AN EVALUATION OF INLET LINER DEACTIVATION SURFACES FOR A WIDE RANGE OF ANALYTES: FROM EPA METHOD 8270 TO ETHANOLAMINES

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ABSTRACT

A c itical aspect of the gas chromatographic (GC system is a lack of interaction between an inlet liner and the analytes which pass through it. Without the appropriate surface deactivation, analytes can be irreversibly adsorbed and/or temporarily retained in the liner. The result of which is poor, inaccurate chromatography reflected as tailing, broad or absent peaks. For example, in an analysis of semivolatile components, several analytes are prone to inlet liner adsorption. 2,4-dinitrophenol, pentachlorophenol, N-nitroso-di-n-propylamine, and hexachlorocyclopentadiene are often the first compounds to show signs of improper inlet deactivation or inlet contamination. This is demonstrated as the relative response ratios of these compounds are non-linear over a calibration curve and/or below the minimum required values dictated by the EPA method.

The analysis of compounds with a highly basic character poses an equally difficult challenge. Improper liner surfaces can interact with basic analytes, resulting in adsorption and therefore chromatograms with severe peak tailing or an artificial loss of response. Ethanolamines and polyamines are particularly prone to this, and selecting the appropriate liner is a key factor in accurate analyses.

Four different types of inlet liners will be evaluated for their performance over a broad spectrum of analytes (i.e., from highly acidic to highly basic in character). Chromatographic and statistical results will be discussed to assist the gas chromatographer in the appropriate choice of inlet liner surface deactivation.

Introduction for Semivolatile testing

US EPA method 8270 is a comprehensive list of compounds varying from basic to neutral to acidic character. The variety of compound functionalities is also highly variable, which therefore makes the 8270 listing an excellent test bed for chromatographic system performance.

The inlet liner geography to be used for semivolatile testing will be a drilled Uniliner. The injection mode will be splitless. Since the samples will be injected at low ppm levels, a liner which prevents interaction between the sample and metal injection port surfaces will allow the isolation of liner performance only. The bottom of the drilled Uniliner physically seals against the head of the analytical column thereby forcing the sample to interact only with the liner surfaces.

Each liner was injected with 6 dilutions of the test mix: 4, 10, 16, 24, 32, and 80ng on column for each component. Test conditions are shown in the protocol listing:

Liner Geometries

Drilled Uniliner (for 8270 Semivolatiles testing – Siltek version shown)

4mm Single Gooseneck (for basic compound testing – Siltek version shown)

Liner Surfaces

1. **Bare borosilicate glass:** Raw glass surface with no deactivation

2. **Standard Intermediate Polarity (IP):** Proprietary polymeric deactivation

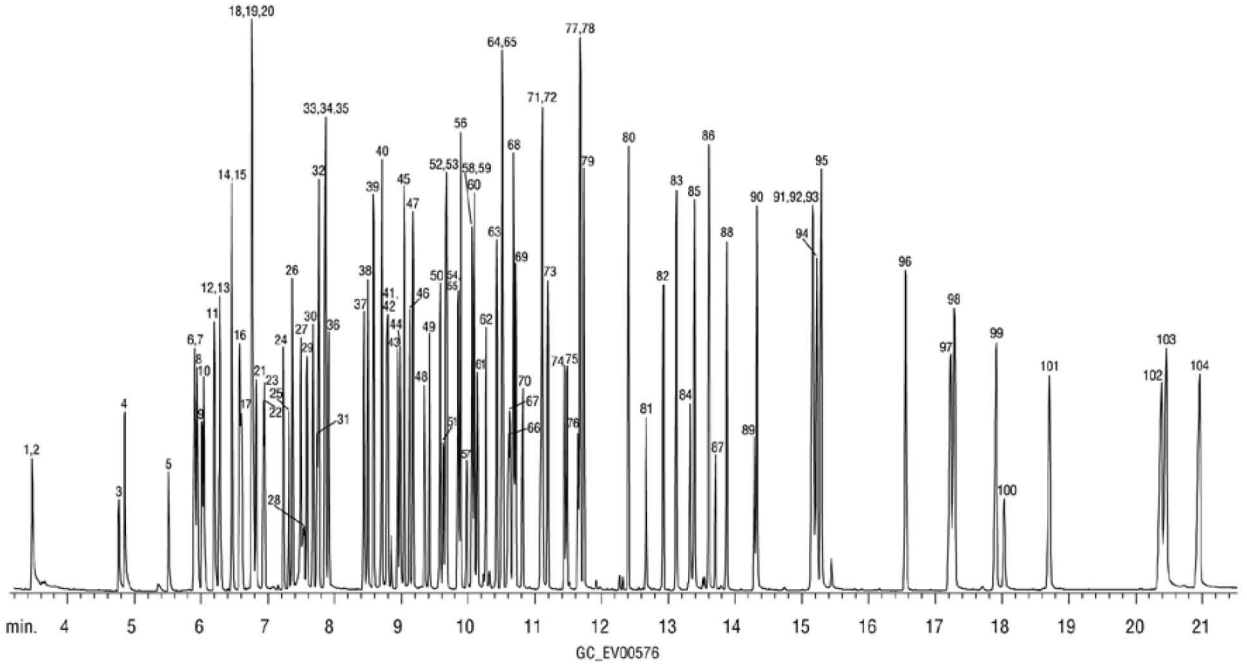
3. **Siltek Deactivated:** Proprietary chemical vapor deposition deactivation

4. **Base Deactivated:** Proprietary deactivation to impart a basic character to the glass surface

Testing Protocol for Semivolatiles (US EPA 8270)

Column: 30m, 0.25mm ID, 0.25um Rtx-5Sil MS
Standard mix: 104 compound mix of US EPA 8270 list
Injection volume: 1µl, 7683 autosampler
Injection type: splitless
Hold time: 0.4 min
Injector temperature: 300°C
Carrier gas: helium (1mL/min. constant flow)
Linear velocity: 34cm/sec.
Oven temperature: 35°C (2min) to 260°C @20°C/min, to 330°C @ 6°C/min (1min)
GC: Agilent 6890
Detector: Agilent 5973 MS
Transfer line temperature: 280°C
Scan range: 35 to 550amu
Ionization: EI
Mode: Full scan

