Evaluation of Capillary Columns for the Analysis of Volatile Organic Compounds Using Computer Modeling Software.

Colton Myers, Chris English, Chris Rattray, Linx Waclaski, Jaap de Zeeuw and Kristi Sellers
Restek Corporation, 110 Benner Circle, 16823 Bellefonte, United States

Introduction

With an ever-expanding target list and many different stationary phases available choosing the correct column can be difficult. Every stationary phase has limitations, whether its temperature, stability or selectivity. With the advent of new revisions to the method target list coelutions of analytes that share common ions is almost certain to be a problem. The first columns used for analyzing volatiles were based on diphenyl/dimethyl polysiloxane stationary phases. The main advantage of these polymers are their resistance to oxidative breakdown and their low bleed, compared to cyanopropylphenyl polysiloxane (i.e. 624) phases. The disadvantage is the incomplete resolution of the early eluting compounds, poor overall selectivity of halogenated-aromatics and branched aromatics.

Modeling software allows precise evaluations of selectivity specific to the user's compound list and chosen stationary phase. It is possible to predict retention times and optimized chromatographic methods without the need to analyze compound sets under many different empirical conditions. The program allows users to adjust: stationary phase type, film thickness, temperature, column length, column internal diameter and flow.

This program will be used to examine the most commonly used stationary phases for the analysis of volatiles and demonstrate advantages of each phase under a given set of conditions.

How Accurate is Pro EZGC?

Peaks	RT (min)	Res.	Peak Width	Peaks	RT (min)	Res.	Peak Width
1. Ethanol	3.20	12.70	0.05	13. Methyl methacrylate	9.07	2.64	0.05
2. Allyl chloride	3.87	8.11	0.06	14. n-Propyl acetate	9.21	2.64	0.05
3. Acetone	4.36	8.11	0.06	15. 2-Chloroethanol	9.37	3.02	0.05
4. Acrylonitrile	5.38	3.30	0.07	16. 4-Methyl-2-pentanone	10.11	3.97	0.05
5. Vinyl acetate	5.61	3.30	0.07	17. Ethyl methacrylate	10.30	3.97	0.05
6. Allyl alcohol	5.92	4.39	0.07	18. n-Butyl acetate	10.77	0.88	0.04
7. Ethyl Acetate	6.66	0.52	0.08	19. 2-Hexanone	10.81	0.88	0.05
8. Methyl acrylate	6.70	0.52	0.07	20. 1-Bromo-4-fluorobenzene	12.06	12.30	0.04
9. 2-Butanone	6.99	2.91	0.08	21. Pentachloroethane	12.60	12.30	0.04
10. Propargyl alcohol	7.21	2.91	0.07	22. Nitrobenzene	14.38	40.30	0.05
11. Isobutyl alcohol	7.94	1.54	0.07				
12. Isopropyl acetate	8.04	1.54	0.06				

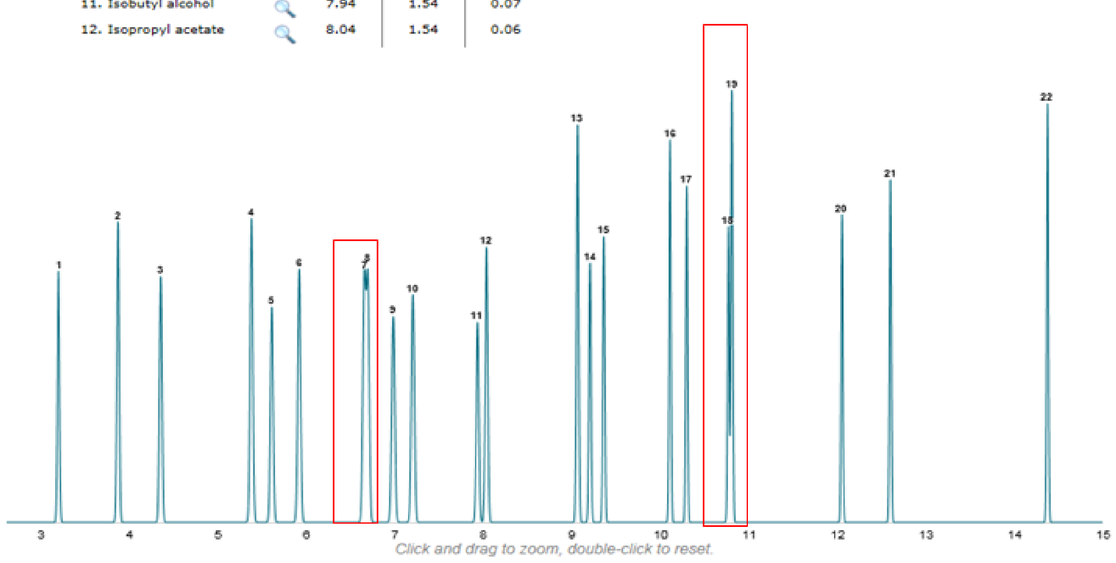


Figure 1: Pro EZGC model of volatiles ranging in polarity from alcohols to aromatics. After entering the compounds the program recommends a column and conditions. In this case the Rtx-VMS column was the first choice although at least 22 of these compounds can be found on four other columns in the database.

