

Importance of Column Inertness for Maximizing Sensitivity for the quantification of traces

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Challenges and Needs of today's lab

Challenges

- Quantification & Qualification of traces
- Keep the selective detector up and running
- Reduced investment of knowledge in the lab

Needs

- Lower detection limits
- Improved stability in GC and GC-MS systems

What can we do:

- Make more inert and stable columns
- Improve Easy of use
- Education



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Lower detection limits

Need to Increase signal to noise..

1 Reducing the Noise

2 Increase the signal



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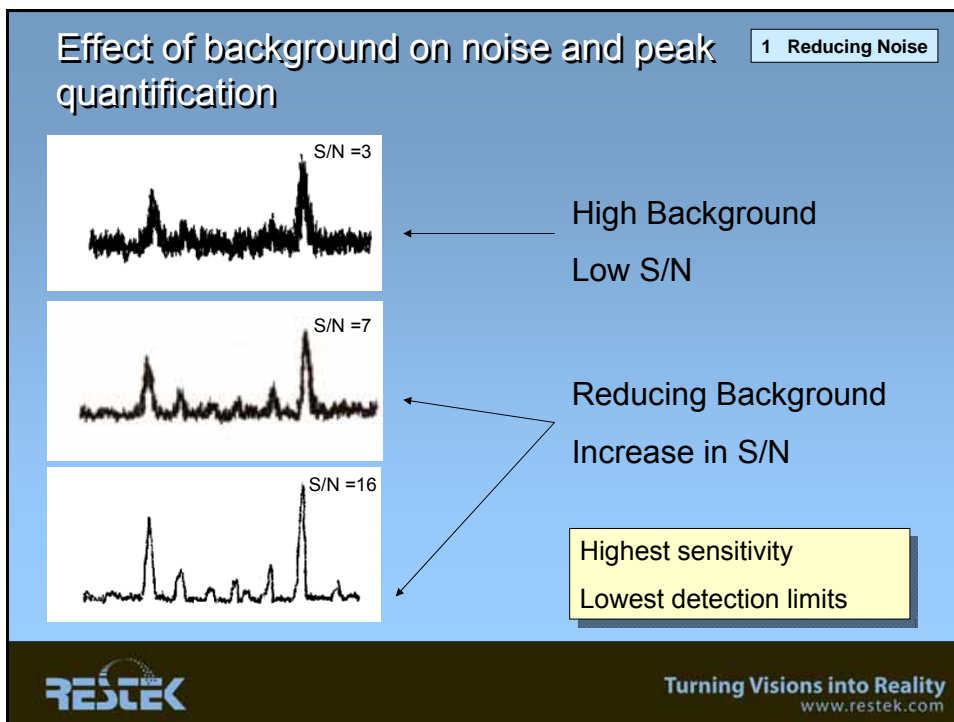
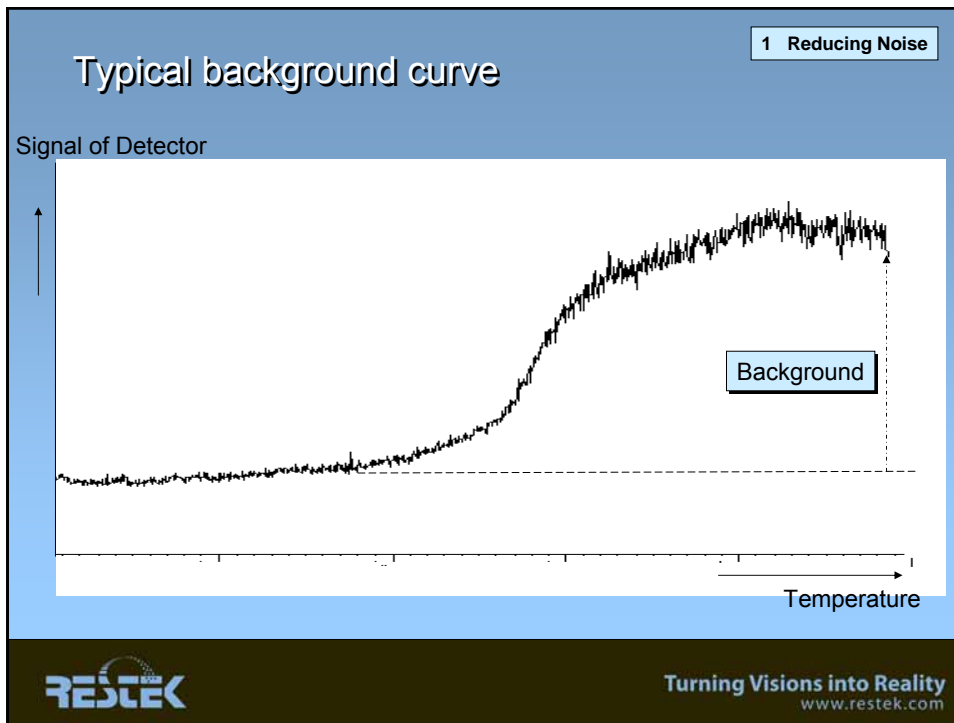
1 Reducing Noise

Noise level is directly related to the background of the GC system

“A system with lower background will also have a better performance”



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Background: area's to look at..

Main Contributions:

- **Injection system**
 - Septa
 - Liners
 - Connections
- **Carrier gas, detector gases**
- **Column outside coating**
- **Leaks and leak checking**
- **Temperature setting**

- **Type of stationary phases**



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Why is a Low background system important?

- Less noise on detector signal
 - higher signal/noise ratio improved trace analysis
 - lower detection limits
- Reduced detector contamination
- Short stabilization times
- Better MS-spectra
- Reduced chance on "ghost" peaks
- Longer column life time



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The stationary phase

Stationary phase will start to decompose when heated at elevated temperature

Absolute bleed level depends on:

- **The nature of the stationary phase**
Type of polymer, stabilization, molecular weight
- **The temperature**
Every 12°C higher, 2 times higher bleed
- **The amount of phase present in the column**
Film thickness, length and diameter



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Stabilization of Stationary Phases

That's an area where Restek can help..

Introducing a New platform GC phases offering a combination of:

Lowest Possible Bleed & Ultra Inertness

**Rxi-polymer
technology**



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Rxi-technology

- Stabilization of stationary phase using stabilizing groups
 - Incorporation of “smart” stabilization/crossbonding groups
 - Long polymers, ladder technology
 - Allow surface bonding
 - High purity polymers
- Minimization of reactive silanol groups in the polymer and fused silica surface
 - End capping
 - Unique surface deactivation
- Surface bonding of all Rxi polymers
- Conditioning under pure carrier gas (water free)



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Rxi Characteristics

- **All advantages for using low bleed columns**
 - Improved trace analysis
 - Lower detection limits
 - Reduced down time
 - Better mass spectra
 - Longer column life time
- **Superior inertness provides High response for polar compounds (alcohols, bases/acids)**
- **Extremely robust: more analysis per column**



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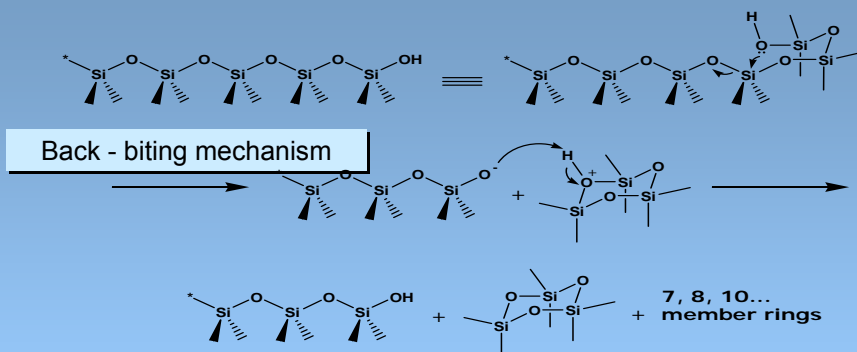
Stabilization of the stationary phases..

All Stationary phases will form degradation product when used at higher temperatures

..need to know the stationary phase breakdown process..



