

Optimized Volatiles Analysis Ensures Fast VOC Separations

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- Optimized analysis allows for 36 runs per 12-hour shift, increasing instrument productivity.
- Rxi-624Sil MS column inertness gives sharper peaks and more accurate data.
- High temperature stability reduces bleed profile, resulting in lower detection limits.

Optimized methods for the analysis of volatile organic compounds (VOCs) can be time-consuming to develop because compound lists can be extensive and analytes vary significantly in chemical characteristics. For example, target compounds in EPA Method 8260 for solid waste matrices include volatiles that range from light gases (fluorocarbons) to larger aromatic compounds (trichlorobenzenes). These differences make column selectivity, thermal stability, and inertness critical to resolving volatiles. Often, "624" type columns are chosen for their selectivity, but thermal stability is usually poor, which can result in phase bleed that decreases detector sensitivity. New Rxi-624Sil MS columns offer reliable resolution of critical VOC pairs and also provide lower bleed and greater inertness than other columns. In order to provide optimized conditions for labs analyzing VOCs, we established parameters that ensure good resolution, while reducing downtime by syncing purge and trap cycles with instrument cycles. In addition, we present comparative data that demonstrate why Rxi-624Sil MS columns are the best choice for volatiles analysis.

Resolve Critical Pairs and Reduce Downtime

In order to achieve desired separations and minimize downtime between injections, several critical pairs were chosen for computational modeling using Pro EZGC software. The temperature program initially determined by the software was 35 °C (hold 5 min.) to 120 °C @ 11 °C/min. to 220°C @ 20 °C/min. (hold 2 min.). While this provided the best resolution of critical pairs, it also extended the analysis time to 19 min. Since the purge and trap cycle time was 16.5 min., we tested other conditions to see if adequate resolution could be maintained, while using a faster instrument cycle time that more closely matched the purge and trap cycle time, in order to maximize sample throughput. In other calculations, the software suggested changing temperature ramps at 60°C; therefore, a program of 35°C (hold 5 min.) to 60°C @ 11 °C/min. to 220°C @ 20 °C/min. (hold 2 min.) was tested. This final program reduced instrument downtime by better synchronizing injection and analysis cycles, and also provided excellent resolution of volatile compounds (Figure 1). Testing of faster conditions determined that the initial hold of 5 minutes at 35°C was critical for the best separation of early eluting compounds, such as the gases, as well as a favorable elution of methanol between gas compounds.



Figure 1: Rxi-624Sil MS columns resolve methyl ethyl ketone and ethyl acetate, a separation not obtained on other 624 columns.