Figure 2: Chromatogram acquired using GC-MS following the conditions recommended by Pro-EZGC. Compounds not fully resolved may show differences compared to the model.

Peak #	Compound	T_R Experiment (min)	T_R Model (min)	Aboslute Error
1	Ethanol	3.30	3.20	0.10
2	Allyl chloride	3.88	3.87	0.01
3	Acetone	4.13	4.36	0.23
4	Acrylonitrile	5.20	5.38	0.18
5	Vinyl acetate	5.54	5.61	0.07
6	Allyl alcohol	5.61	5.92	0.31
7	Ethyl acetate + Methyl acrylate	6.57	6.70	0.13
8	2-Butanone	6.81	6.99	0.18
9	Propargyl alcohol	6.93	7.21	0.28
10	Isobutyl alcohol	7.63	7.94	0.31
11	Isopropyl acetate	7.91	8.04	0.13
12	Methyl methacrylate	8.89	9.07	0.18
13	n-Propyl acetate	9.05	9.21	0.16
14	2-Chloroethanol	9.19	9.37	0.18
15	4-Methyl-2-pentanone	9.93	10.11	0.18
16	Ethyl methacrylate	10.12	10.30	0.18
17	n-Butyl acetate	10.59	10.77	0.18
18	2-Hexanone	10.66	10.81	0.15
19	1-Bromo-4-fluorobenzene	11.87	12.06	0.19
20	Pentachloroethane	12.41	12.60	0.19
21	Nitrobenzene	14.17	14.38	0.21
			Average Error	0.18
			RMSE	0.07

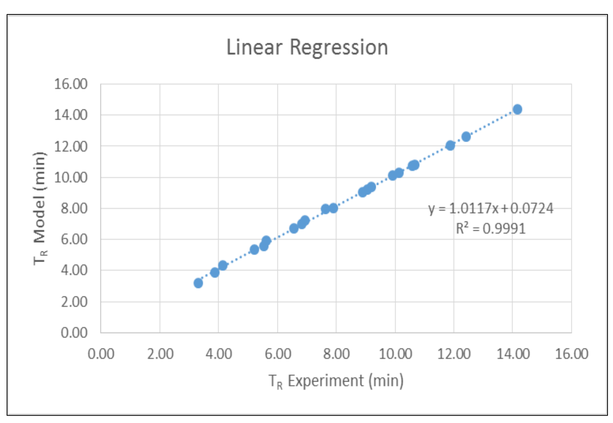
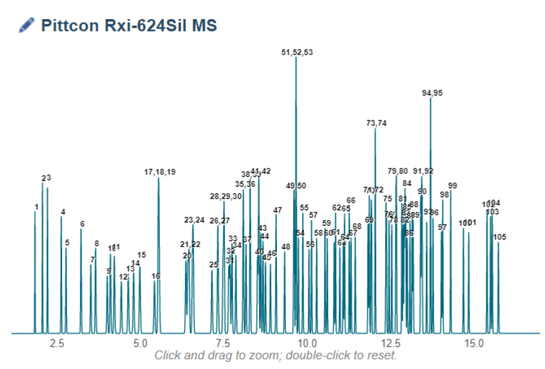
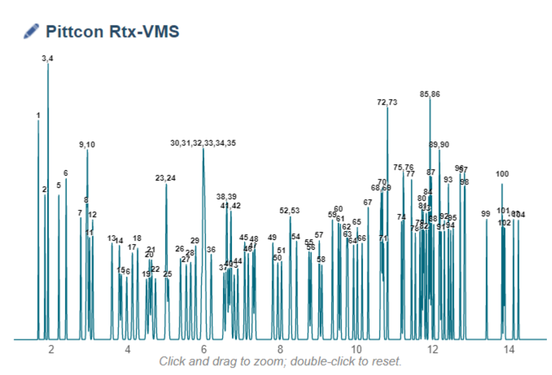


Figure 3: Pro EZGC comparison between experimental and predicted retention times with a correlation coefficient fit of 0.9991.