The stationary phase breakdown process



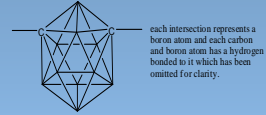
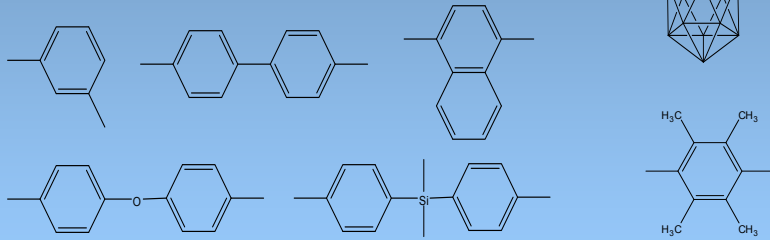
Initiated by terminal silanol groups



New *FUSION* line using Rxi-technology.. Stabilization of Stationary Phases

Incorporation of stabilizing groups

Incorporation of “smart” cross bonding



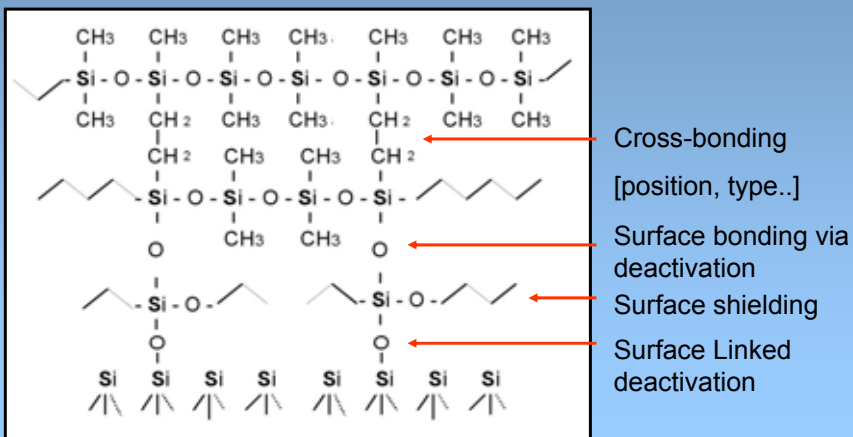
The “back-biting” is made more difficult:
polymer is more stable and bleeds less..



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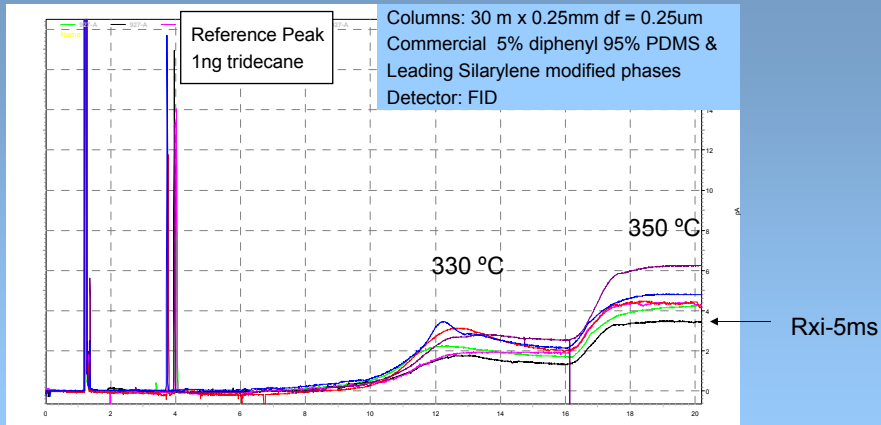
Rxi technology Stabilization/ deactivation

Cross-bonding, Surface-bonding, Deactivation and Shielding for
minimization impact of (re)active silanols



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Impact of Rxi technology on bleed



- Differences on bleed not very big for most “ms” type columns
- Rxi-technology results in lowest bleed..



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Lower detection limits

2 Increase the signal

Need to Increase signal to noise..

1 Reducing the Noise

2 Increase the Signal



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Increase of signal can be obtained by

- Concentrate sample
- Inject more onto the column
- Optimization of detector settings (flows)
- Inert injection and detection port sleeves/liner
- Position of column in the detector
- Increase gas velocity or temperature program rate

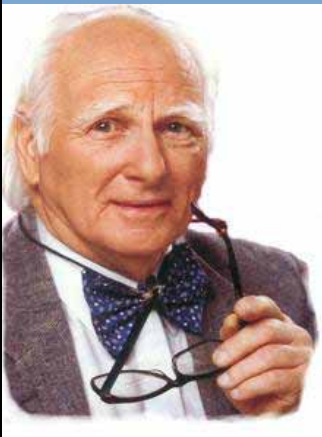
But also:

Using the most inert capillary column..



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What is the challenge for the next generation capillary columns ?



Inertness !

Professor Walt Jennings,
ISCC Conference 2004..



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Why is an inert system important?

2 Increasing signal

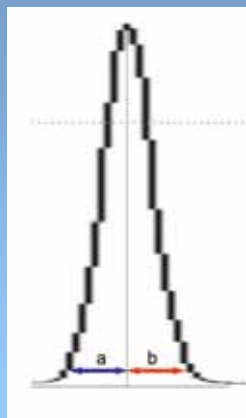
- The components will elute as sharper peaks
 - Higher response
 - Higher peak area's (less adsorption)
 - No retention time shifting
- Allows polar compounds to be measured at increasing low levels
- Derivatization often not necessary
- More analysis without maintenance



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Peak height vs asymmetry

2 Increasing signal



Symmetrical peaks;

- Provide highest response (sensitivity)
- Are better for quantitation

Activity in the column will affect symmetry and response will decrease..



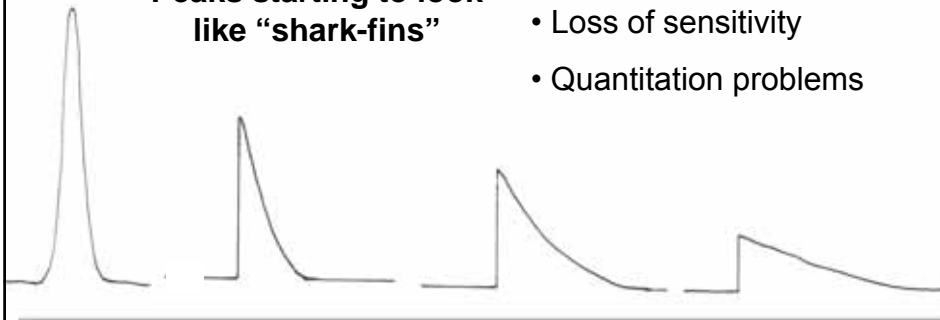
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Strong interaction with residual active sites in the column

2 Increasing signal

Peaks starting to look like “shark-fins”

- Loss of sensitivity
- Quantitation problems



There is also an other effect: shifting of retention times..



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Shifting of retention times

2 Increasing signal

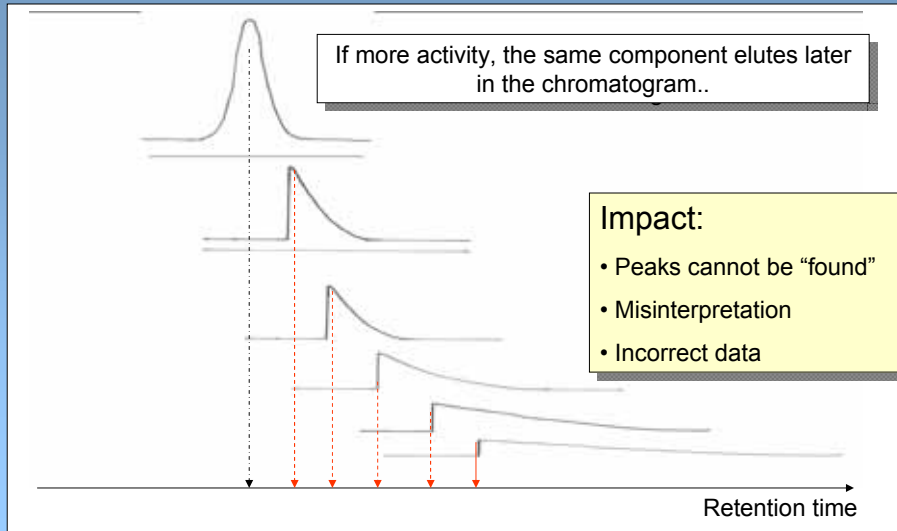
- Activity in the column will act as a 2nd retention mechanism
 - Retention (and RI) depend on degree of activity
 - Variations on activity, each column can show a different RI
- Retention time will become a function of concentration
 - High levels elute earlier



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Impact of column activity on retention times