Peak		DT ()	02 / 1/ 0:		12 / 06	00	-Butylbenzene		1/ 570
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16.	Dichlorodifluoromethane (CFC-12) Chloromethane Vinyl chloride Bromomethane Chloroethane Trichlorofluoromethane (CFC-11) Diethyl ether (ethyl ether) 1,1-Dichloroethene 1,1,2-Trichlorotrifluoroethane (CFC-113) Acetone Iodomethane Carbon disulfide Acetonitrile Allyl chloride Methyl acetate Methylene chloride tert-Butyl alcohol Acrylonitrile	RT (min.) 2.198 2.459 2.659 3.226 3.434 3.876 4.440 4.909 4.998 5.029 5.195 5.323 5.637 5.715 5.723 5.981 6.234 6.451	83. trans-1,4-Dic 84. Bromobenzer 85. 1,2,3-Trichlor 86. n-Propylbenz 87. 2-Chlorotolu 88. 1,3,5-Trimeth 99. 4-Chlorotolu 90. tert-Butylber 91. Pentachloroe 92. 1,2,4-Trimeth 93. sec-Butylben 94. 4-Isopropylto 95. 1,3-Dichlorob 97. 1,4-Dichlorob	ne opropane tene ene tylbenzene ene tylbenzene thane tylbenzene zene oluene (p-cymene) openzene	13.496 13.515 13.526 13.565 13.657 13.699 13.751 13.965 14.007 14.010 14.140 14.254 14.263 14.321 14.340	99. 1 100. 1 101. N 102. 1 103. H 104. N 105. 1	"2-Díchlorobenzene "2-Dibromo-3-chloro litrobenzene "2,4-Trichlorobenzer lexachloro-1,3-butao Japhthalene "2,3-Trichlorobenzen	ne diene	14.579 14.635 15.252 15.407 15.935 16.040 16.196 16.396 wet needle
19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31.	Methyl tert-butyl ether (MTBE) trans-1,2-Dichloroethene 1,1-Dichloroethane Vinyl acetate Diisopropyl ether (DIPE) Chloroprene Ethyl tert-butyl ether (ETBE) 2-Butanone (MEK) cis-1,2-Dichloroethene 2,2-Dichloropropane Ethyl acetate Propionitrile Methyl acrylate Methacrylonitrile	6.509 6.512 7.315 7.359 7.407 7.429 7.970 8.193 8.193 8.265 8.276 8.318 8.476	8.10 8.20	29 XIC — = m/z 43 — = m/z 72	23,24 20 26,27, 25	42, 40,41	43 44,45 50°,51,52 59 66 61 64	71,72 91,92 73,74 175,76 84,85 98 84,85 97 98	104
34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52.	Bromochloromethane Tetrahydrofuran Chloroform 1,1,1-Trichloroethane Dibromofluoromethane Carbon tetrachloride 1,1-Dichloropropene 1,2-Dichloroethane 1,2-Dichloroethane 1sopropyl acetate 1sobutyl alcohol tert-Amyl methyl ether (TAME) Fluorobenzene Trichloroethene 1,2-Dichloropropane Methyl methacrylate 1,4-Dioxane (ND) Dibromomethane Propyl acetate 2-Chloroethane In-Dichloropropane Methyl methacrylate 1,4-Dioxane (ND) Dibromomethane Propyl acetate 2-Chloroethanol (ND) Bromodichloromethane	8.507 8.521 8.651 8.843 8.848 9.026 9.037 9.246 9.262 9.334 9.421 9.421 9.421 9.598 9.976 10.243 10.299 10.326 10.346 10.346 10.346	j	14.15 7 9.10 8 12 13 4 6	29,30 22 31 21	36,37 36,37 38, 39, 22 35	49 60 62 49 60 62 48 56 47 54	70 90 99 69 87 87 88 88 88 88 88 88	103
	2-Nitropropane cis-1,3-Dichloropropene	10.698 10.904		3.00 4.00 5.00 6.00	7.00 8.00	9.00	10.00 11.00 12	00 13.00 14.00 15.0	0 16.00 Time (min)
57.	4-Methyl-2-pentanone (MIBK)	11.026				GC_EV	/1169		
	Toluene-D8 Toluene	11.148 11.210	Column:	Rxi-624Sil MS, 30 m, 0.25 mm II	D, 1.40 μm		Oven		
60.	trans-1,3-Dichloropropene	11.407	Sample:	(cat.# 13868) 8260A Surrogate Mix (cat.# 302	240)			35 °C (hold 5 min.) to 60 220 °C at 20 °C/min. (ho	
62.	Ethyl methacrylate 1,1,2-Trichloroethane	11.435 11.585	•	8260A Internal Standard Mix (c. 8260B MegaMix Calibration Mix	at.# 30241)	١		He, constant flow	•
	Tetrachloroethene 1,3-Dichloropropane	11.662 11.729		VOA Calibration Mix #1 (ketone	s) (cat.# 3000		Flow Rate:	1.0 mL/min.	
65.	2-Hexanone	11.749		8260B Acetate Mix (revised) (ca California Oxygenates Mix (cat.	# 30465)			MS Scan	
	Butyl acetate Dibromochloromethane	11.837 11.921	Conc.:	502.2 Calibration Mix #1 (gases) 25 ppb in RO water) (cat.# 30042	2)	Transfer Line	230 °C	
68.	1,2-Dibromoethane (EDB)	12.035	Injection	purge and trap split (split ratio 3	30:1)		Analyzer Type:	Quadrupole	
	Chlorobenzene-d5 Chlorobenzene	12.412 12.440	Inj. Temp.: Purge and Trap	225°C				230 °C 150 °C	
71.	Ethylbenzene	12.507	Instrument:	OI Analytical 4660			Electron Energy:	70 eV	
	1,1,1,2-Tetrachloroethane <i>m</i> -Xylene	12.507 12.612	Trap Type: Purge:	10 Trap 11 min. @ 20 °C			Solvent Delay Time:	1.5 min.	
74.	<i>p</i> -Xylene	12.612	Desorb Preheat Temp.:	180 °C			Tune Type:	BFB EI	
	o-Xylene Styrono	12.935	Desorb:	0.5 min. @ 190 °C			Scan Range:	36-260 amu	
	Styrene n-Amyl acetate	12.949 13.018	Bake: Interface	5 min. @ 210 °C			Instrument: Notes	Agilent 7890A GC & 59	75C MSD
78.	Bromoform	13.118	Connection:	injection port			Other Purge and Tra	ap Conditions:	
	Isopropylbenzene (cumene) cis-1,4-Dichloro-2-butene	13.226					Sample Inlet:	40°C	
	4-Bromofluorobenzene	13.268 13.385					Sample: Water	40°C	
	1,1,2,2-Tetrachloroethane	13.456						Purge 110°C, Desorb 0°	C, Bake, 240°C