Using Pro-EZGC to Evaluate Phase Coelutions

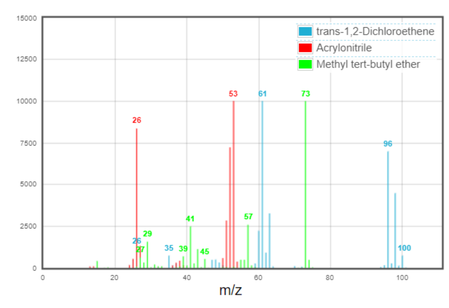
For this demonstration we can compare different stationary phases using the overlay spectra feature of the program to determine if compound coelutions can be resolved by quantification ions in the mass spectra. Optimized conditions specific to each phase will be used for the Rtx-VMS (chromatogram # GC_EV1352) and Rxi-624Sil MS (chromatogram # GC_EV1169) with a focus on US EPA 8260 and commonly added compounds.



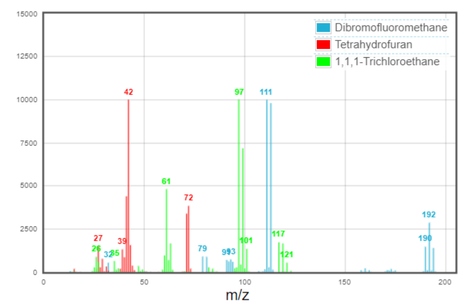


Figures 4 & 5: Compounds presented will also display mass spectra and coelutions can be displayed as an overlay, which helps the analyst determine if the compounds can be resolved by MS.

Rxi-624Sil MS Resolved

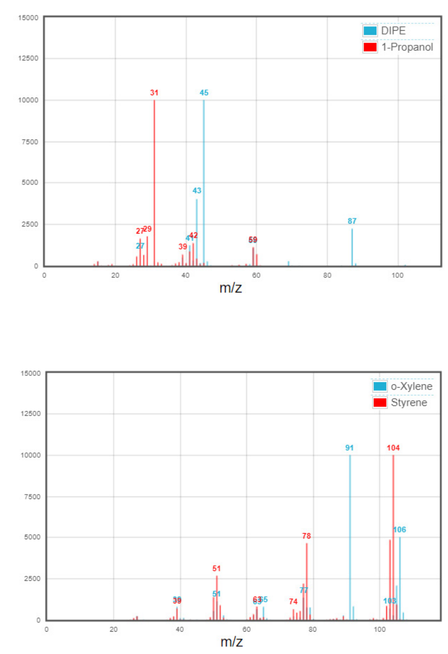


Rtx-VMS Resolved

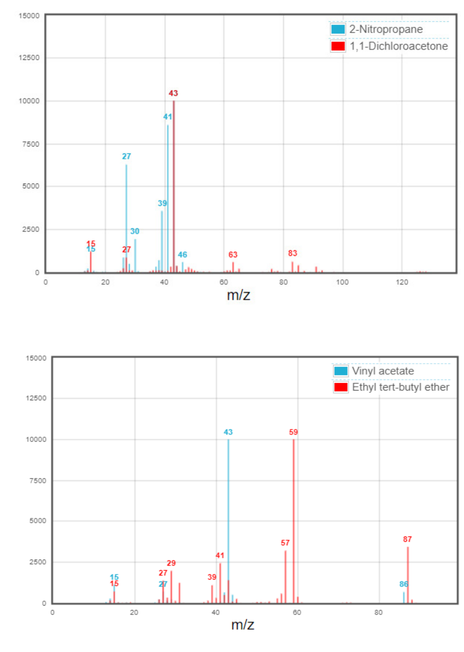


Figures 6 & 7: Examples where both columns successfully resolve multiple coelutions. For example using the Rxi-624Sil MS trans-1,2-Dichloroethene, Acrylonitrile and Methyl-tert-butyl ether (peak #s 17, 18, 19) are resolved by fragmentation ion. For the Rtx-VMS Dibromofluoromethane, Tetrahydrofuran and 1,1,1-Trichloroethane (peak #s 33,34,35) do not have any interfering ions.

Rxi-624Sil MS Coelutions



Rtx-VMS Coelutions



Figures 8-11: Examples of coelutions where there is overlapping ions for either identification or quantification.

Many capillary columns have been designed for the analysis of volatiles. Column selection is normally based on the analytical method, compound list, and detection system used. Pro-EZGC is an excellent tool in determining the best volatile column and conditions for your specific compound list. There is a comprehensive library of volatiles on a variety of stationary phases to include the following: Rtx-VMS, Rtx-624Sil MS, Rtx-502, Rtx-624, and Rtx-1. For instance the Rtx-VMS column library contains 471 compounds and the Rxi-624Sil MS contains 591. This allows the analyst to choose the best column and target specific separations using Pro-EZGC.