2 Increasing signal

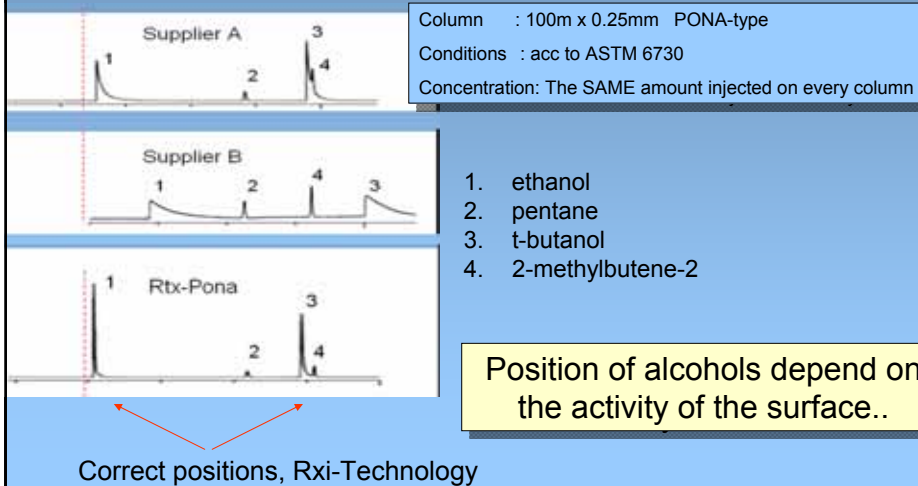


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Example: position of Alcohols on 100% PDMS-type column, ASTM Method D6730

2 Increasing signal



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Retention time will become a function of concentration

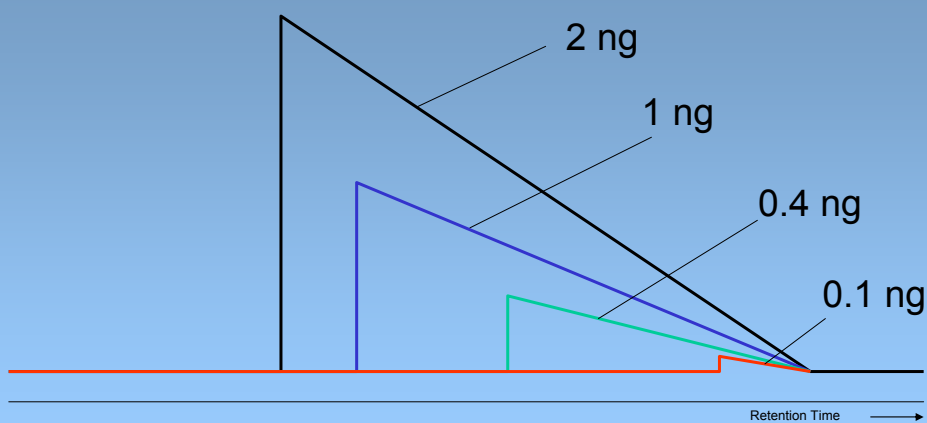
High levels elute earlier..



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Impact of activity on retention times

2 Increasing signal

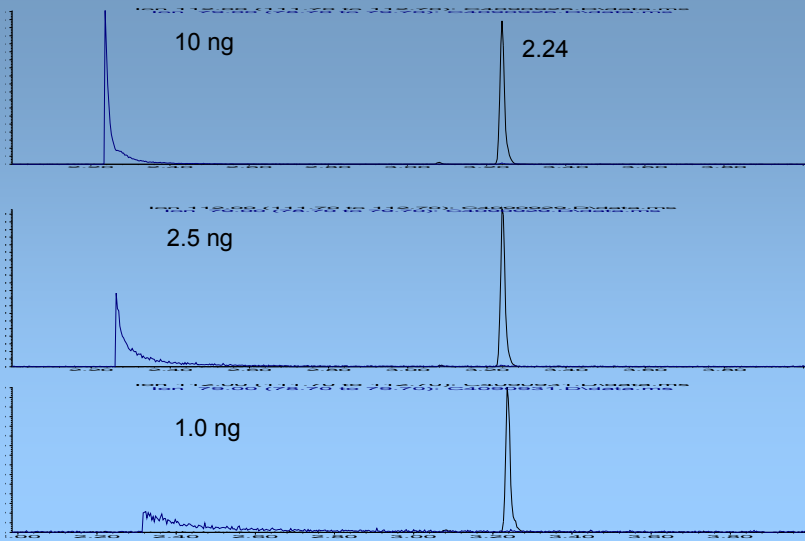


Retention Time depend on the amount of component present



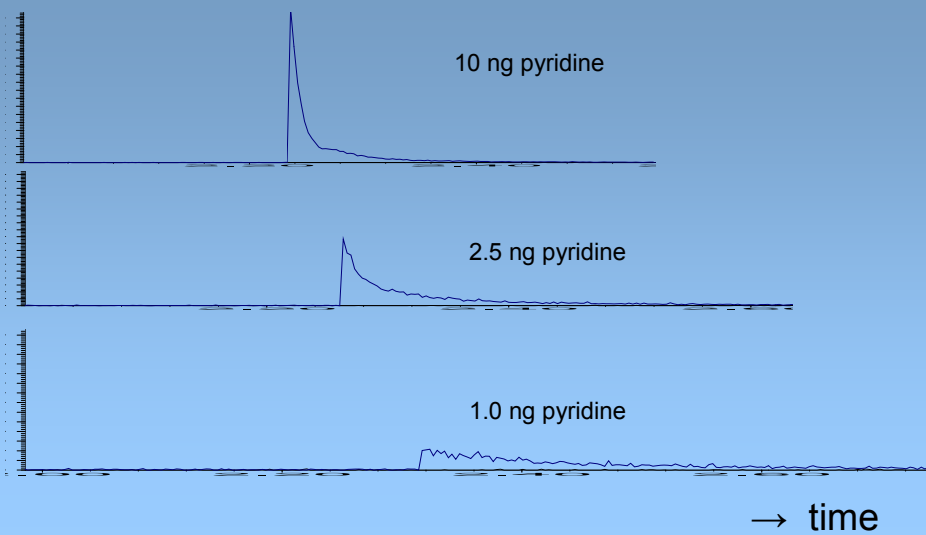
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Pyridine retention on a typical commercially available column

