RESTEK environmental

Applications note

Rtx®-CLPesticides and Rtx®-CLPesticides2 Columns: The Ideal Confirmational Pair for Analyzing Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a group of industrial organochlorine chemicals that have become a major environmental concern. Since the 1950's, over one million metric tons of PCBs have been produced. They are very persistent in the environment and bioaccumulate in living systems. All PCBs are practically insoluble in water, but they are soluble in hydrophobic media like fats or oily substances. They were used commercially because they are chemically inert liquids and are difficult to burn; they have low vapor pressures, are inexpensive to make, and are excellent electrical insulators. As a result, they were used extensively as coolant fluids in transformers and capacitors; and later as plasticizers, de-inking solvents, heat transfer fluids in machinery, and water-proofing agents, among other uses.

Because of their persistence and their solubility in fatty tissue, PCBs in food chains undergo biomagnification. Strong heating of PCBs in the presence of oxygen can lead to the formation of polychlorodibenzofurans (PCDF), which are structurally and toxicologically similar to dioxins. Commercial PCB mixtures (e.g., Aroclor® mixtures) contain small amounts of PCDF as a result of the synthesis. PCB mixtures are not highly toxic, but toxicity due to the PCDF concentration has caused concern.

Certain PCB congeners can be highly toxic; toxicity depends on where the chlorine substitution resides on the biphenyl molecule. The congeners without chlorine substitution on the ortho positions are the most toxic. These are termed "coplanar PCBs" because the phenyl rings can maintain a planar geometry to each other. This makes these compounds "dioxin-like," and the most toxic of these PCB congeners is one-tenth the toxicity of the 2,3,7,8-tetrachloro dibenzo dioxin. The coplanar PCBs also have been implicated as endocrine disrupters.[1]

It is important, therefore, when designing a PCB analysis method to determine if the separation will be by specific congener (for toxicity) or by commercial Aroclor® mixture. The commercial synthesis of PCBs results in chlorination of the biphenyl molecule, and this reaction produces a mixture of many of the 209 congeners of the PCB family.

Naming of the specific congeners follows the positional numbering shown in Figure 1. Because the IUPAC names for these compounds are long, the congeners are normally referred to by their IUPAC number or BZ number as defined by Ballschmitter and Zell.[2] The exact proportions of congeners in the Aroclor® mixtures depends on the ratio of chlorine to biphenyl, the reaction time, and the temperature. Although many of the PCB compounds are solids, the mixtures usually are liquids or low-melting-point solids. Commercially, the PCB compounds were not isolated. Instead, they were sold as partially separated mixtures, with the average chlorine content in different products ranging from 21% to 68%. These Aroclor® mixtures are, therefore, composed of a number of individual PCB congeners and have a characteristic profile depending on the percent of chlorine substitution. The Aroclor® mixtures are named by the number of carbons (12), followed by the weight % of chlorine (42). Thus Aroclor® 1242 represents a mixture of PCB compounds with an average weight percent of 42.

There are 9 common Aroclor® mixtures: 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268, and 1016. Aroclor® 1016 does not follow the same naming sequence, and appears chromatographically similar to 1242. Samples from contamination sites often are quantitated and reported as concentration of PCBs, i.e., as Aroclor® mixtures. This analysis requires the individual PCB Aroclor® mixtures to be analyzed as standards, then the sample extract chromatograms are compared to the standards to qualitatively identify the Aroclor® mixtures. Once this identification has been made, the quantitation can be performed by selecting five of the largest peaks and treating them as individual compounds, then reporting the average concentration.

