



Application of Pearson Correlation Coefficient to Two-Dimensional Gas Chromatography High-Resolution Time-of-Flight Mass Spectrometry as a Comparison and Discovery-Based Technique

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High Explosives and Plasticizers

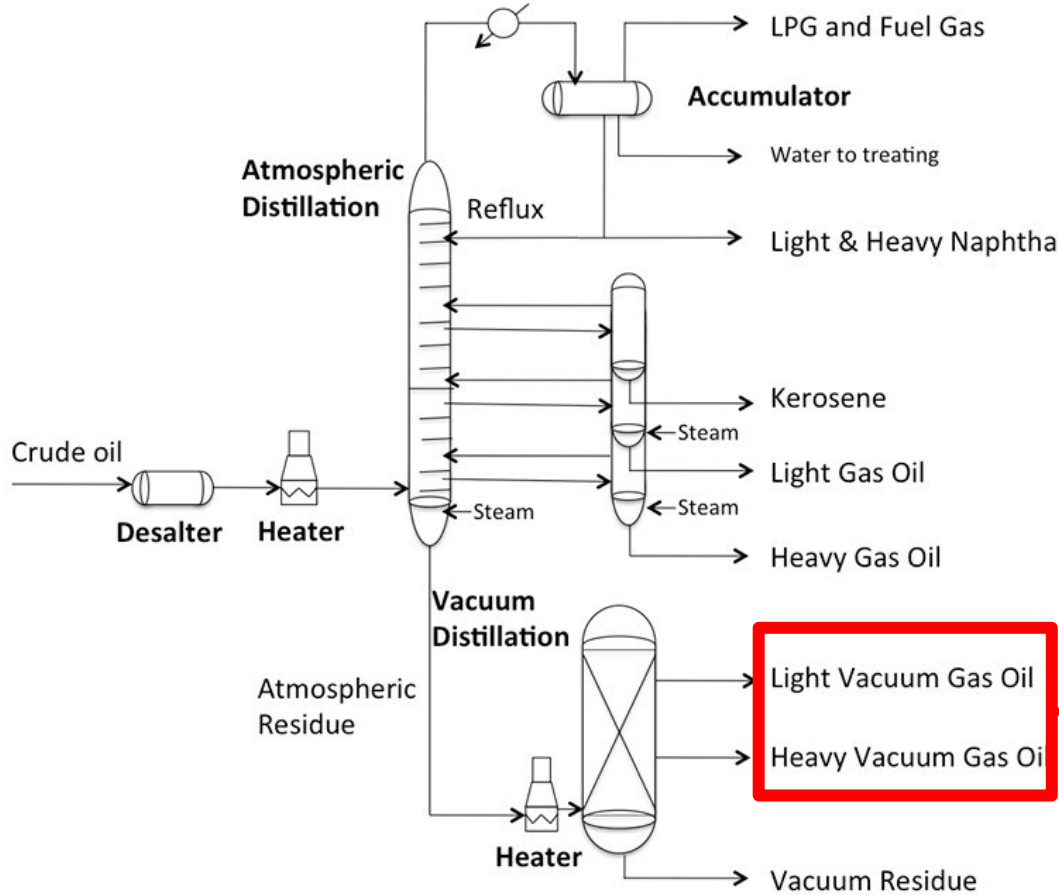
- Plastic-bonded explosives (PBXs): powdered explosives coated in polymeric binders
 - Increases safety of explosives
 - May also contain plasticizer
- Plasticizer effects on PBXs
 - Increases elasticity (plastic deformation)
 - Decreases viscosity
 - Reduces friction during handling increasing safety
- In April 2022, HyVac Products, Inc. (oil manufacturer) went out of business



HyVac® Oils

Our goal: find a suitable replacement for HyVac oil while analyzing physical and chemical characteristics needed for future plasticizer selection

What is Vacuum Pump Oil?