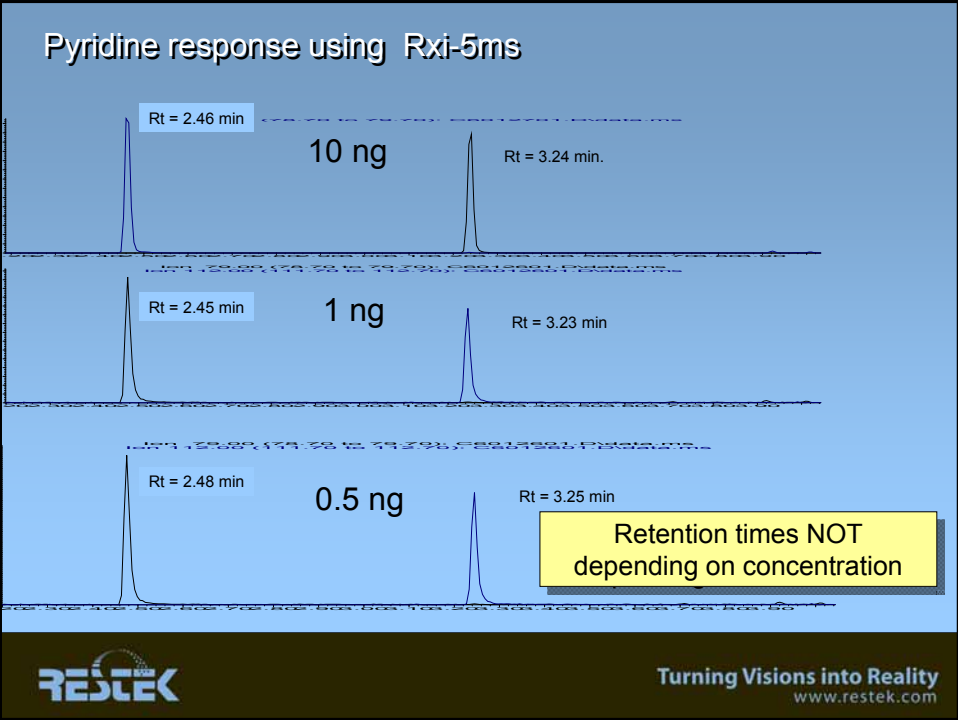
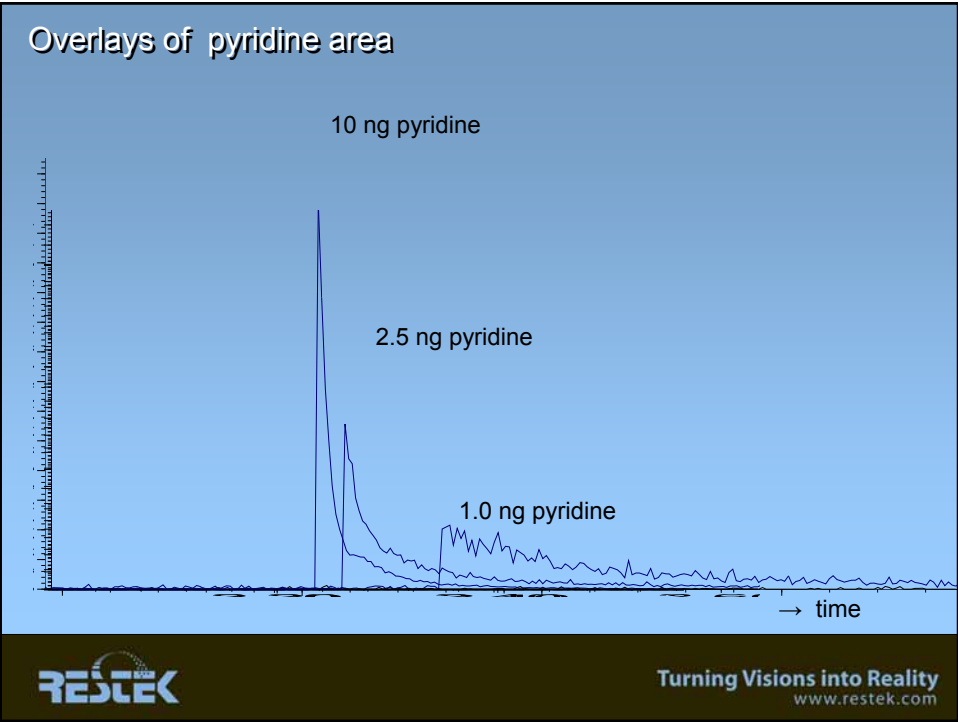


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Expansion of pyridine area



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Rxi-Technology: Deactivation

2 Increasing signal

New deactivation

- Resulting in a “neutral” surface
- Reproducible
- Temperature stable
- Usable for a series of stationary phases



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Rxi-technology

2 Increasing signal

- Stabilization of stationary phase using stabilizing groups
 - Incorporation of stabilization / cross bonding groups
 - Long polymers, ladder technology
 - Allow surface bonding
 - High purity polymers
- Minimization of reactive silanol groups in the polymer and fused silica surface
 - End capping
 - Unique surface deactivation
- Surface bonding of all Rxi polymers
- Conditioning under pure carrier gas (water free)



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Critical Test for measuring inertness of columns

Running the standard mixtures all suppliers use it seems that all columns are inert..

We need components that are really CRITICAL and will provide additional value to the inertness-status of a capillary column (or system)..

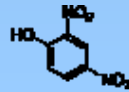
Basic Test

Pyridine



Acidic Test

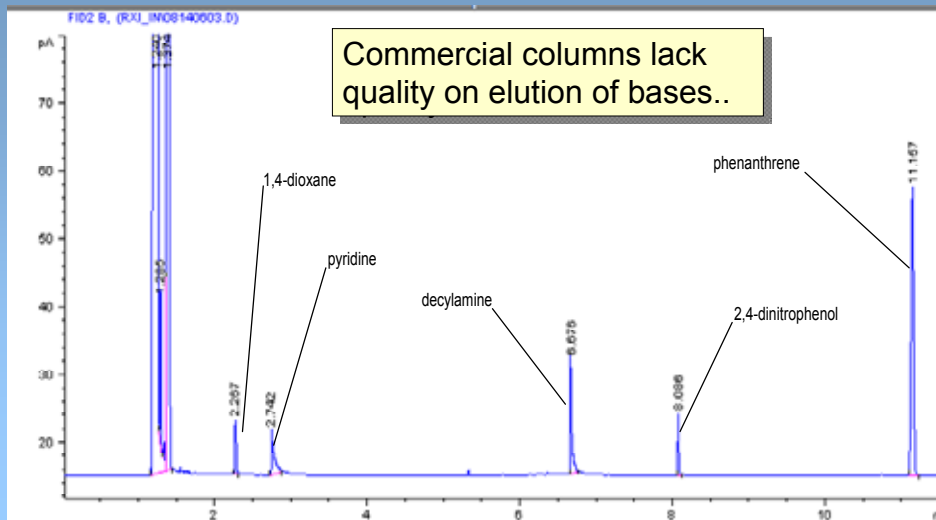
2,4-dinitro phenol



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"State of the art" deactivation technology

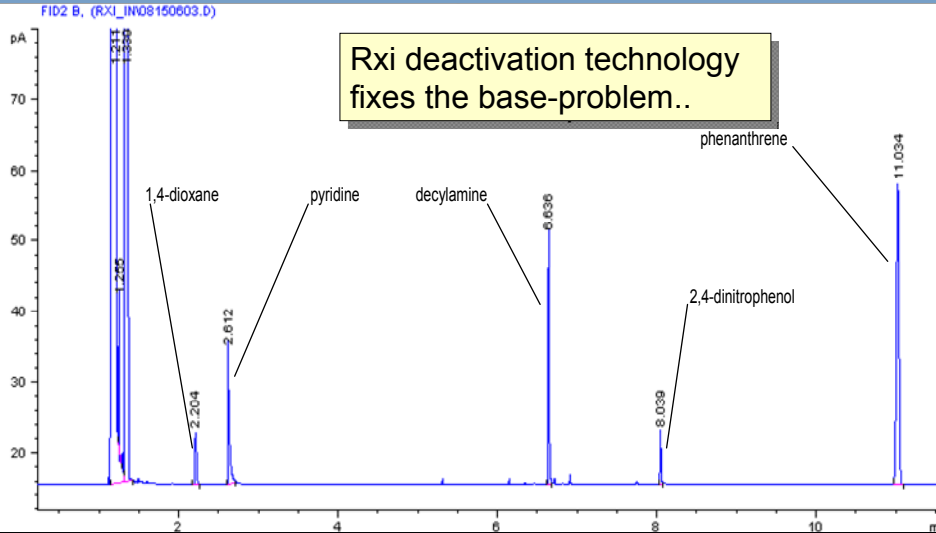
2 Increasing signal



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New Rxi-deactivation technology

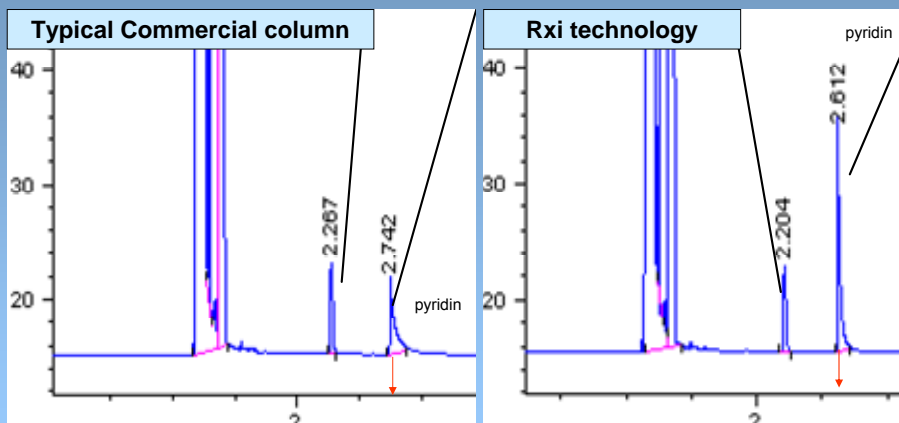
2 Increasing signal



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Zooming in on impact of Rxi-deactivation

2 Increasing signal



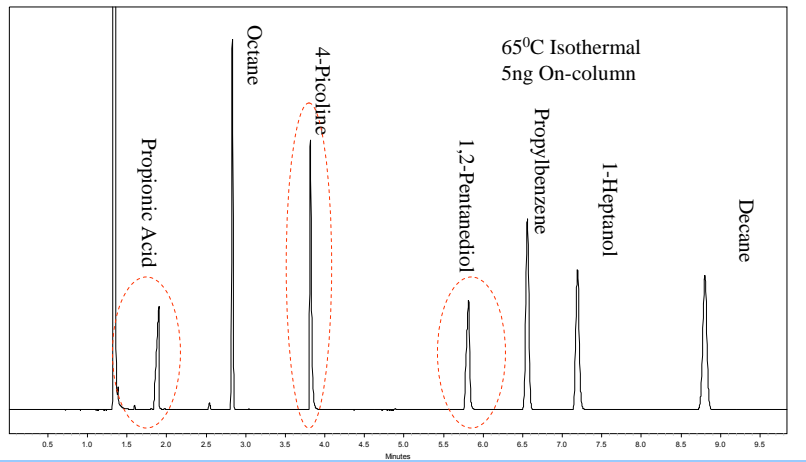
Note the improvement in peak shape and peak height for pyridine peak..(and the position..!!)



