The Role of the Carbon Cartridge in the One-Pass System

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Introduction

Biotage is a leader in sample preparation using solid phase extraction (SPE) for semi/nonvolatile extraction. One recent introduction is a system to extract a full range of acid/base neutral compounds from various types of water samples using a One-Pass system. In this case, rather than extract water at pH 2, adjust the pH of the water to 12 and re-extract, the water is passed once through a multi-media SPE disk and then a carbon cartridge before being delivered to waste. The elegance of this approach is the elimination of the basification step, which requires additional labor adjusting the pH and time passing the sample through the disk a second time after the first elution of acids and neutrals. The additional benefit of omitting the basification step eliminates the formation of insoluble metal hydroxides that can restrict the flow of sample through the disk or add significant time if a liquid-liquid extraction is used.

A schematic of the system is shown in Figure 1.

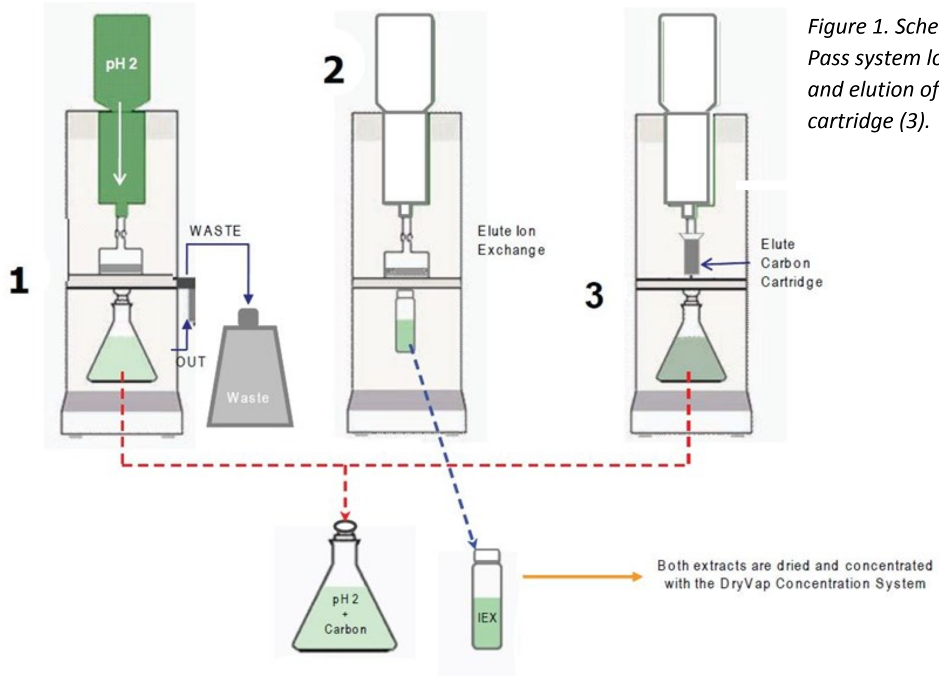


Figure 1. Schematic of the One-Pass system loading of sample (1) and elution of the disk (1,2) and cartridge (3).

The solubility range of compounds for a wide suite of semivolatile analytes, such as seen in US EPA method 625 or 8270 is amazingly disparate and includes compounds from infinitely soluble methyl methanesulfonate to benzo(k)fluoranthene @ 8.00×10^{-7} g/L.[1,2]

Liquid-liquid extraction (LLE) cannot be expected to efficiently extract very water soluble compounds into a non-polar solvent like methylene chloride. Recovery of highly water soluble compounds is very dependent on the matrix properties, such as the ionic strength.

In SPE there is no single sorbent that can handle this range of solubility or charged state of the analytes, so a multimodal media disk (Hydrophilic/Lipophilic groups along with cation exchange sites on the resin) is used for the majority of compounds. Compounds that are unretained on the disk are captured by the Max Detect Carbon Cartridge. These compounds typically have water solubility of $\geq$10g/L or may be anionic in nature, e.g. N-Nitroso compounds like N-Nitrosodimethylamine (NDMA) and short chain alkyl-sulfonates.