Figure 1. Sample Chromatogram of US EPA Method 8270 compounds at 24ug/ml with a Siltek drilled Uniliner



1. N-nitrosodimethylamine
2. pyridine
3. methyl methanesulfonate
4. 2-fluorophenol
5. ethyl methanesulfonate
6. phenol-d6
7. phenol
8. aniline
9. bis(2-chloroethyl)ether
10. 2-chlorophenol
11. 1,3-dichlorobenzene
12. 1,4-dichlorobenzene-d4
13. 1,4-dichlorobenzene
14. 1,2-dichlorobenzene
15. benzyl alcohol
16. 2-methylphenol
17. bis(2-chloroisopropyl)ether
18. acetophenone
19. 4-methylphenol/3-methylphenol
20. N-nitroso-di-*n*-propylamine
21. hexachloroethane
22. nitrobenzene-d5
23. nitrobenzene
24. isophorone
25. 2-nitrophenol
26. 2,4-dimethylphenol
27. bis(2-chloroethoxy)methane
28. benzoic acid
29. 2,4-dichlorophenol
30. 1,2,4-trichlorobenzene
31. naphthalene-d8
32. naphthalene
33. 2,6-dichlorophenol
34. 4-chloroaniline
35. hexachloropropene
36. hexachlorobutadiene
37. 4-chloro-3-methylphenol
38. isosafrole
39. 2-methylnaphthalene
40. 1-methylnaphthalene
41. hexachlorocyclopentadiene
42. 1,2,4,5-tetrachlorobenzene
43. 2,4,6-trichlorophenol
44. 2,4,5-trichlorophenol
45. 2-fluorobiphenyl
46. safrole
47. 2-chloronaphthalene
48. 2-nitroaniline
49. 1,4-naphthoquinone
50. dimethylphthalate
51. 1,3-dinitrobenzene
52. 2,6-dinitrotoluene
53. acenaphthylene
54. acenaphthene-d10
55. 3-nitroaniline
56. acenaphthene
57. 2,4-dinitrophenol
58. pentachlorobenzene
59. 4-nitrophenol
60. dibenzofuran
61. 2,4-dinitrotoluene
62. 2,3,4,6-tetrachlorophenol
63. diethyl phthalate
64. fluorene
65. 4-chlorophenyl phenyl ether
66. 4-nitroaniline
67. 4,6-dinitro-2-methylphenol
68. diphenylamine
69. azobenzene
70. 2,4,6-tribromophenol
71. phenacetin
72. 4-bromophenyl phenyl ether
73. hexachlorobenzene
74. pentachlorophenol
75. pentachloronitrobenzene
76. phenanthrene-d10
77. dinoseb
78. phenanthrene
79. anthracene
80. di-*n*-butylphthalate
81. 4-nitroquinoline-1-oxide
82. isodrin
83. fluoranthene
84. benzidine
85. pyrene
86. *p*-terphenyl-d14
87. aramite
88. chlorbenzilate
89. kepone
90. butyl benzyl phthalate
91. benzo(a)anthracene
92. 3,3'-dichlorobenzidine
93. chrysene-d12
94. chrysene
95. bis(2-ethylhexyl)phthalate
96. di-*n*-octyl phthalate
97. benzo(b)fluoranthene
98. benzo(k)fluoranthene
99. benzo(a)pyrene
100. perylene-d12
101. 3-methylcholanthrene
102. indeno(1,2,3-cd)pyrene
103. dibenzo(a,h)anthracene
104. benzo(ghi)perylene

Figure 2. Average Response Factors for key semivolatile components:

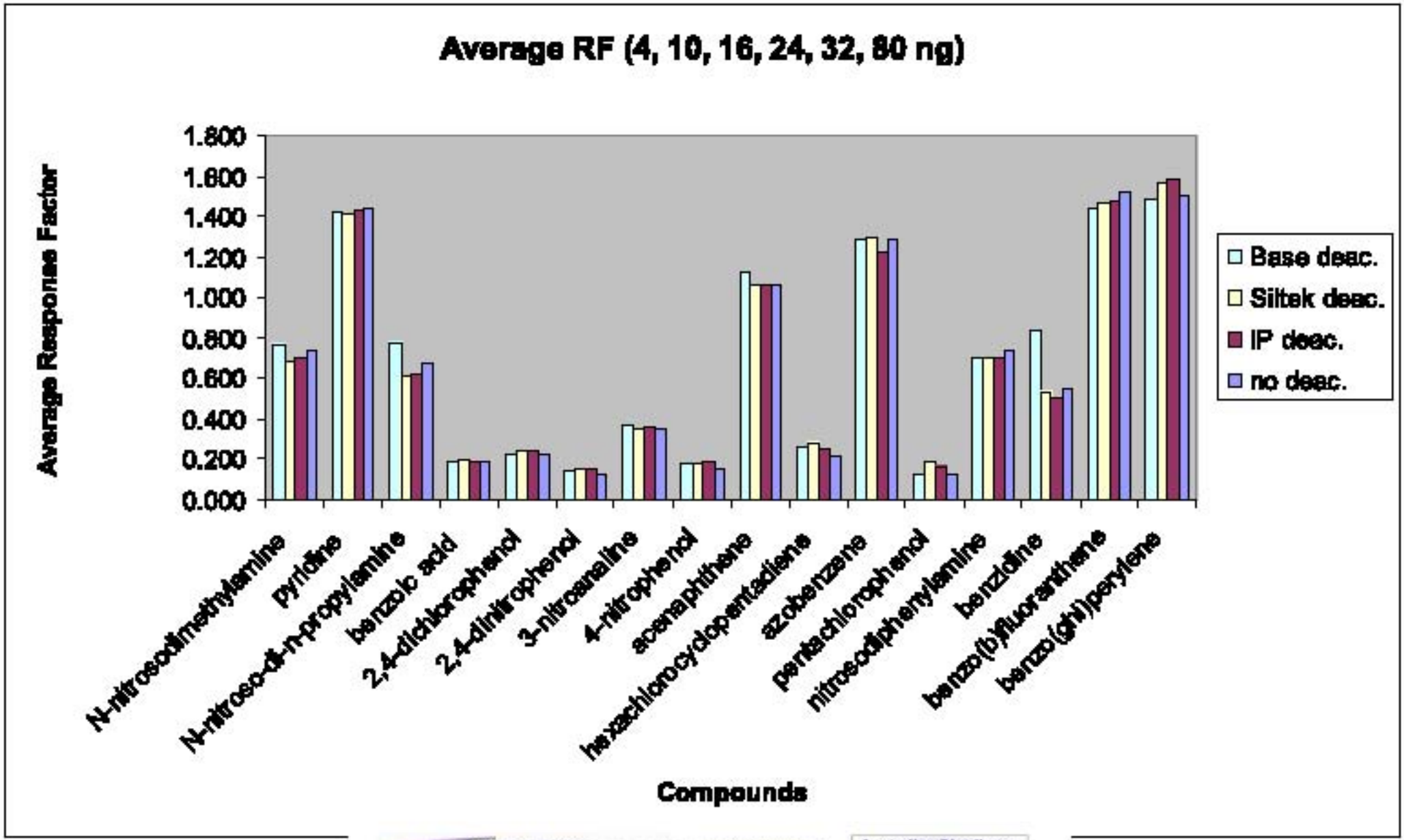


Figure 3. Average Response Factors for key semivolatile components at 4ng on column:

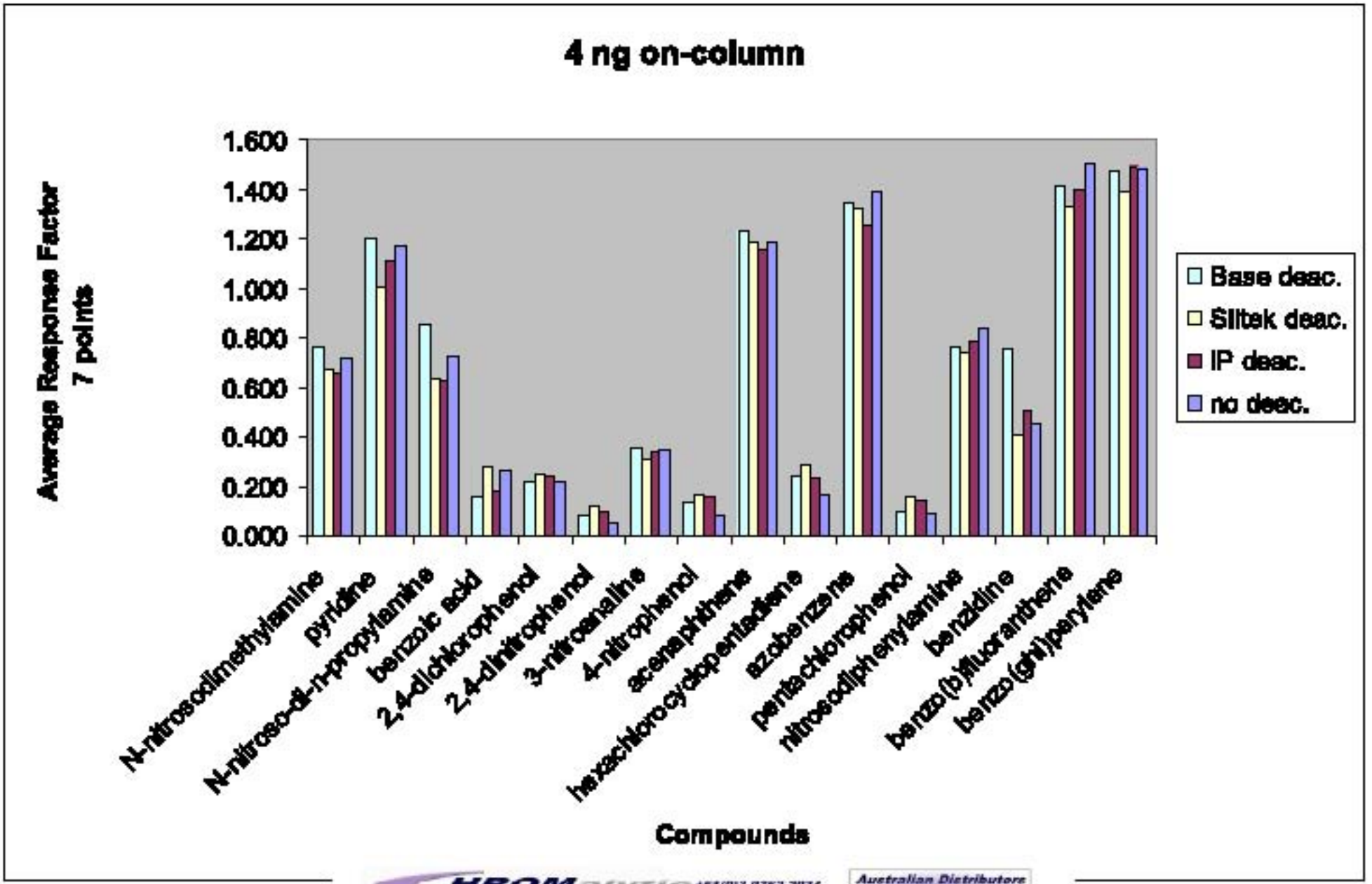


Table I. %RSD comparison of semivolatile subset

	no deact.	IP deact.	Siltek deact.	Base deact.
N-nitrosodimethylamine	5%	4%	1%	3%
pyridine	13%	11%	14%	5%
aniline	7%	4%	5%	7%
N-nitroso-di-n-propylamine	17%	6%	13%	11%
benzoic acid	28%	16%	21%	26%
2,4-dichlorophenol	7%	8%	6%	4%
2,4-dinitrophenol	38%	20%	17%	33%
3-nitroanaline	8%	5%	5%	5%
4-nitrophenol	29%	9%	7%	7%
acenaphthene	13%	10%	12%	11%
hexachlorocyclopentadiene	12%	9%	5%	5%
azobenzene	11%	5%	12%	11%
pentachlorophenol	20%	9%	5%	10%
nitrosodiphenylamine	12%	11%	12%	10%
benzidine	35%	10%	13%	12%
benzo(b)fluoranthene	17%	7%	8%	12%
benzo(ghi)perylene	14%	8%	7%	9%

Discussion on results for various liner surfaces with Semivolatiles:

1. Undeactivated borosilicate liner

   The liner with no deactivation, exhibited surprising response factors that at times were superior or equal to one or more of the deactivated liners (Figures 2 and 3). In general, the amine compounds responded well on this liner, even at 4ng concentrations. This is unusual as borosilicate glass can typically display an acidic character. The %RSD values, however, for this liner were appreciably higher than the deactivated liners as shown in Table I. Therefore, individual values may be deceiving as data over a variety of concentrations will excessively deviate unpredictably from the desired linear average.