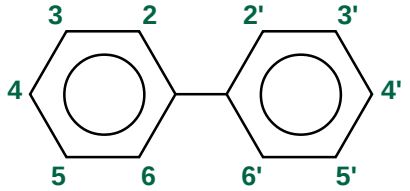
Due to the unreactive nature of the PCBs, instrument conditions and column choice is less critical than when analyzing chlorinated pesticides. When choosing columns, it is important to select stationary phases that have low bleed and high thermal stability; allowing the columns to be baked out at the end of the run to prevent carryover from one injection to the next. Because many instruments used for the analysis of PCBs also may be used for pesticide and herbicide analyses, the column pair of choice is the Rtx®-CLPesticides and Rtx®-CLPesticides2 columns. This column pair provides excellent separation of the pesticide and herbicide compounds, low bleed, high thermal stability, and they are designed to compliment each other for primary column analysis and secondary column confirmation.

Figure 2 shows the chromatograms obtained for seven commercial Aroclor® mixtures injected on the Rtx®-CLPesticides column. Figure 3 shows the chromatograms for the same mixtures injected on the Rtx®-CLPesticides2 column.

Table 1 (on back) lists the retention times for the individual 209 PCB congeners on these same stationary phases. The analysis of PCBs by congener requires each peak to be treated like an individual component; making a standard curve for each of the congeners of interest. While many laboratories are interested in the analysis of PCBs by congener, most do not need, or desire, to analyze all 209. For this reason, the retention table is listed, and conditions may be modified to better suit the particular separation in your laboratory. If you have questions regarding the analysis of PCBs by congener, contact Restek's technical service team at 800-356-1688 or 814-353-1300, ext. 4, or contact your local Restek representative.

Figure 1

Structure of polychlorinated biphenyls.

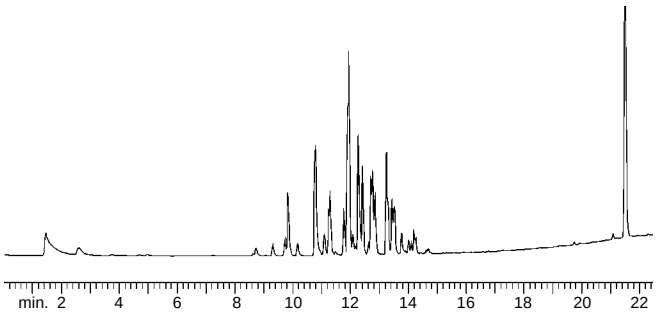


environmental

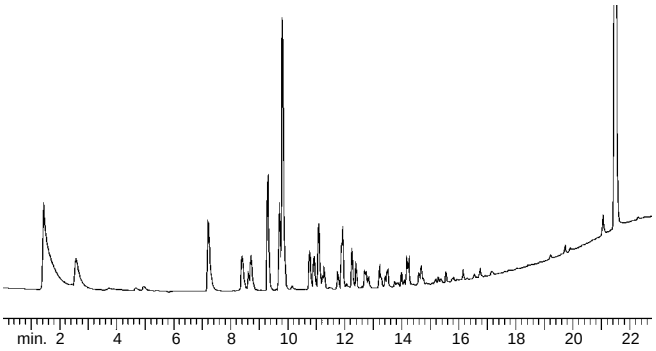
Figure 2

Aroclor® standards run on the Rtx®-CLPesticides column at 320ppb.