The One-Pass disk is resin-based, offering several benefits over silica-based sorbents like C18. The sorbent requires no activation with methanol and is stable with samples at extreme acidic and basic conditions. The resin has several times more reversed-phase retention capacity over silica, as the resin backbone is the sorbent whereas the bonding capacity of C18 is only found on the surface. Silica C18 loses C18 through hydrolysis at pH <2 and the silica begins to dissolve at a pH above 7.

The Max Detect Carbon cartridge has been designed to be complementary to the One-Pass disk as it can capture analytes passing through as fast as 100 mL/min. The cartridge contains activated carbon, not non-porous graphitized carbon, making it especially suitable for this purpose. In addition the cartridge captures compounds through a backflush process to minimize the solvent used in elution.

In some cases the carbon cartridge is not needed in the One-Pass system when the compounds retained on the carbon cartridge are not of interest.

Table 1 shows a table of selected compounds showing the distribution in their elution between the acid fraction, ion exchange fraction and the carbon fraction.

The utility of the carbon cartridge can also be seen in Figures 2 and 3. Figure 2 shows a full suite of compounds extracting using liquid-liquid (blue) compared to the One-Pass process (red). The compounds are named in Appendix 1, but include a full suite of semivolatile compounds. It is easily seen in the compound by compound comparison that the SPE One-Pass procedure works very well and in many cases gives a more accurate recovery. Figure 3 shows the same set of compounds extracted with the One-Pass system and the compound bar graph colored to indicate which fraction contained the analyte of interest. You can readily see that each component contributes to the compound recovery and makes the system effective.

Table 1. Selected Compound Elution Percentage in Acid/Neutral, Cation Exchange, or Carbon Carbridge Fraction.

Target Compounds	CAS No.	Analyte Number	ACID/Neutral	CATION EXCHANGE	CARBON
N-Nitrosodimethylamine (NDMA)	62-75-9	1	0	0	100
Pyridine	110-86-1	2	0	100	0
2-Picoline (2-Methylpyridine)	109-06-8	3	0	100	0
N-Nitrosomethylethylamine	10595-95-6	4	5	0	95
Methyl methanesulfonate	66-27-3	5	2	5	93
N-Nitrosodiethylamine	55-18-5	7	20	0	80
Ethyl methanesulfonate	62-50-0	8	8	0	92
Phenol-d6 (surr)	13127-88-3	9	78	0	22
Phenol	108-95-2	10	80	0	20
Aniline	62-53-3	11	0	100	0
Benzyl alcohol	100-51-6	18	50	0	50
N-Nitroso-pyrrolidine	930-55-2	21	7	0	93
N-Nitroso-morpholine	59-89-2	22	16	0	84
o-Toluidine	95-53-4	27	0	100	0
N-Nitrosopiperidine	100-75-4	30	42	0	58
4-Chloroaniline	106-47-8	40	2	98	0
3-Nitroaniline	99-09-2	61	40	60	0
2-Naphthylamine	91-59-8	69	0	100	0
1-Naphthylamine	134-32-7	70	0	100	0
5-Nitro-o-toluidine	99-55-8	75	72	28	0
Azobenzene	103-33-3	78	97	3	0
4-Aminobiphenyl	92-67-1	86	3	97	0
Methapyrilene	91-80-5	93	0	100	0
Benzidine	92-87-5	95	0	100	0
p-Dimethylaminoazobenzene	60-11-7	98	2	98	0
3,3'-Dimethylbenzidine	119-93-7	99	0	100	0
3,3'-Dichlorobenzidine	91-94-1	102	0	100	0

Figure 2. Full suite of analytes from US EPA Method 8270 recovered from spiked reagent using Liquid-Liquid extraction (blue) compared to the One-Pass system (red)