2. Base deactivated liner

   Overall, this liner displayed excellent relative response factors. As expected, the basic semivolatile compounds had the highest response and best linearity on this liner. Unfortunately, as shown in Figures 2 and 3, acidic compounds displayed lower response factors and higher %RSD values (Table I). Benzo(b)fluoranthene and benzo(ghi)perylene also showed low response factors. These undesirable values are the direct result of an inherent basic character of the modified glass surface for this liner.

Discussion on results for various liner surfaces with Semivolatiles (continued):

3. Intermediate Polarity (IP) and Siltek deactivated liners

The IP liners and Siltek liners generally exhibited the highest average response factors (Figures 2-6) in conjunction with the lowest %RSD values (Table I). This is the most desirable situation in a test lab environment where the data needs to be both accurate and consistent. Individually, the IP liners showed marginal superiority in overall average response factors for some of the early eluting compounds (Figure 2), but this statement does not necessarily hold true for the same compounds at 4ng (Figure 3). Also, %RSD values were relatively identical throughout the EPA 8270 subset. The Siltek liners did show slightly superior response factors (both overall and at 4ng) for the mid- to late-eluting compounds (Figures 2 and 3). For this half of the study, Siltek and IP liners are shown to have equivalent performance for low level semivolatile analysis.

Introduction for Amines testing

The gas chromatographic analysis of low level amines, in particular polyamines and ethanolamines, is considered to be one of the most challenging. Without a properly deactivated chromatographic pathway, severe peak tailing and adsorption can occur, thereby ruining quantitative results. Inlet liners with the same four different surface as the semivolatile study were evaluated with a low level (2.5-5.0 ng on column) test mix with various amine compounds to determine each surfaces' performance. Compounds of particular interest were diethylenetriamine and diethanolamine, as these are compounds representative of the most difficult basic compounds to be analyzed by gas chromatography.

The inlet liner geography to be used for amine testing will be a single gooseneck. The injection mode will be splitless. Since the samples will be injected at low ppm levels, a liner which prevents interaction between the sample and metal injection port surfaces will allow the isolation of liner performance. The bottom funnel (gooseneck) of the liner will prevent this interaction so the variation of resultant data is reflective of the various liner surface composition.

Each liner was injected 6 times with the test mix. Data analysis will compare results with and without the initial injection in order to determine the degree of priming required by each surface. Test conditions are shown in the protocol listing:

Testing Protocol for Amines

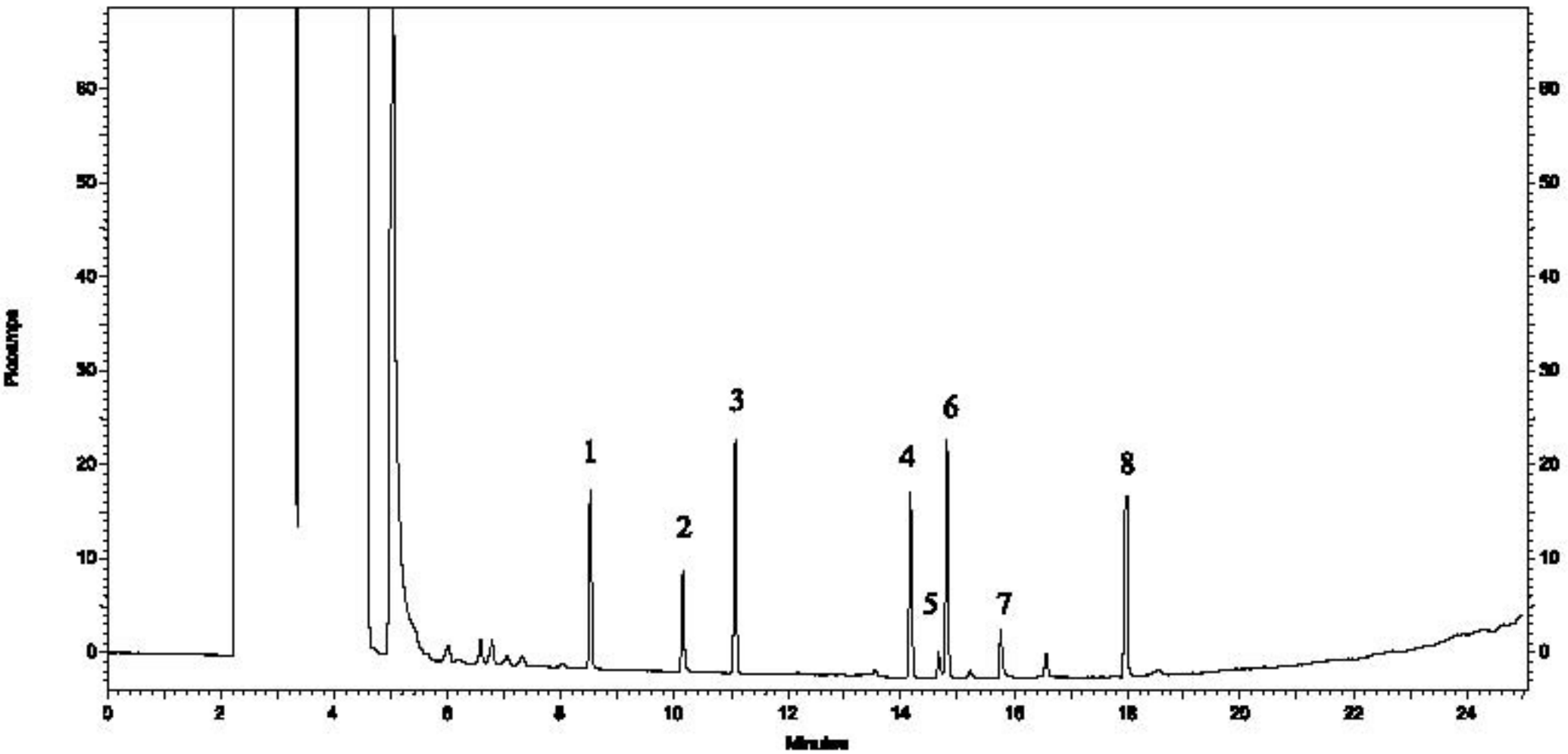
Column: 30m, 0.32mm ID, 1.0um Rtx-35 Amine
Standard Mix: Amine test mix in 50:50 CH_2Cl_2/MeOH