Not all "624s" are Equivalent

While optimizing instrument conditions can improve sample throughput, obtaining adequate resolution depends largely on column selectivity, thermal stability, and inertness. Rxi-624Sil MS columns are optimized across these parameters, and therefore provide reliable separation of critical VOCs.

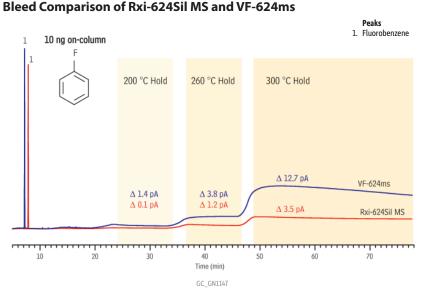
Lower Bleed Means Improved Sensitivity and Longer Column Lifetime

While 624 type columns generally provide good selectivity for most volatiles, they are limited by their low thermal stability. Poor thermal stability results in phase bleed that can reduce column lifetime, decrease detector sensitivity (especially ion trap mass spectrometers), and interfere with the quantification of later eluting compounds. Rxi-624Sil MS columns have the highest thermal stability and lowest bleed among 624 type columns due to the incorporation of phenyl rings in the polymer backbone (Table I, Figure 2). The conjugated ring system of this silarylene phase provides a more rigid structure that increases thermal stability compared to nonsilarylene phases.

Table I: The Rxi-624Sil MS column has the highest thermal stability of any 624 column.

Column	Manufacturer	Highest Temperature Limit (Isothermal)	
Rxi-624Sil MS	Restek	320 °C	
VF-624ms	Varian	300 °C	
DB-624	Agilent J&W	260 ℃	
ZB-624	Phenomenex	260 ℃	

Figure 2: The Rxi-624Sil MS column has the lowest bleed of any column in its class and provides true GC/MS capability.