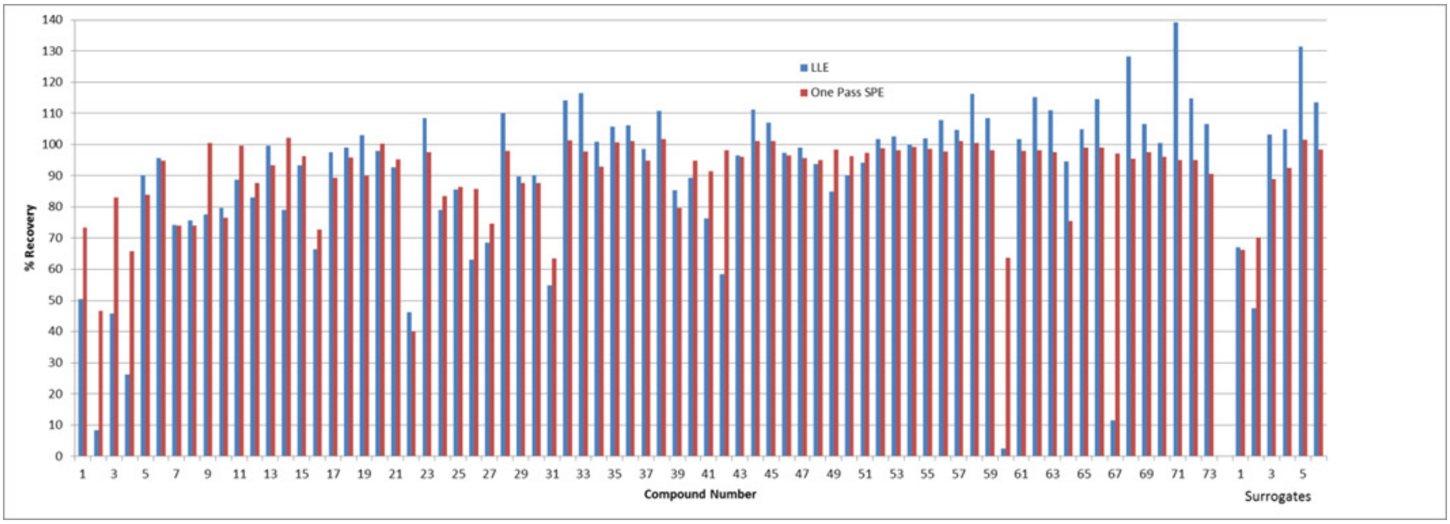