Injection volume: 1µl, 7673 autosampler
Injection type: splitless
Hold time: 1min
Injector temperature: 250°C

Carrier gas: helium (9psi head pressure, constant pressure)
Oven temperature: 40°C (1min) to 165°C (1min) @10°C/min, to 280°C(10min) @ 10°C/min

GC: Agilent 5890
Detector / Temperature: FID / 310°C

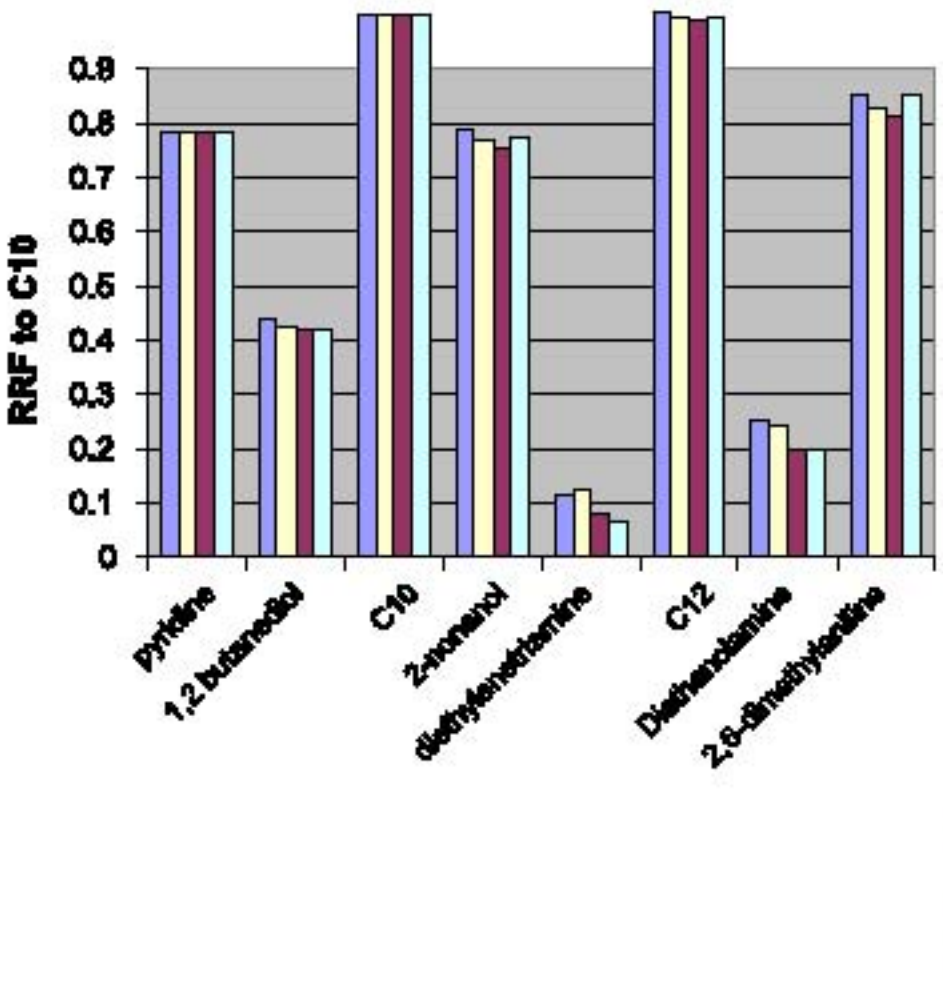
Figure 4. Sample Chromatogram for Amines (2.5 / 5.0ng)



1. pyridine (2.5ng)
2. 1,2-butanediol (2.5ng)
3. C10 (2.5ng)
4. 2-nonanol (2.5)
5. diethylenetriamine (5.0ng)
6. C12 (2.5ng)
7. diethanolamine (5.0ng)
8. 2,6-dimethylaniline (2.5ng)