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Rxi Deactivation technology: neutral column

2 Increasing signal



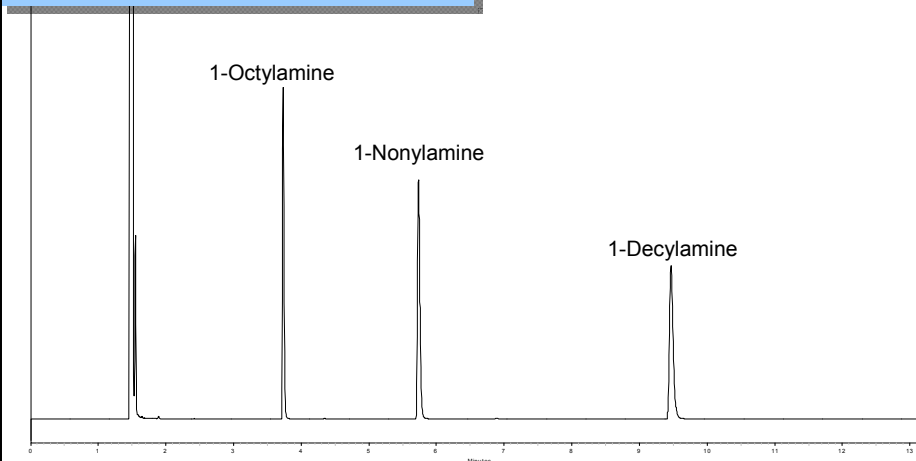
Elutes acids, bases and alcohols..



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Primary Amines

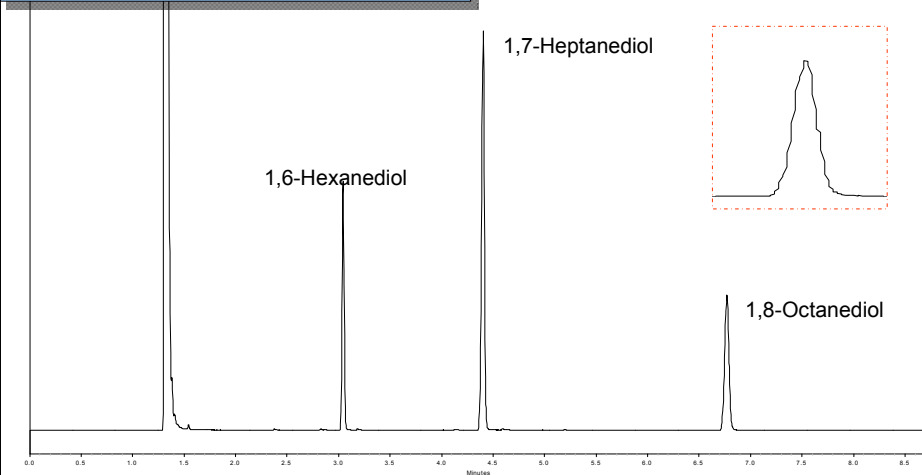
Column : 30 m x 0.25mm Rxi 5ms, Df=0.25um
Sample : 5ng On Column
Oven : 105°C



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Diols

Column : 30 m x 0.25mm Rxi 5ms, df=0.25um
 Sample : 5ng On Column
 Oven : 125°C

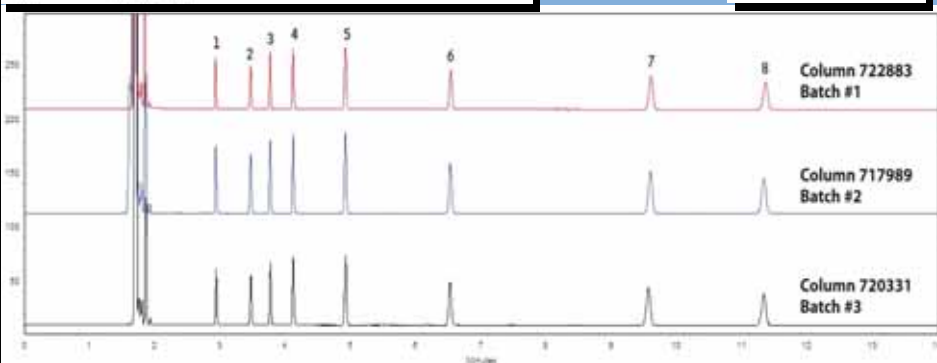


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Rxi: tested with CHALLENGING compounds

Column: Rxi™ 5ms 30m, 0.25 ID, 0.25µm (cat. # 13423)
 Sample: 500µg/mL Isothermal Column Test Mix (cat. # 35241) in toluene
 Inj.: 1.0µL, split injection (split ratio 1:100), 4mm single gooseneck inlet liner with wool (cat. # 22405)
 Inj. temp.: 250°C
 Carrier gas: hydrogen, constant flow
 Linear velocity: 38cm/sec. @ 135°C
 Oven temp.: 135°C
 Det.: FID @ 330°C

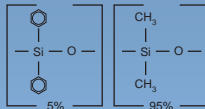
- 1. 1,6-hexanediol
- 2. 4-chlorophenol
- 3. methyl nonanoate
- 4. 1-decylamine
- 5. tridecane
- 6. 1-undecanol
- 7. acenaphthylene
- 8. pentadecane



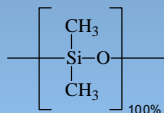
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Rxi- stabilization technology is successfully applied with:

Rxi-5ms

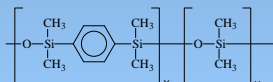


Rxi-1ms

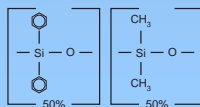


Rxi-5Sil MS

Rxi-XLB



Rxi-17



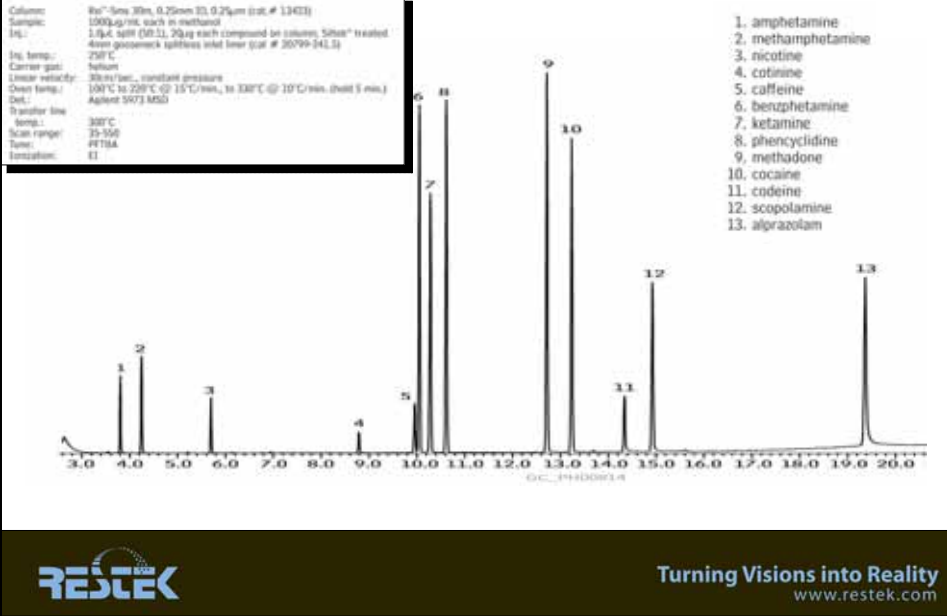
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Applications of columns made with Rxi-technology