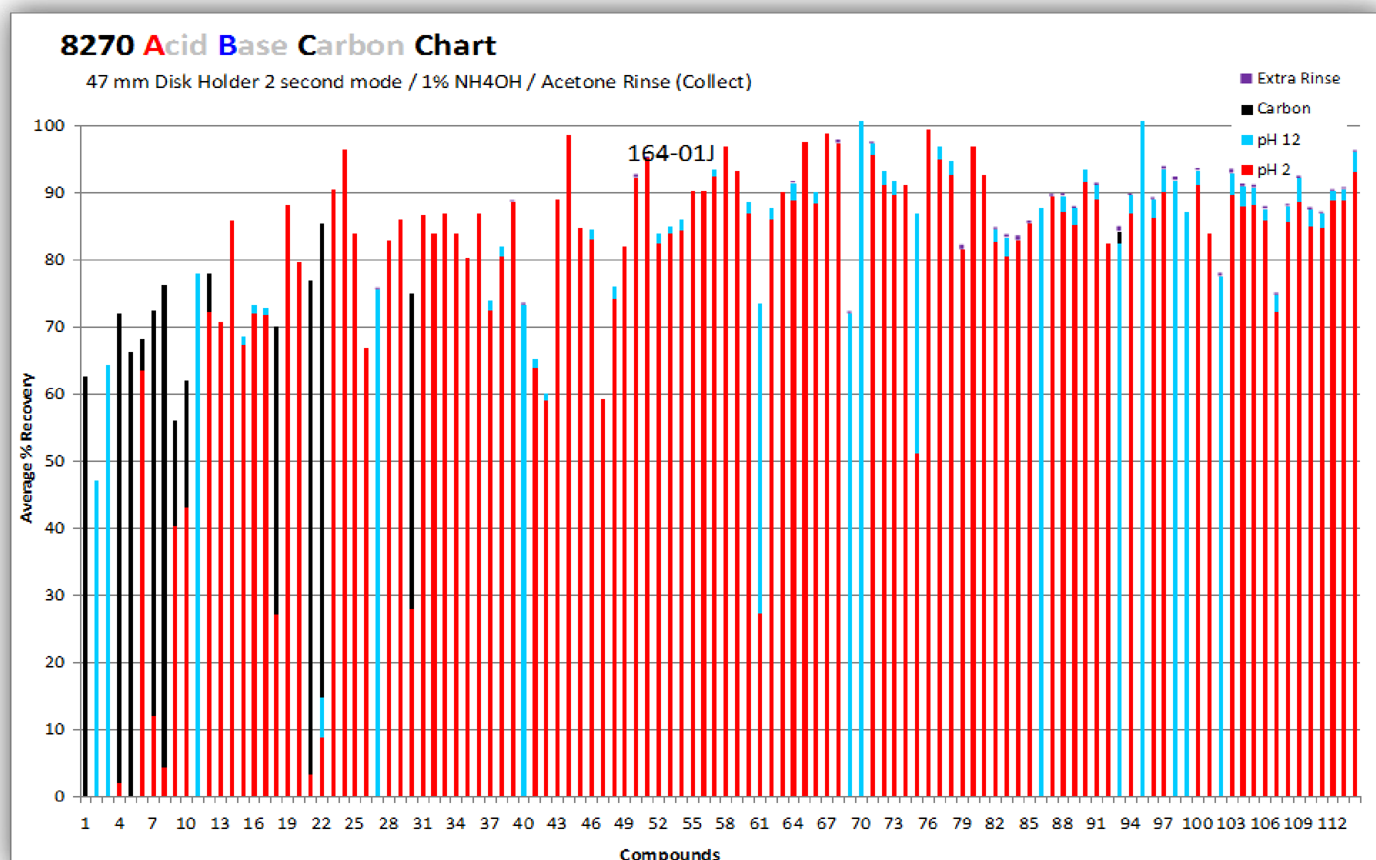