Figure 5A-B. Results for Amine Evaluation, Injections 2-6

A. Average Response Factors for Injections 2-6



B. %RSD for Injections 2-6

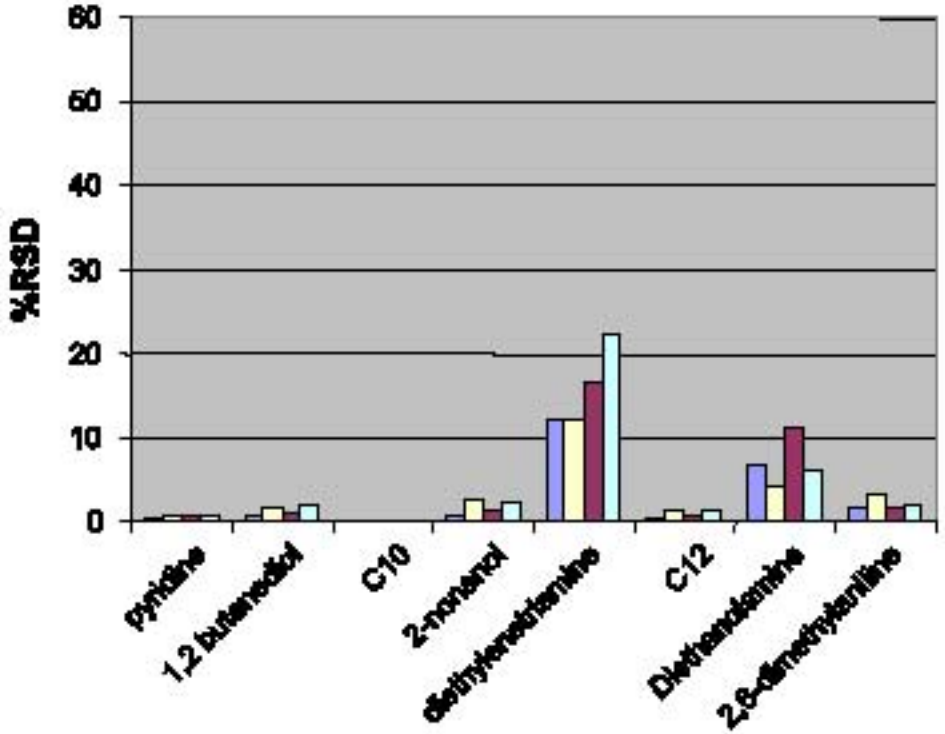
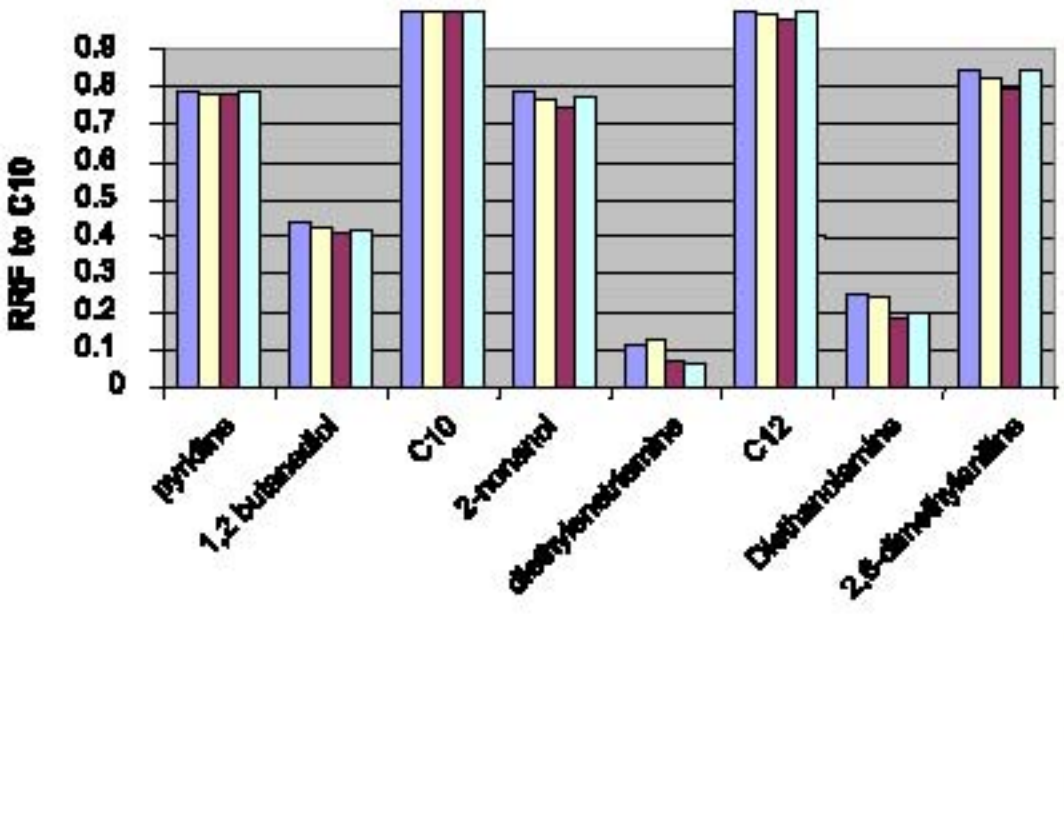
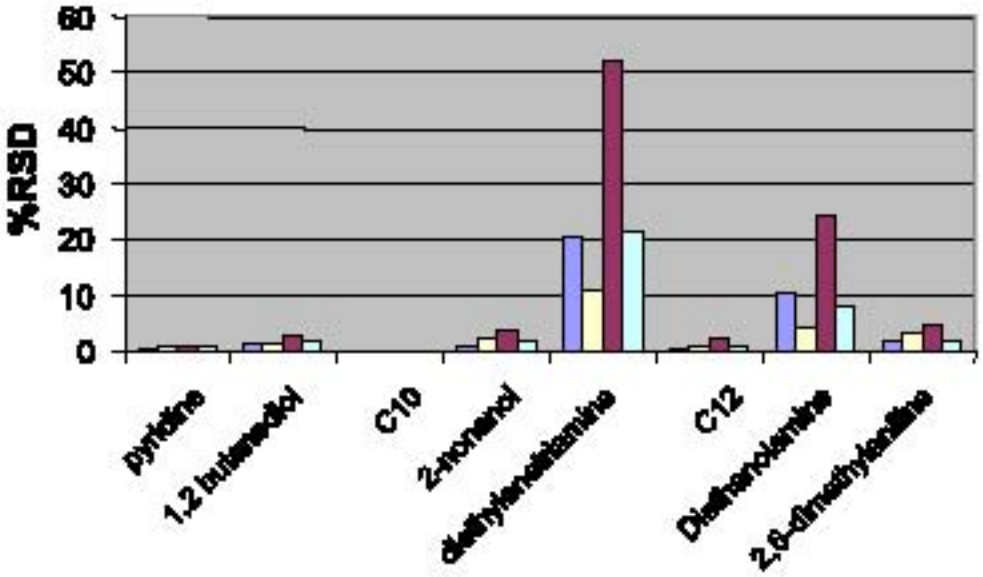


Figure 6A-B. Results for Amine Evaluation, Injections 1-6

A. Average Response Factors for Injections 1-6



B. %RSD for Injections 1-6



Discussion on results for various liner surfaces with Amines (Figures 5-6):

1. Undeactivated borosilicate liner

   When analyzing basic compounds at low ppm levels, the liner without any deactivation again displayed surprisingly high relative response factors. For the most demanding compounds (diethylenetriamine and diethanolamine), however, these liners predictably showed the lowest response factors and high %RSD values. Also, this liner surface did not show significant priming when comparing RRF and %RSD values from runs 2-6 vs. 1-6.