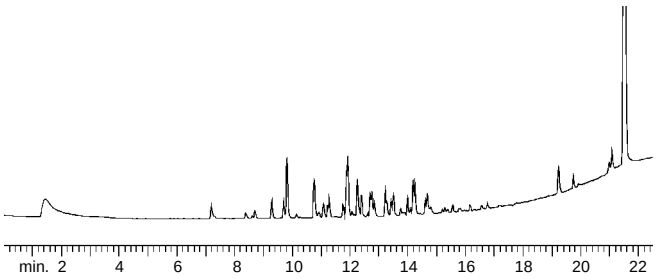
Aroclor® 1016



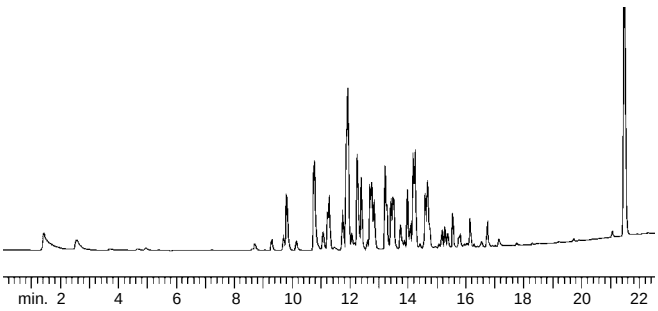
Aroclor® 1221



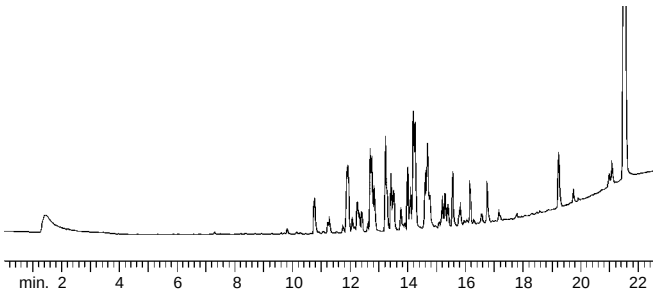
Aroclor® 1232



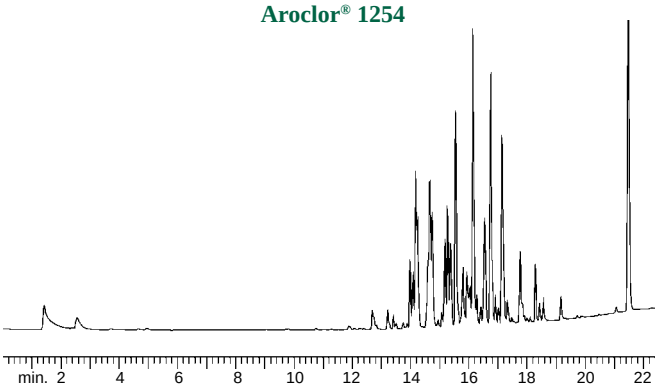
Aroclor® 1242



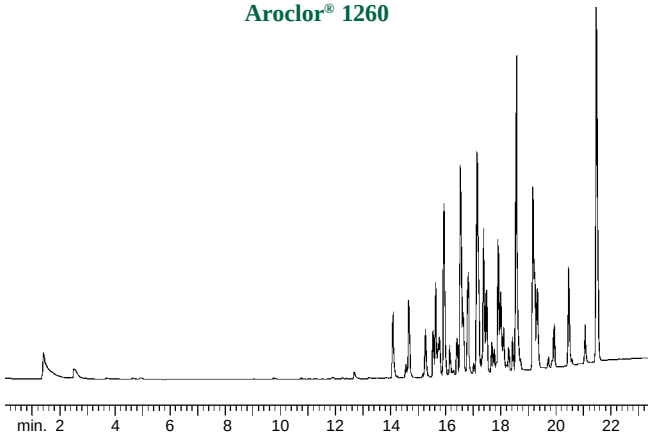
Aroclor® 1248



Aroclor® 1254



Aroclor® 1260

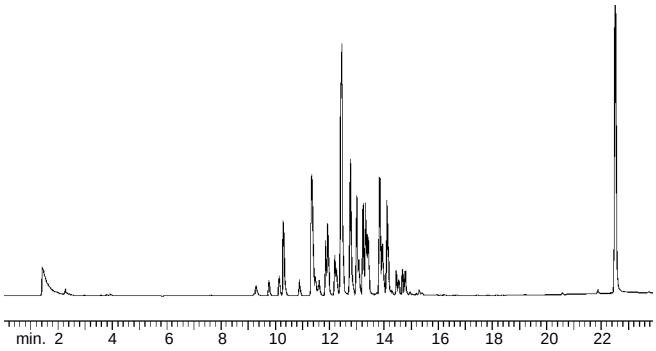


30m, 0.32mm ID, 0.50µm Rtx®-CLPesticides (cat.# 11139). 0.5µL direct injection of commercial Aroclor® mixtures, 160pg on-column concentration. **Oven temp.:** 120°C (hold 1 min.) to 300°C @ 9°C/min. (hold 10 min.); **Inj. temp.:** 210°C; **Det.:** ECD with anode purge, 310°C; **Carrier gas:** He.