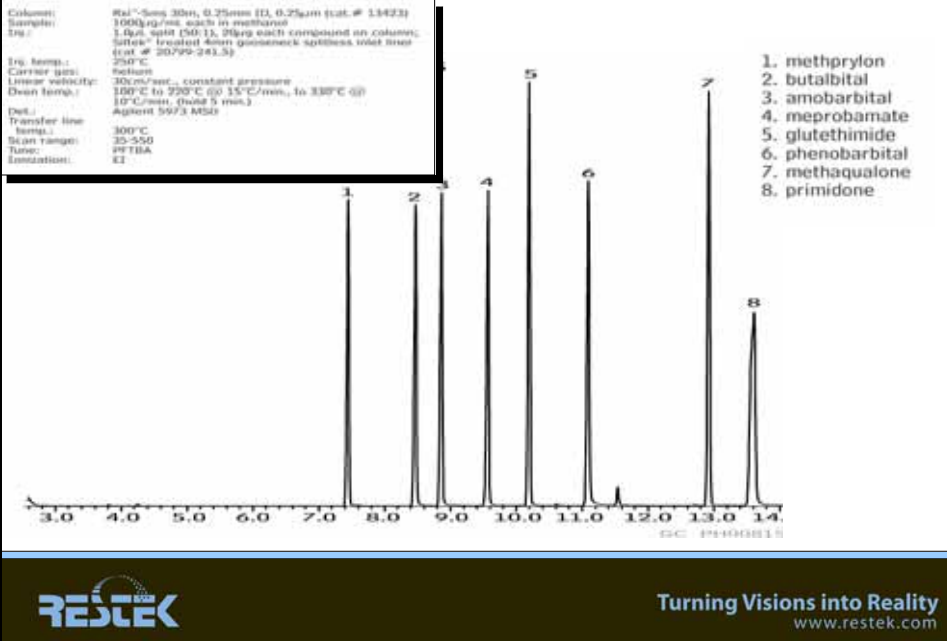


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Basic drugs, no derivatisation



Acidic Drugs

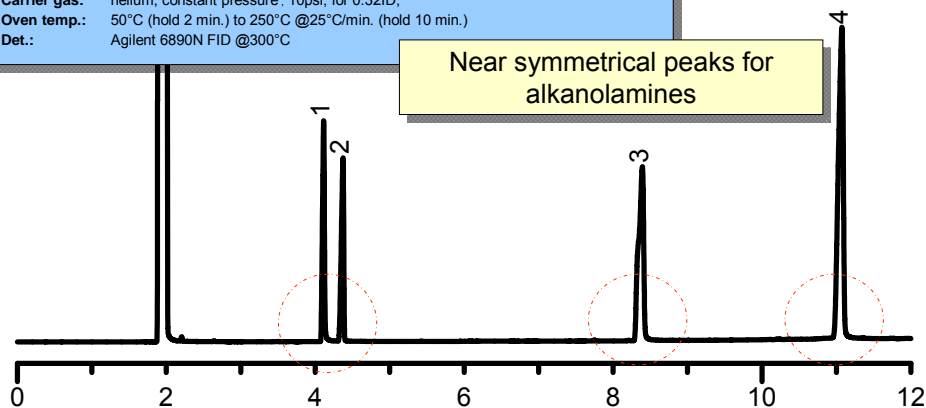


Alkanolamines and glycol on Rxi-5ms

Column: Rxi-5 MS 30m, 0.32 ID, 1.0 μ m (cat.#13454)
Sample: 0.2% solution Ethanolamine standard (custom) in methanol
Inj.: 1.0 μ L split (split ratio varied), 20:1 for 0.32ID; 100:1 for 0.25ID
 4mm base deactivated, single gooseneck, split/splitless inlet liner (cat.#20799-210.5)
Inj. temp.: 200°C
Carrier gas: helium, constant pressure . 10psi, for 0.32ID;
Oven temp.: 50°C (hold 2 min.) to 250°C @25°C/min. (hold 10 min.)
Det.: Agilent 6890N FID @300°C

1. monoethanolamine
2. ethylene glycol
3. diethanolamine
4. triethanolamine

Near symmetrical peaks for alkanolamines

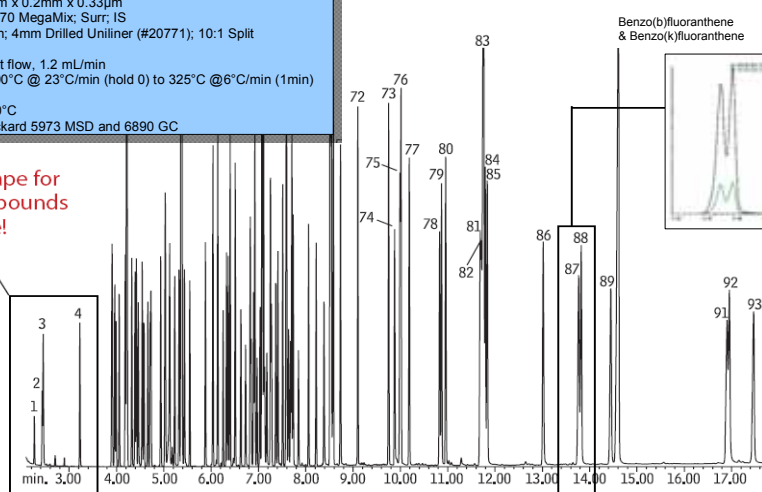


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EPA 8270D analytes on Rxi-5ms

Standard: 10 μ g/mL of EPA 8270
Column: Rxi-5ms 25m x 0.2mm x 0.33 μ m
Standard: 10 μ g/mL 8270 MegaMix, Surr, IS
Inject: 1 μ L injection, 4mm Drilled Uniliner (#20771); 10:1 Split
Inj. temp.: 250°C
Carrier gas: He, constant flow, 1.2 mL/min
Oven temp.: 50(0.5) to 290°C @ 23°C/min (hold 0) to 325°C @ 6°C/min (1min)
Scan range: 35-550 amu
Det.: MSD @ 280°C
Instrument: Hewlett-Packard 5973 MSD and 6890 GC

Excellent peak shape for early eluting compounds including pyridine!



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Symmetrical peaks for all chemical classes analyzed

1. 1,4-dioxane	26. nitrobenzene-d5 (int.)	39. 2-fluorobiphenyl (sur.)	58. 4-chlorophenyl phenyl ether	75. 3,3'-dimethylbenzidine
2. N-nitrosodimethylamine	27. nitrobenzene	40. 2-chloronaphthalene	59. fluorene	76. styrene
3. pyridine	28. isophorone	41. 2-nitroanisole	60. 4-nitroanisole	77. p-terphenyl-d14 (sur.)
4. 2-fluorophenol (sur.)	29. 2,4-dimethylphenol	42. 1,4-dinitrobenzene	61. 4,6-dinitro-2-methylphenol	78. butyl benzyl phthalate
5. phenol	24. 2-nitrophenol	43. dimethyl phthalate	62. N-nitrosodiphenylamine (isohentamine)	79. styrene-d10 (sur.)
6. phenol-d6 (sur.)	25. benzoic acid	44. 1,3-dinitrobenzene	63. 1,2-diphenylhydrazine (as azobenzene)	80. bis(2-ethylhexyl) adipate
7. aniline	26. bis(2-chloroethyl) methane	45. 2,6-dinitroanisole	64. 2,4,6-tribromophenol (sur.)	81. 1,3-dichlorobenzidine
8. bis(2-chloroethyl) ether	27. 2,4-dichlorophenol	46. acenaphthylene	65. 4-bromophenyl phenyl ether	82. bis(2-ethylhexyl) phthalate
9. 2-chlorophenol	28. 1,2,4-trichlorobenzene	47. 1,2-dinitrobenzene	66. hexachlorobenzene	83. benz(a)anthracene
10. 1,3-dichlorobenzene	29. naphthalene-d8 (int. std.)	48. 3-nitroanisole	67. pentachlorophenol	84. chrysene-d12 (int. std.)
11. 1,4-dichlorobenzene-d4 (int. std.)	30. naphthalene	49. acenaphthene-d10 (int. std.)	68. pentafluorophenol	85. chrysene
12. 1,4-dichlorobenzene	31. 4-chloroanisole	50. 2,4-dibromophenol (int. std.)	69. pentafluorobenzene-d10 (int. std.)	86. di-n-butyl phthalate
13. benzyl alcohol	32. hexachlorobutadiene	51. acenaphthene	70. anthracene	87. benzofluoranthene
14. 2-methylphenol	33. 4-chloro-3-methylphenol	52. 4-nitrophenol	71. carbazole	88. benzofluoranthene
15. 1,2-dichlorobenzene	34. 2-methylnaphthalene	53. 2,4-dinitroanisole	72. di-n-butyl phthalate	89. benzo(a)pyrene
16. bis(2-chloroisopropyl) ether	35. 1-methylnaphthalene	54. dibenzofuran	73. fluoranthene	90. perylene-d12 (int. std.)
17a. 4-methylphenol/3-methylphenol	36. hexachlorocyclopentadiene	55. 2,3,5,6-tetrachlorophenol	74. benzidine	91. benzo(b)fluoranthene
17b. N-nitroso-N-propylamine	37. 2,4,6-trichlorophenol	56. 2,1,4,6-tetrachlorophenol		
19. hexachloroethane	38. 2,4,5-trichlorophenol	57. diethyl phthalate		