Hydrocracking

Hydrowaxing

Hydrotreating



Important Characteristics

Vapor Pressure

Viscosity

Distillation process

Additives

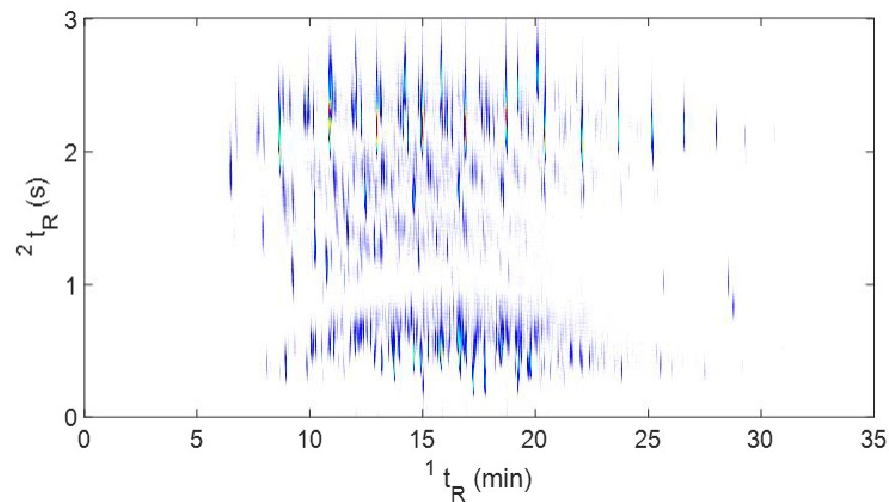
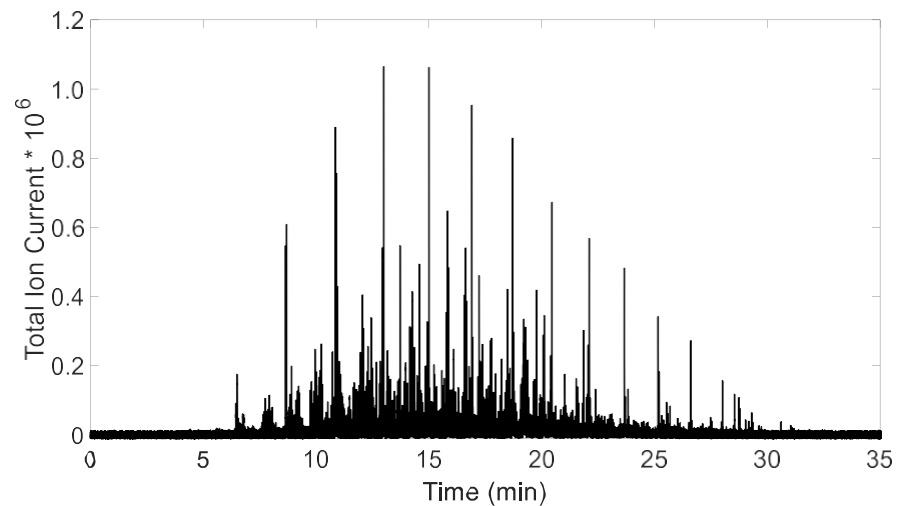
Physical Characteristics

Top Ten Oil Replacement Candidates

- Measured density and viscosity of 20 oils
- Density within range of 0.86-0.88g/cm³ at 20°C
- Dynamic viscosity of 128-297mPa-s at 20°C
 - Highly variable