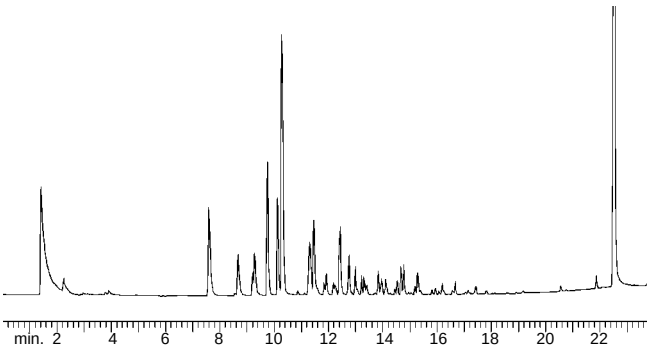
Figure 3

Aroclor® standards run on the Rtx®-CLPesticides2 column at 320ppb.

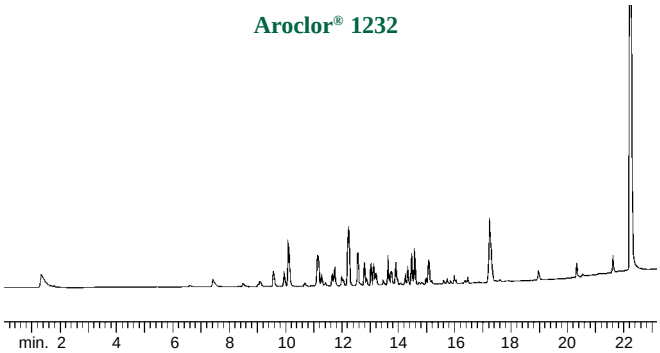
Aroclor® 1016



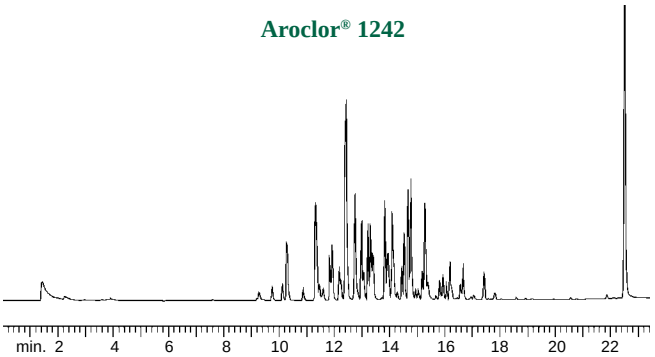
Aroclor® 1221



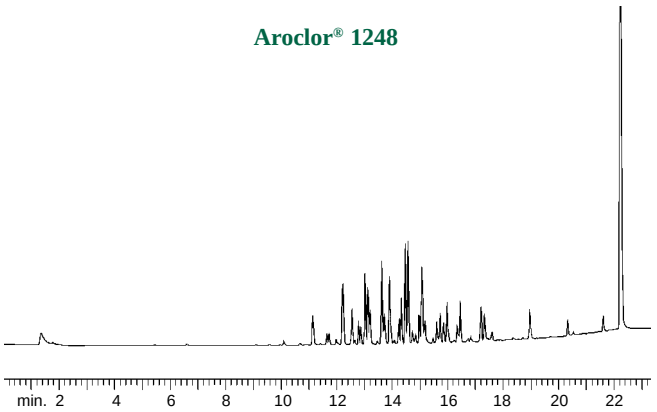
Aroclor® 1232



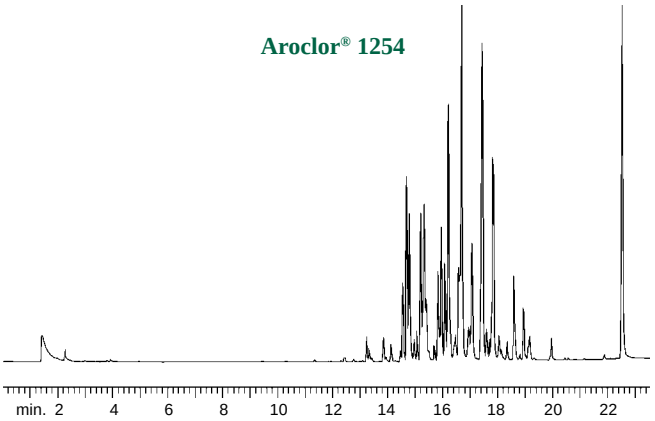
Aroclor® 1242



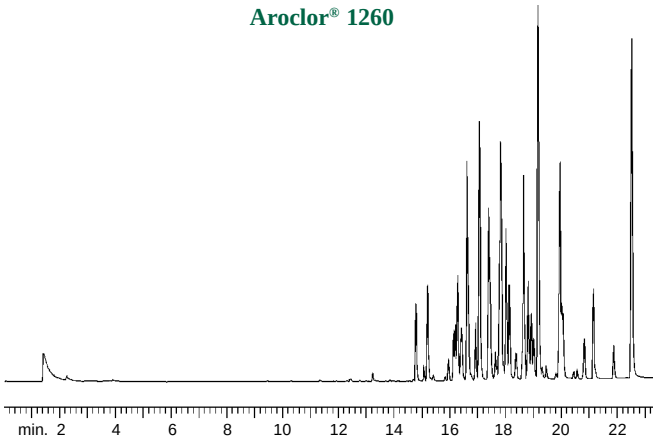
Aroclor® 1248



Aroclor® 1254



Aroclor® 1260



30m, 0.32mm ID, 0.25µm Rtx®-CLPesticides2 (cat.# 11324). 0.5µL direct injection of commercial Aroclor® mixtures, 160pg on-column concentration. **Oven temp.:** 120°C (hold 1 min.) to 300°C @ 9°C/min. (hold 10 min.); **Inj. temp.:** 210°C; **Det.:** ECD with anode purge, 310°C; **Carrier gas:** He.