Amines

Phenols

Ethers

Chlorinated hydrocarbons

Alcohols

Nitro compounds

Acids

Hydrocarbons

Aromatics

Polyaromatic hydrocarbons



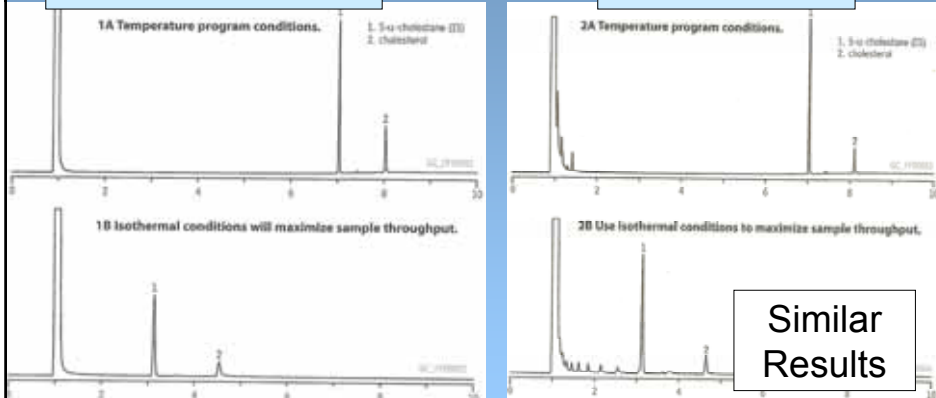
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Cholesterol

15m x 0.25mm Rxi-5ms, df = 0.25 um

Without derivatization

With derivatization



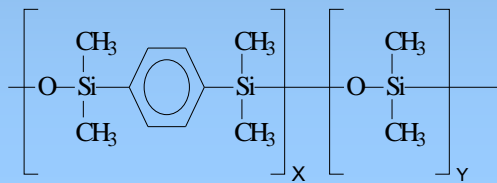
Inertness of Rxi-5ms allows determination of cholesterol without derivatization



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Rxi technology applied with:

Rxi-5Sil MS

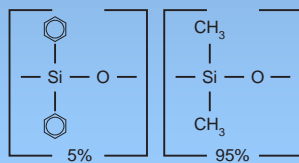


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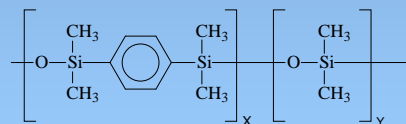
Why offering a Rxi-5Silms next to a Rxi-5ms phase?

- Both phases are different in selectivity
- Most companies consider these phases to be similar

They are NOT !!



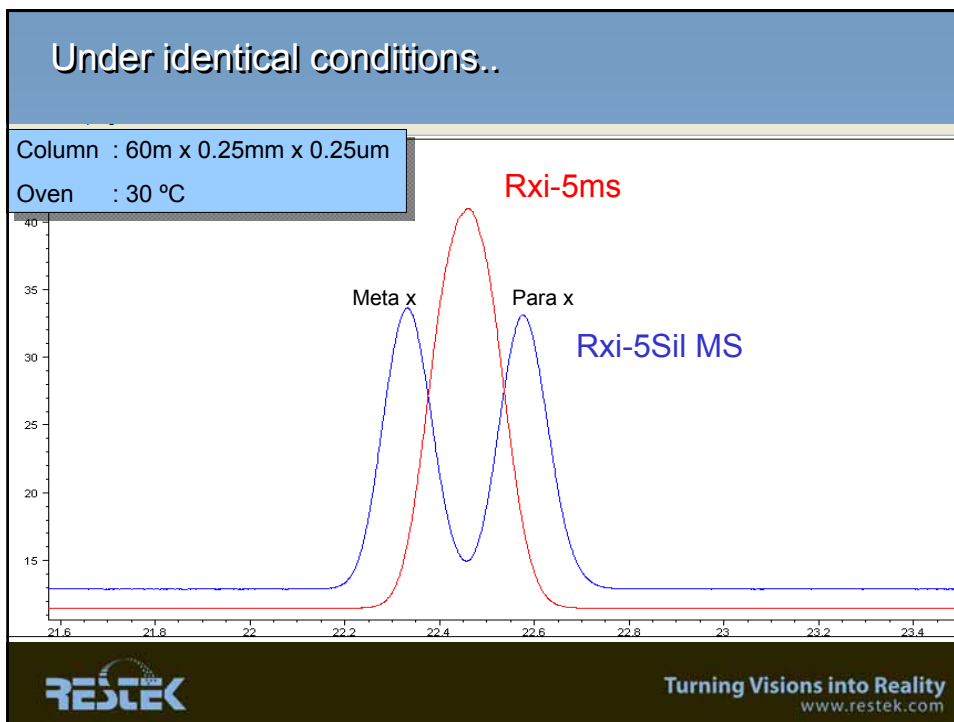
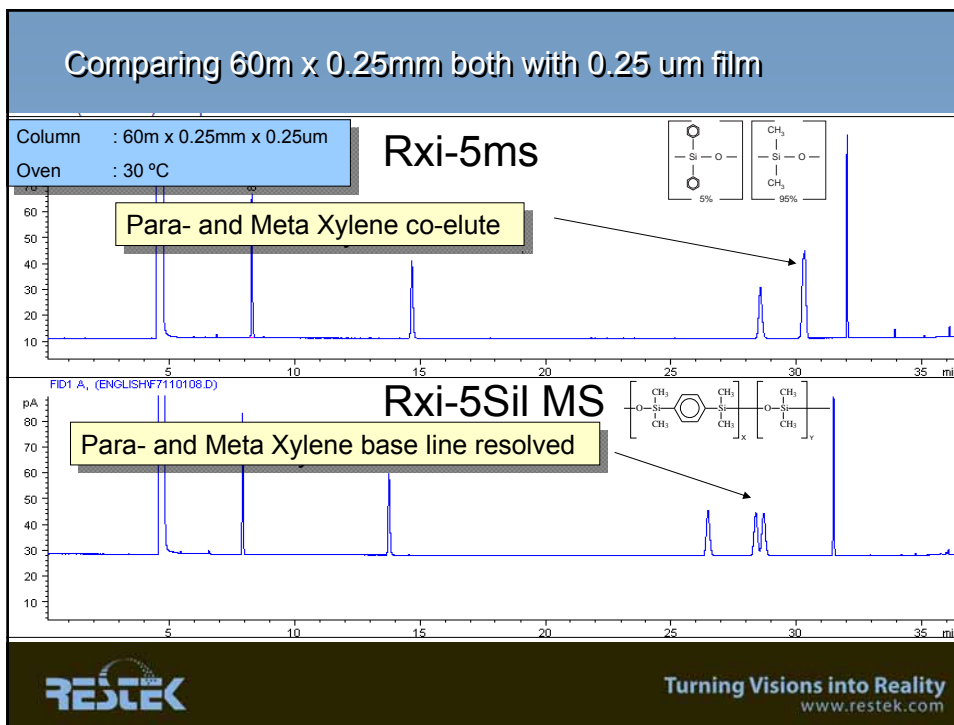
Rxi-5ms



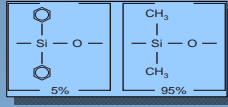
Rxi-5Sil MS



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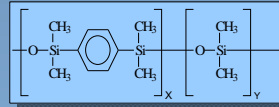