Column Rxi-624Sil MS (see notes), 30 m, 0.25 mm ID, 1.4 μm (cat.# 13868)

Sample Fluorobenzene (cat.# 30030)

Diluent: methanol Conc.: 200 µg/mL Injection

Inj. Vol.: 1 µL split (split ratio 20:1)

Liner: 4mm Split Liner with Wool (cat.# 20781)

Inj. Temp.: 220 °

Oven
Oven Temp: 40 °C (hold 5 min.) to 60 °C at 20 °C/min. (hold 5 min.) to 120 °C at 20 °C/min. (hold 5 min.)

to 200°C at 20°C/min. (hold 10 min.) to 260°C at 20°C/min. (hold 10 min.) to 300°C at 20°C/min. (hold 20 min.) He. constant flow

Carrier Gas He, constant flow Linear Velocity: 40 cm/sec. Detector FID @ 250 °C Instrument Agilent/HP6890 GC

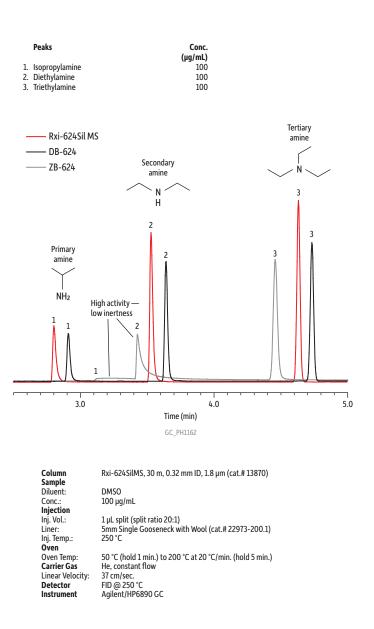
Notes Columns are of equivalent dimensions and were tested after equivalent conditioning



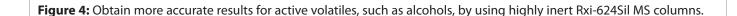
Better Peak Shape Means More Accurate Results

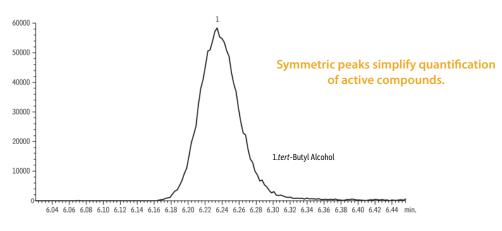
Rxi-624Sil MS columns are the most inert 624 column available. Figure 3 shows the differences between vendor columns using primary amines, which are good indicators of column activity. The unique Rxi deactivation results in symmetric peaks with minimal tailing, which improves quantitative accuracy. Minimizing tailing is especially important with concentration techniques, such as purge and trap, since the act of desorbing analytes off of the packing material results in some tailing. If a column is not inert, additional tailing due to column activity can magnify this problem. The sharp, symmetric peaks seen on Rxi-624Sil MS columns allow greater resolution, higher signal-to-noise ratios, and more accurate results for active volatiles such as alcohols (Figure 4).

Figure 3: Highly inert Rxi-624Sil MS columns provide better peak shape and more accurate results for active compounds.









GC EV1175

Column Rxi-624Sil MS, 30 m, 0.25 mm ID, 1.40 µm (cat.# 13868)

Sample Conc.: 25 ppb in RO water

Injection purge and trap split (split ratio 30:1) 225 °C

Inj. Temp.:

Purge and Trap Instrument:

OI Analytical 4660 Trap Type: 10 Trap 11 min. @ 20 °C Purge: Desorb Preheat

180°C Temp.:

0.5 min. @ 190 °C 5 min. @ 210 °C Desorb: Bake: Interface Connection: injection port

Oven Temp: 35 °C (hold 5 min.) to 60 °C at 11 °C/min. to 220 °C at 20 °C/min. (hold 2 min.) Carrier Gas

1.0 mL/min. Flow Rate: Detector MS Mode: Transfer Line Scan 230 °C Temp.: Quadrupole 230 °C Analyzer Type: Source Temp.: Quad Temp.: Electron Energy: 70 eV Solvent Delay 1.5 min.

Tune Type: Ionization Mode: Scan Range: 36-260 amu

Agilent 7890A GC & 5975C MSD Other Purge and Trap Conditions: Instrument Notes

Sample Inlet: Sample: Water 40°C

Purge 110°C, Desorb 0°C, Bake, 240°C

Conclusions

Labs interested in optimizing resolution and sample throughput can adopt the conditions established here on Rxi-624Sil MS columns to maximize productivity and assure accurate, reliable results.





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