Table I—PCB Congener Retention Time Data

Rtx®-CLP PCB IUPAC#	Rtx®-CLP RT (min)	Rtx®-CLP2 PCB IUPAC#	Rtx®-CLP2 RT (min)	Rtx®-CLP PCB IUPAC#	Rtx®-CLP RT (min)	Rtx®-CLP2 PCB IUPAC#	Rtx®-CLP2 RT (min)	Rtx®-CLP PCB IUPAC#	Rtx®-CLP RT (min)	Rtx®-CLP2 PCB IUPAC#	Rtx®-CLP2 RT (min)	Rtx®-CLP PCB IUPAC#	Rtx®-CLP RT (min)	Rtx®-CLP2 PCB IUPAC#	Rtx®-CLP2 RT (min)	Rtx®-CLP PCB IUPAC#	Rtx®-CLP RT (min)	Rtx®-CLP2 PCB IUPAC#	Rtx®-CLP2 RT (min)
1	13.36	1	14.33	52	25.24	73	26.47	155	28.50	88	29.89	135	31.90	147	33.60	182	35.37	129	36.95
2	ND	2	ND	65	25.27	52	26.56	66	28.54	155	30.07	139	32.10	82	33.69	187	35.38	159	36.95
3	15.86	3	16.61	43	25.29	46	26.70	80	28.77	91	30.22	149	32.22	108	33.75	183	35.60	126	37.00
4	16.57	10	17.79	62	25.30	43	26.71	55	28.90	55	30.39	140	32.35	107	33.79	126	35.67	166	37.06
10	16.38	4	17.94	73	25.33	49	26.73	60	29.28	92	30.54	124	32.37	139	33.80	159	35.76	183	37.16
7	17.84	7	18.98	49	25.34	75	26.79	92	29.28	101	30.81	108	32.37	149	33.86	185	35.98	162	37.34
9	17.86	9	18.99	39	25.34	38	26.86	84	29.34	90	30.85	107	32.43	123	33.89	162	36.12	167	37.61
6	18.73	6	19.80	75	25.40	65	26.87	89	29.42	60	30.91	123	32.49	106	33.96	128	36.14	185	37.65
5	18.91	8	20.13	47	25.48	47	26.88	90	29.44	56	30.96	106	32.51	118	34.01	181	36.32	128	38.08
8	18.96	5	20.21	48	25.52	62	26.92	56	29.48	113	30.96	118	32.65	140	34.06	167	36.37	181	38.20
19	19.64	14	20.56	104	25.53	48	26.93	101	29.51	99	31.07	142	32.67	133	34.25	202	36.50	174	38.24
14	19.80	30	21.17	38	25.78	104	27.31	150	29.60	84	31.16	188	32.68	165	34.31	174	36.50	202	38.27
30	19.82	19	21.36	44	26.32	35	27.61	99	29.68	89	31.26	143	32.68	143	34.36	177	36.69	177	38.56
18	21.00	11	21.93	59	26.34	59	27.80	113	29.76	79	31.28	134	32.69	188	34.39	201	36.85	201	38.70
17	21.06	12	22.24	42	26.44	44	27.82	152	30.01	119	31.42	131	32.88	134	34.46	204	36.89	204	38.74
11	21.10	13	22.34	35	26.56	72	27.85	112	30.02	150	31.43	114	32.93	161	34.49	171	36.92	171	38.81
24	21.27	18	22.40	64	26.71	42	28.00	119	30.08	112	31.46	184	33.00	142	34.54	173	37.09	192	38.86
12	21.31	17	22.46	96	26.71	37	28.07	109	30.10	109	31.58	133	33.03	146	34.57	197	37.18	156	38.88
13	21.34	15	22.66	41	26.86	68	28.11	116	30.18	78	31.83	165	33.19	114	34.60	156	37.27	173	39.04