Equivalency



Rxi®-5ms

5% diphenyl- PDMS



Rxi®-5Sil MS

Arylene stabilized equivalent of 5% diphenyl-PDMS

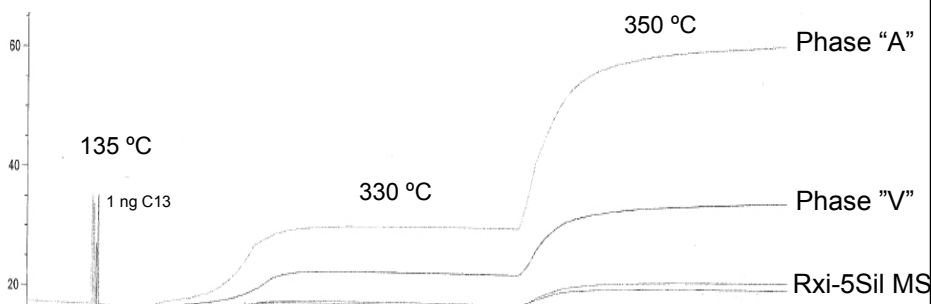
Restek	Rtx-5	Rtx-5Sil MS
Agilent	HP-5, HP-5ms, DB-5, Ultra-2	DB-5ms
Varian	CP-Sil 8 CB	VF-5ms, CP-Sil 8 CB LB/MS
Alltech	AT-5	AT-5ms
Supelco	Equity-5	
SGE	BP-5	BPX-5
Phenomenex	ZB-5	ZB-5ms
Mackery nagel	Optima-5	Optima-5ms



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Bleed behavior of arylene stabilized phases

Columns: all "fresh" 30m x 0.25mm Arylene stabilized phases;
Same conditioning treatment..

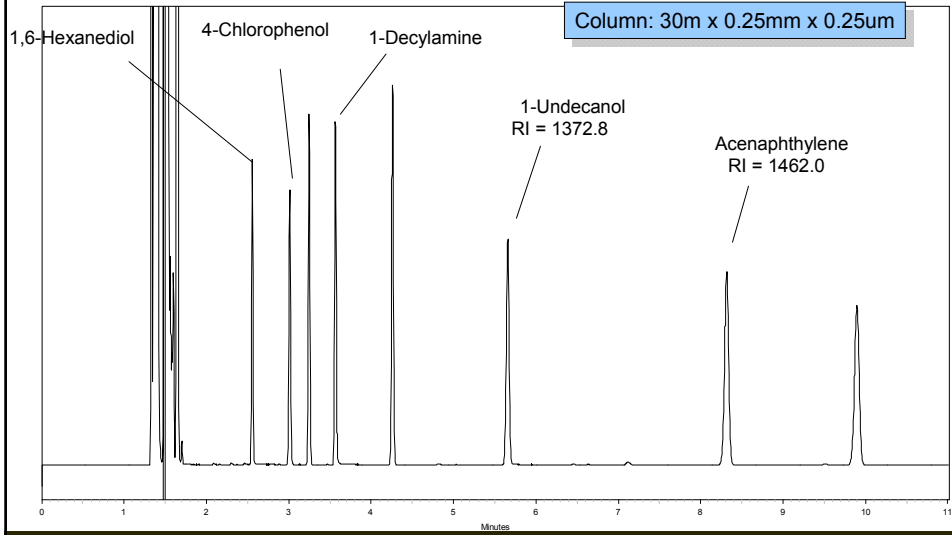


Rxi-5Sil MS shows clearly the lowest degradation

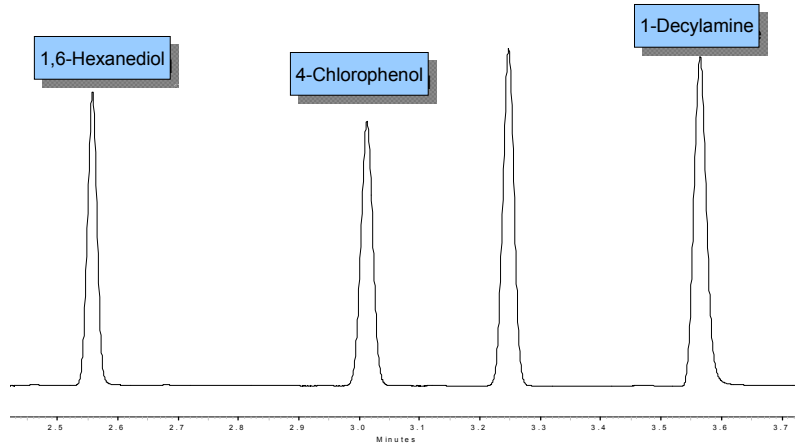


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Isothermal test with Rxi-5Sil MS



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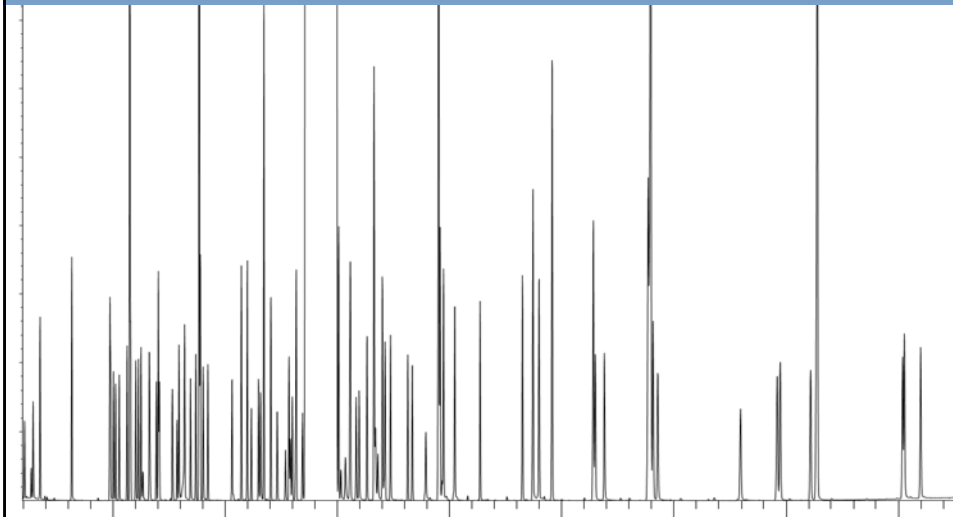


Note perfect peak shape for diols, acids and bases..



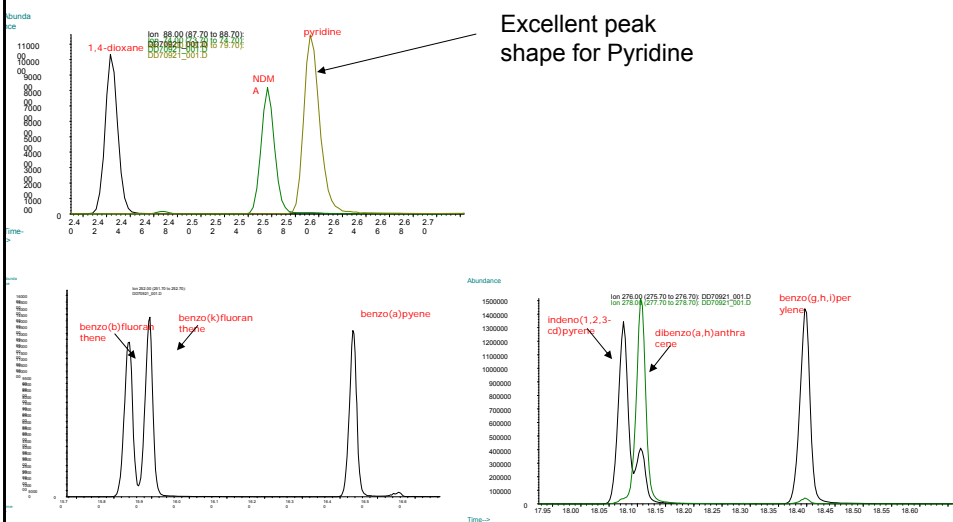
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EPA 8270 volatiles using Rx-5Sil MS



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EPA 8270 volatiles: key separations



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Rxi technology: What does it bring?

Better value

Low bleed

- Better signal to noise, quicker conditioning times
- All advantages of low background
- Longer column life time [phase doesn't bleed out]

Inertness

- Run active compounds at lower concentrations
- Better sensitivity
- Wider application [better data]

Reproducible

- Same retention times & peak elution order : No surprises!!



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