2. Intermediate polarity (IP) deactivated liner

   Since the IP liner has a characteristically neutral-to-acidic nature, it predictably performed worst of the four types. Most notably with the diethylenetriamine and ethanolamine, the %RSD comparison from runs 2-6 vs. 1-6 showed significant priming. The %RSD of the triamine increase from 17% to 52% when the first injection is factored in. Likewise for diethanolamine, the %RSD increased from 11% to 25%. This liner surface also had the lowest overall response factors in the amines experiment.

Discussion on results for various liner surfaces with Amines (continued):

3. Siltek and Base deactivated liners

The Siltek and base deactivated liners performed to give relatively equivalent response factors for all test probes. These liners also had superior performance over the raw and IP liners. It is interesting to note, however, that the Siltek liners displayed less priming effect. The %RSD for base deactivated liners increased from 12% to 20% for diethylenetriamine and from 7% to 11% for diethanolamine when factoring in the first of six injections. Correspondingly, the Siltek liner decreased from 12% to 11% for diethylenetriamine and remained constant at 4% for diethanolamine. This result suggest a slightly superior overall performance of Siltek over base deactivated liners for the analysis of basic compounds.

Conclusions

The choice of a correct liner deactivation has hinged on the type of analytes that are to be analyzed. Typically, if the analytes are acidic, a liner tailored to have an acidic character would be used in order to avoid the possibility of peak tailing or adsorption. Conversely, a base deactivated liner would be selected to analyze compounds with a basic character. This study has shown that liners with surface characteristics which match those of the analytes do in fact give excellent analytical performance when operating in their designated environments. However, the study also shows that Siltek deactivated liners perform equivalently or better than the older generation surfaces. Within the design of this comprehensive study, the Siltek surface is capable of optimum performance whether analyzing acidic semivolatile or basic amine compounds.

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A Comparison of Surface Inertness in Process Analytical Systems

Introduction

Recent innovations in coating technologies have dramatically improved the analytical sensitivity and test precision of process sample transfer and analytical systems. Poor surface inertness can result in performance issues ranging from poor sensitivity and resolution, to adsorption/ desorption and catalytic effects. The overall impact to the customer includes regulatory compliance issues, lost product, poor process yields, and ultimately lost customers.

This study compares the surface inertness of 2 coatings on the inner walls of 1/8" stainless steel tubing: SilcoNert™2000 (SilcoTek™Corporation) and Silonite (Entech Instruments Inc.). The data show significant differences in surface inertness of the two coatings.

Experimental

SilcoNert™2000 and Silonite coated tubing sections (1.0m long x 1/8" OD x 0.85" ID) were tested for various active compounds (see appendix A for test compounds and test results). The test tubing was connected to the end of an MXT-5 analytical column (Restek Corp.), and tested on an Agilent gas chromatograph model 6890 (Figure 1) See appendix B for test conditions.

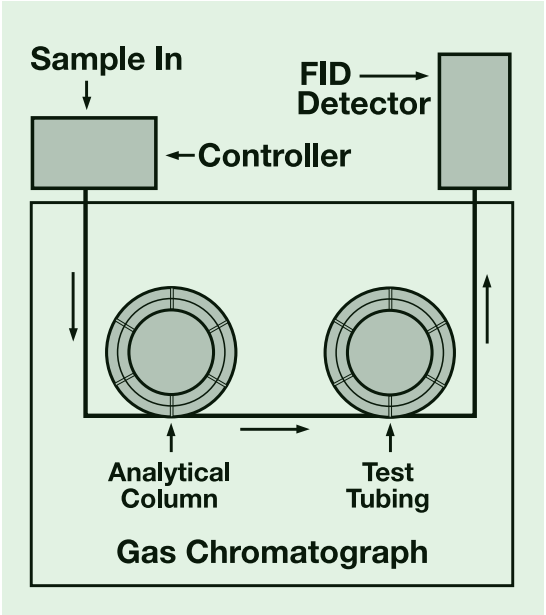


Figure 1 - Experimental setup comparing the inertness of SilcoTek™2000 and Silonite tubing.

A test mix containing active and non-active compounds was first injected into a control analytical column without any connected 1/8" tubing. Test results show superior results with all compounds resolved (Figure 2).

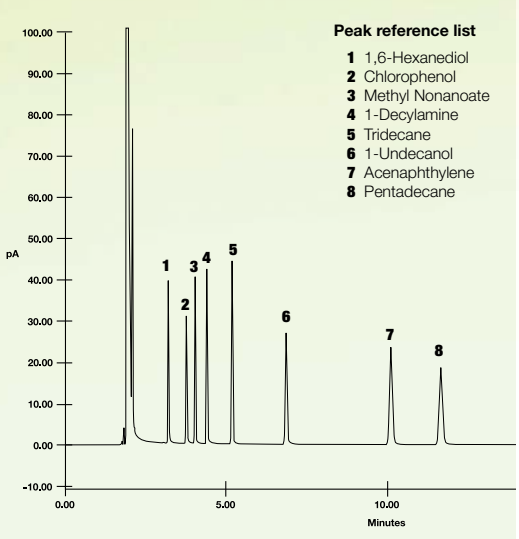
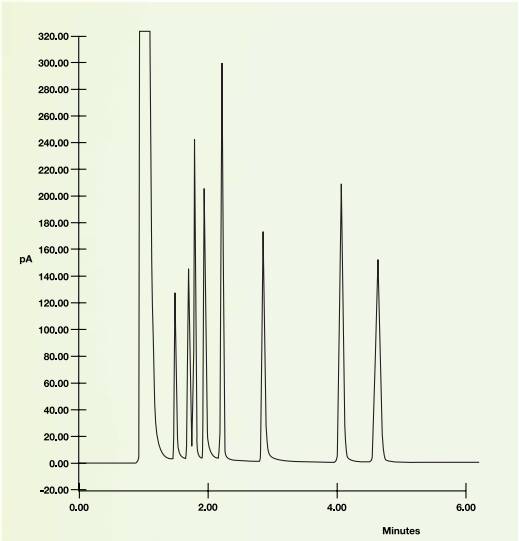


Figure 2 - Control analytical column shows superior results, with all compounds resolved.