27	21.67	24	22.88	37	26.89	103	28.38	79	30.27	83	31.84	146	33.30	131	34.68	192	37.57	172	39.08
15	21.68	27	23.00	72	26.90	71	28.40	145	30.29	111	31.87	161	33.30	184	34.73	157	37.61	197	39.09
32	22.01	32	23.49	103	26.97	64	28.41	83	30.33	152	31.89	122	33.40	153	34.86	172	37.65	157	39.26
16	22.11	23	23.63	71	26.98	41	28.50	86	30.46	116	32.00	132	33.55	122	34.88	200	37.87	180	39.42
54	22.36	16	23.65	68	27.00	57	28.61	117	30.49	148	32.04	153	33.56	168	34.98	180	37.95	193	39.51
23	22.37	34	23.69	100	27.22	100	28.70	97	30.56	86	32.07	179	33.74	127	35.11	193	38.11	191	39.71
29	22.52	29	23.78	57	27.44	96	28.72	115	30.57	97	32.13	168	33.75	132	35.46	191	38.25	200	39.93
34	22.69	26	24.27	40	27.44	67	28.83	148	30.69	120	32.14	105	33.95	141	35.60	198	39.17	169	40.54
50	23.01	54	24.37	67	27.61	40	29.10	136	30.72	117	32.19	176	34.07	105	35.61	170	39.19	198	40.76
26	23.15	25	24.39	61	27.73	58	29.13	78	30.73	125	32.19	141	34.15	179	35.63	190	39.19	190	40.95
25	23.20	50	24.55	63	27.76	63	29.18	87	30.79	145	32.20	127	34.16	137	35.96	169	39.30	199	41.04
31	23.46	31	24.74	94	27.78	61	29.29	125	30.84	115	32.26	137	34.34	176	36.01	199	39.38	170	41.07
28	23.56	28	24.81	58	27.92	94	29.30	111	30.91	87	32.40	186	34.39	130	36.20	203	39.56	203	41.23
21	23.79	21	25.32	93	28.00	74	29.37	85	30.98	81	32.43	130	34.58	160	36.27	196	39.62	196	41.33
53	23.85	53	25.44	74	28.00	80	29.42	154	31.07	154	32.45	160	34.66	163	36.37	208	40.44	189	42.17
51	24.04	33	25.48	98	28.07	121	29.47	81	31.10	85	32.65	163	34.80	164	36.39	189	40.71	208	42.38
33	24.22	20	25.53	102	28.13	98	29.68	120	31.13	136	32.74	138	34.81	186	36.41	207	40.82	207	42.82
20	24.23	51	25.68	88	28.16	102	29.68	110	31.38	110	32.95	158	34.90	178	36.44	195	40.86	195	42.92
45	24.33	36	25.85	95	28.22	70	29.70	151	31.60	77	33.06	164	34.93	138	36.48	194	42.05	194	43.68
22	24.53	22	25.97	70	28.39	93	29.72	144	31.79	151	33.14	178	34.99	158	36.50	205	42.28	205	43.83
46	24.93	45	26.12	76	28.44	76	29.74	77	31.79	144	33.35	166	35.15	175	36.73	206	43.34	206	45.15
69	24.96	69	26.21	121	28.46	95	29.86	82	31.87	135	33.44	175	35.22	182	36.90	209	44.19	209	46.32
36	25.05	39	26.39	91	28.47	66	29.88	147	31.89	124	33.56	129	35.23	187	36.91				