Figure 3. Full suite of analytes from US EPA Method 8270 recovered from spiked reagent water using a One-Pass system and drying and evaporation using the DryVap® system. The bar color indicates the fraction in which the compound was eluted.



Conclusion

The One-Pass system using the One-Pass disk and carbon cartridge is an effective way to extract a large suite of analytes with different characteristics with good recovery. The carbon cartridge can be used to capture additional analytes that are more polar and have large water solubility. If these compounds are not of interest, the One-Pass system can be used without the carbon cartridge.

In addition, the ability to avoid formation of emulsions is an important step in making the extraction more predictable and avoiding time spent to break an emulsion.

References

1. US EPA Method 8270E, can be obtained from https://www.epa.gov/sites/production/files/2017-04/documents/method_8260d_update_vi_final_03-13-2017_0.pdf
2. US EPA Method 625.1, can be obtained from https://nepis.epa.gov/Exe/ZyPDF.cgi?P100LVHC.PDF?Dockey=P100LVHC.PDF.

		LLE	One Pass SPE
1	N-Nitrosodimethylamine (NDMA)	50.5	73.3
2	Pyridine	8.4	46.6
3	Phenol	45.8	83.0
4	Aniline	26.3	65.7
5	Bis(2-chloroethyl) ether	90.3	83.8
6	2-Chlorophenol	95.8	94.7
7	1,3-Dichlorobenzene	74.3	73.9
8	1,4-Dichlorobenzene	75.8	74.0
9	Benzyl alcohol	77.5	100.5
10	1,2-Dichlorobenzene	79.8	76.5
11	2-Methylphenol	88.8	99.6
12	Bis(2-chloroisopropyl) ether	83.0	87.6
13	Acetophenone	99.8	93.3
14	3-Methylphenol & 4-Methylphenol	79.0	102.2
15	N-Nitrosodi-n-propylamine	93.3	96.3
16	Hexachloroethane	66.5	72.8
17	Nitrobenzene	97.5	89.4
18	Isophorone	99.0	95.9
19	2-Nitrophenol	103.0	90.1
20	2,4-Dimethylphenol	98.0	100.2
21	Bis(2-chloroethoxy)methane	92.8	95.2
22	Benzoic acid	46.3	40.2
23	2,4-Dichlorophenol	108.5	97.5
24	1,2,4-Trichlorobenzene	79.0	83.5
25	Naphthalene	85.5	86.4
26	4-Chloroaniline	63.0	85.7
27	Hexachlorobutadiene	68.5	74.7
28	p-Chloro-m-methylphenol	110.3	98.0
29	2-Methylnaphthalene	89.8	87.6
30	1,2,4,5-Tetrachlorobenzene	90.3	87.7
31	Hexachlorocyclopentadiene	54.8	63.4
32	2,4,6-Trichlorophenol	114.3	101.4
33	2,4,5-Trichlorophenol	116.5	97.8
34	2-Chloronaphthalene	101.0	92.9
35	2-Nitroaniline	105.8	100.8
36	Dimethyl phthalate	106.3	101.1
37	Acenaphthene	98.5	94.9
38	2,6-Dinitrotoluene	110.8	101.7
39	3-Nitroaniline	85.3	79.6
40	Acenaphthylene	89.3	94.7
41	2,4-Dinitrophenol	76.3	91.5

		LLE	One Pass SPE
42	4-Nitrophenol	58.5	98.2
43	Dibenzofuran	96.5	96.1
44	2,4-Dinitrotoluene	111.3	101.1
45	Diethyl phthalate	107.0	101.2
46	Fluorene	97.3	96.6
47	4-Chlorophenyl phenyl ether	99.0	95.7
48	4-Nitroaniline	93.8	95.1
49	4,6-Dinitro-2-methylphenol	85.0	98.4
50	NDPA/DPA	90.1	96.3
51	Azobenzene	94.3	97.4
52	4-Bromophenyl phenyl ether	101.8	98.7
53	Hexachlorobenzene	102.5	98.1
54	Pentachlorophenol	100.0	99.1
55	Phenanthrene	102.0	98.5
56	Anthracene	107.8	97.7
57	Carbazole	104.8	101.0
58	Di-n-butyl phthalate	116.3	100.5
59	Fluoranthene	108.5	98.1
60	Benzidine	2.6	63.8
61	Pyrene	101.8	97.9
62	Butyl benzyl phthalate	115.3	98.1
63	Benz(a)anthracene	111.0	97.6
64	3,3'-Dichlorobenzidine	94.6	75.4
65	Chrysene	105.0	99.1
66	Bis(2-ethylhexyl) phthalate	114.5	99.1
67	Di-n-octyl phthalate	11.5	97.0
68	Benzo(b)fluoranthene	128.3	95.5
69	Benzo(k)fluoranthene	106.5	97.6
70	Benzo(a)pyrene	100.5	96.0
71	Indeno(1,2,3-cd)pyrene	139.3	95.0
72	Dibenz(a,h)anthracene	114.8	94.9
73	Benzo(g,h,i)perylene	106.5	90.6

		LLE	One Pass SPE
1	2-Fluorophenol (surr)	67.0	66.1
2	Phenol-d6 (surr)	47.4	70.3
3	Nitrobenzene-d5 (surr)	103.2	89.0
4	2-Fluorobiphenyl (surr)	104.8	92.4
5	2,4,6-Tribromophenol (surr)	131.4	101.4
6	p-Terphenyl-d14 (surr)	113.6	98.3

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Literature Number: PPS537.V.1