A SilcoNert™2000 coated tube was then installed in series after the analytical column. The test compounds were then injected into the column combination under similar conditions as the control run. Results show nearly identical peak resolution and response with the SilcoNert™2000 tubing with little to no loss of active compounds (Figure 3).

Figure 3 - SilcoNert™2000 coated tubing provides exceptional inertness with nearly exceptional transfer of compounds.

The SilcoNert™ 2000 tubing was then removed and replaced with the Silonite tubing. Test compounds were then injected into the column combination under similar conditions as the previous run. Results show significant loss of active compounds with a high distortion of signal (peak tailing and broadening) and loss of peak area (Figure 4).

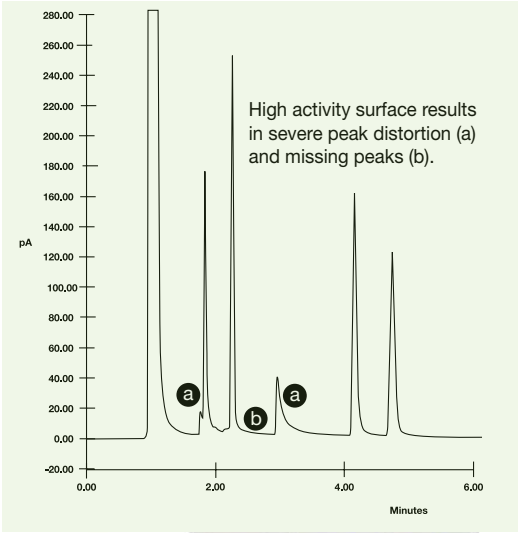
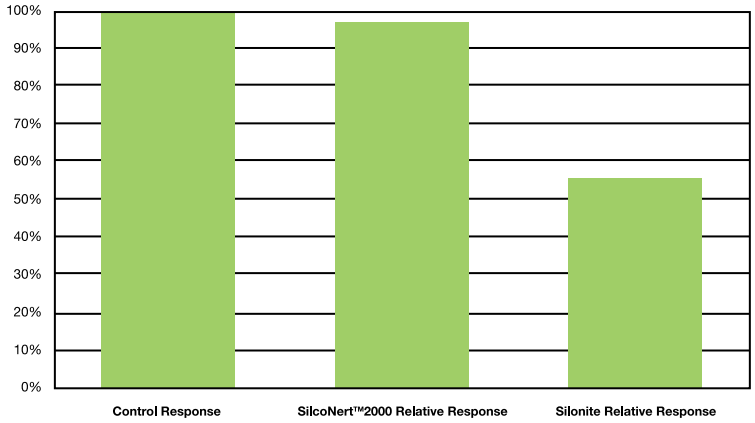


Figure 4 - Silonite coated tube shows significant loss of compounds with high peak tailing.

Results

Tests show the SilcoNert™2000 treated tube is the least active surface for analytical and process sampling. The Silonite surface is drastically more active. Exhibiting significant surface activity with very poor resolution of active compounds. Figure 5 shows the relative activity of each coating based on test results of the 8 active compounds. For a mildly active compound such as 4-chlorophenol, the SilcoNert™2000 surface showed nearly 6.7 times better response than the Silonite surface. For a more active compound such as 1,6-hexanediol, the SilcoNert™ 2000 column surface showed a response nearly equal to the response seen on the analytical column alone. With high activity compounds the Silonite column system showed total adsorption of 1,6-hexanediol. See Appendix A for comparative analytical data.

Figure 5: SilcoNert™2000 demonstrates superior inertness compared to Silonite.



Conclusion

SilcoNert™2000 surface is demonstratively the most inert surface for sampling, transporting, or analyzing active compounds containing active functional groups such as diols, nitrophenols, sulfurs, and mercury compounds.

Appendix A: Comparative analytical test results of SilcoNert™2000 vs, Silonite coated tubes,

Test Compound	Analytical Column (Control)	Peak area ratio	Control Response	SilcoNert™2000 Coated Tube	Peak area ratio	SilcoNert™2000 Relative Response	Silonite Coated Tube	Peak area ratio	Silonite Relative Response
1,6-Hexanediol	154650	0.61		277855	0.55	90%		0	0%
4-Chlorophenol	150581	0.59		291236	0.58	98%	57631	0.07	12%
Methyl Nonanoate	177997	0.7		358693	0.7	100%	582963	0.69	99%
1-Decylamine	206534	0.81		394075	0.78	96%	34138	0.04	5%
Tridecane	255610	1		504389	1	100%	844897	1	100%
Undecanol	213964	0.84		414297	0.82	98%	454764	0.54	64%
Acenaphthylene	283097	1.11		558834	1.11	100%	782758	0.93	84%
Pentadecane	270241	1.06		516370	1.02	96%	715064	0.85	80%
	1712674		100%	3315750		97%	3472215		55%

Appendix B: Analytical Test Conditions Comparing SilcoNert™ 2000 Coated Tubing with Silonite Coated Tubing

Analytical Column: Mxt-5, 30m x 0.53mm x 0.50µm (Restek Corporation)
Inj.: 1.0µl split injection of Rxi-500 Isothermal Test Mix (Restek Coporation)
Oven Temp: 135°C isothermal
Inj./Det. Temp.: 250°C/330°C
Linear Velocity: 55cm/sec hydrogen
Detector: FID
Split Flow: 100ml/min

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- **Moisture control and high purity in semiconductor operations.**

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