30m, 0.32mm ID Rtx®-CLPesticides (cat.# 11139) and Rtx®-CLPesticides2 (cat.# 11324) columns.
Oven temp.: 100°C (hold 1 min.) to 290°C @ 4°C/min.; **Inj. temp.:** 210°C; **Det. temp.:** 310°C; **Carrier gas:** He @ 36cm/sec.

References (not available from Restek):

1 Environmental Chemistry, Colin Baird, W.H. Freeman and Co., 1998, pp. 337-353.

2 Ballschmiter, K, and Zell, M., Fresenius Z. *Anal. Chem.*, 302, 20, (1980)

Product Listing

Rtx®-CLPesticides Columns

ID	df (µm)	Stable to	15m	30m
0.25mm	0.25	340°C	11120	11123
0.32mm	0.50	340°C	11136	11139
0.53mm	0.50	340°C	11137	11140
ID	**df (µm)**	**Stable to**	**10m**	**20m**
0.18mm	0.18	340°C	42101	42102

Rtx®-CLPesticides2 Columns

ID	df (µm)	Stable to	15m	30m
0.25mm	0.20	340°C	11320	11323
0.32mm	0.25	340°C	11321	11324
0.53mm	0.42	340°C	11337	11340
ID	**df (µm)**	**Stable to**	**10m**	**20m**
0.18mm	0.14	340°C	42301	42302

RESTEK ISO 9001 REGISTERED

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Applications note

Siltek™ Deactivation Delivers Inertness to Analyte Breakdown and Reactivity, and Durability to Physical and Chemical Challenges

A common concern in gas chromatographic (GC) analyses is the interaction of analytes with active surfaces in the GC pathway. The injection port is the first source of active sites, often leading to adsorption and breakdown of analytes. However, not all analyses are affected by reactivity within the injection port. Hydrocarbons, typically, are not susceptible to adsorption or breakdown. In contrast, active compounds such as pesticides, drugs, phenols, amines, and alcohols, which are often injected via splitless mode, are more prone to these problems. With a splitless injection, carrier gas flow rate through the liner is very slow, increasing the sample residence time in the injector and the chance for reactivity. Complete and effective liner deactivation is crucial to minimize available active sites and ensure repeatable results.

