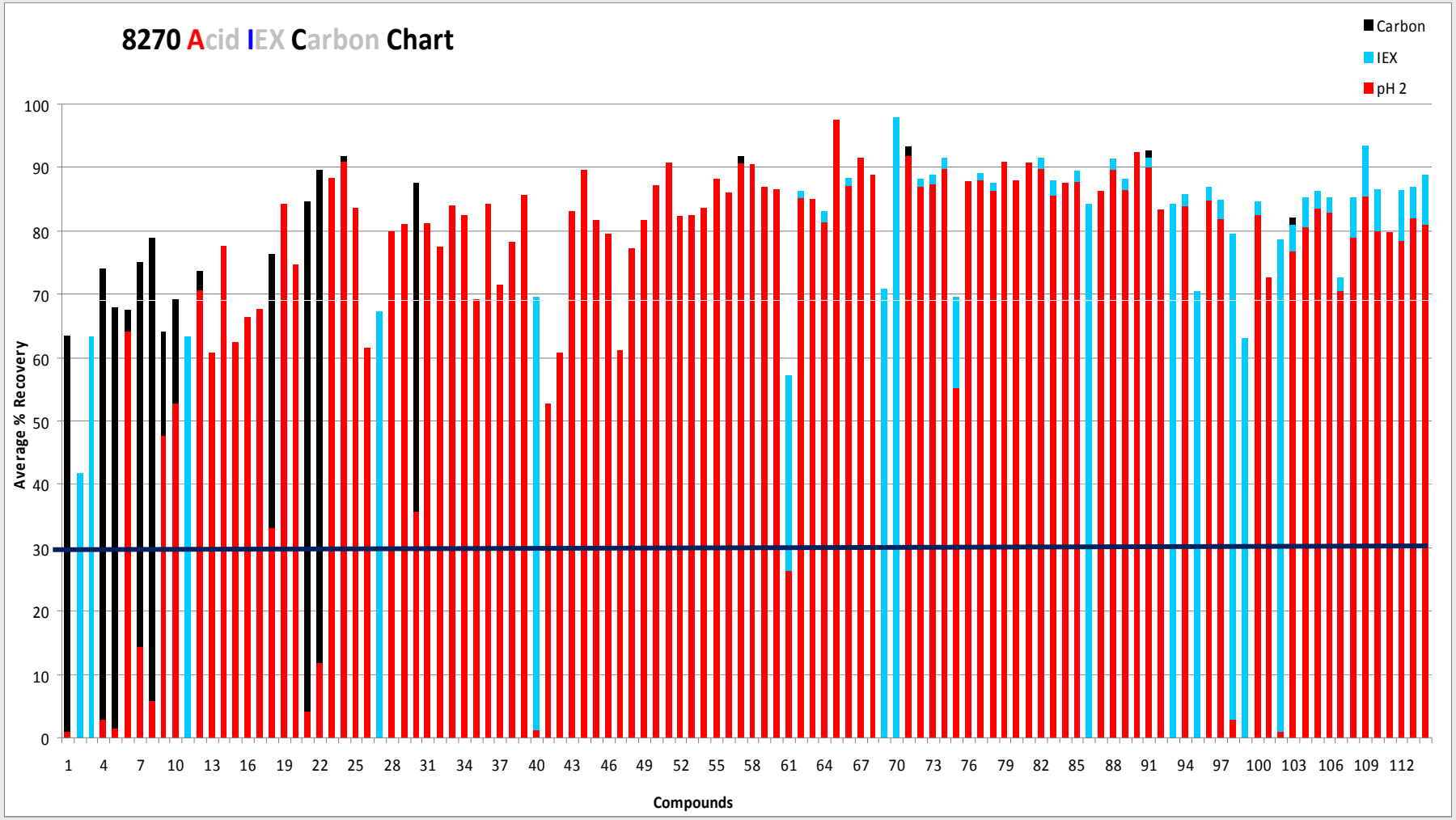
Final Combined Elution Solvent Volume is approximately 180 mL

Horizon technology

8270 One Pass Disk Solvents

- Prewet Solvents:
  - Acetone
  - Reagent Water
- Rinse Solvents:
  - Methylene Chloride
  - Acetone
  - Ammonium Hydroxide (1 % NH_4OH)

Performance of Atlantic™ 8270 One Pass SPE Disk



Conclusions – 8270 One Pass Method

- Eliminates the high pH precipitates when alkaline earths and transition metals are present in the sample.

- Faster by 1 hour over dual pH SPE for 8270 for samples that have low metal content . (Extraction time ~1 hr 45 min).

- Substantially more time saved over dual pH method with high amounts of water hardness.

- Less Solvent Consumption with FFSDH

- Speed of processing comparable to Separatory Funnel but with automation, leaving time for other activities.

- Improved recovery of light ends over Separatory Funnel.

- No problems with emulsions as with LLE.

- Significantly faster than CLLE with comparable recoveries.

Questions?