Restek has designed Siltek® deactivation to deliver both enhanced inertness and durability. Gas chromatography accessories coated with Siltek® deactivation provide durability for matrices of extreme pH or high-temperature applications.

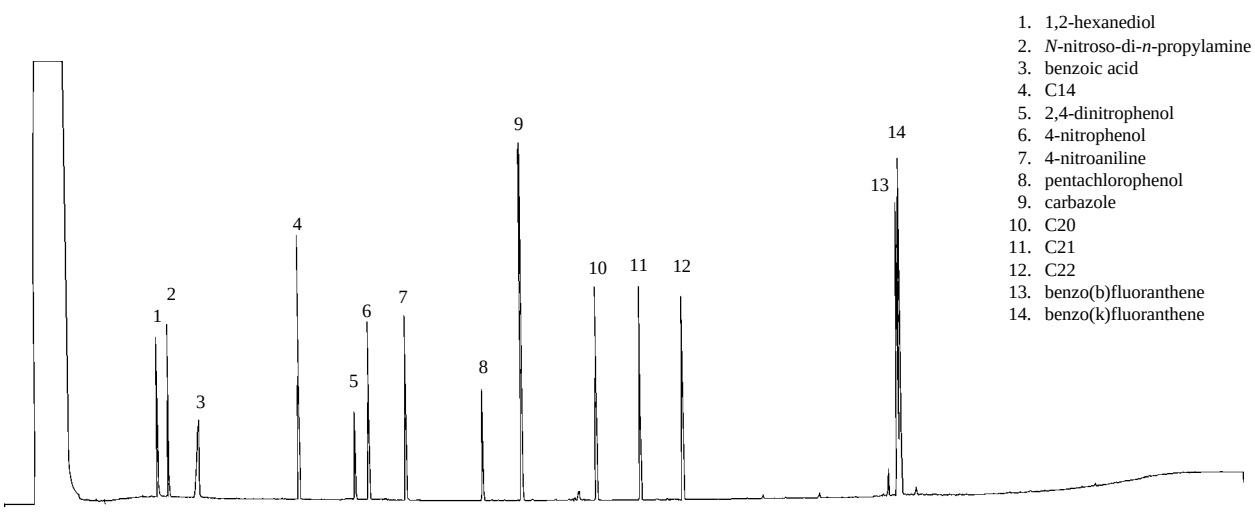
Inertness

Semivolatile analysis places extreme demands on the GC system. One key to successfully analyzing semivolatiles is having the capability to handle basic and acidic compounds in the GC system. The analytical column must provide selectivity for both classes without resulting in poor peak shape. Additionally, liner deactivation is critical to analytical success because the vaporized sample comes in contact with the inlet liner first.

The Restek XTI test mix was chosen to evaluate the inertness of a Siltek™-deactivated liner. This mix contains both acidic and basic probes, some of which are pollutants monitored in US Environmental Protection Agency (EPA) Method 8270 (4-nitroaniline, *N*-nitroso-di-*n*-propylamine, 2,4-dinitrophenol, pentachlorophenol, benzoic acid, benzo(b)- and benzo(k)fluoranthene). A splitless injection of the XTI mix with an on-column concentration of 4-10ng shows an excellent response for all of the probes, including the active compounds dinitrophenol, 1,2-hexanediol, and benzoic acid (Figure 1).

Figure 1

Siltek™-deactivated liner shows excellent inertness for acidic and basic probes.



30m, 0.25mm ID, 0.25µm XTI®-5 (cat.# 12223) with a Siltek™-deactivated 4mm splitless single gooseneck sleeve (cat.# 20798-214.1). **Oven temp.:** 40°C (hold 2 min.) to 100°C @ 30°C/min., to 180°C @ 9°C/min., to 330°C @ 30°C/min. (hold 10 min.); **Inj. temp.:** 250°C; **Det.:** 330°C; **Carrier gas:** He.