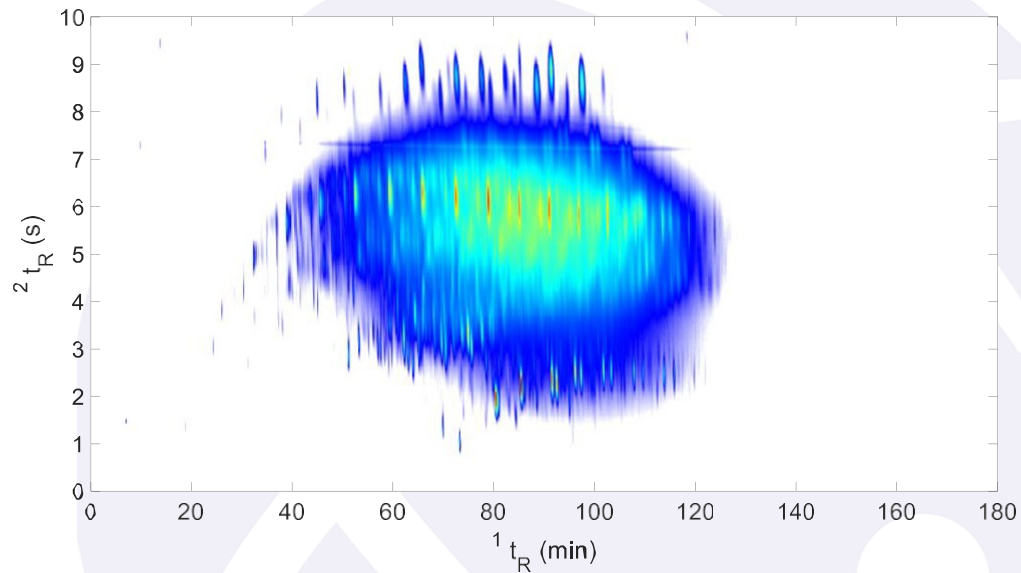
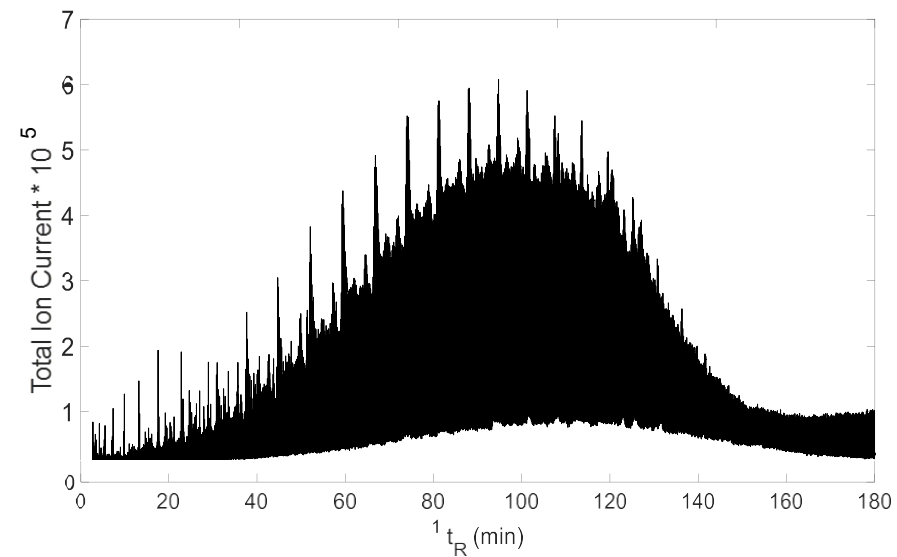
Oil Name	Density (g/cm ³) @20°C	Dynamic Viscosity (mPa-s) @20°C
HyVac Oil	0.87822	218.33
Edwards Ultragrade 70	0.86671	179.77
KJLSS70	0.86252	180.17
Leybonol LVO 710	0.88925	264.20
Leybonol LVO 100	0.87624	283.15
Leybonol LVO 130	0.86311	172.17
Duratex 68	0.86308	179.45
Edwards Ultragrade 19	0.86024	138.32
KJLSS19	0.86094	143.20
VWR 19	0.86445	147.38
Edwards Ultragrade 20	0.86559	290.71

Chemical Characterization of Diesel Fuel



Analysis of diesel fuel via GCxGC is relatively straightforward

Chemical Characterization of HyVac Oil

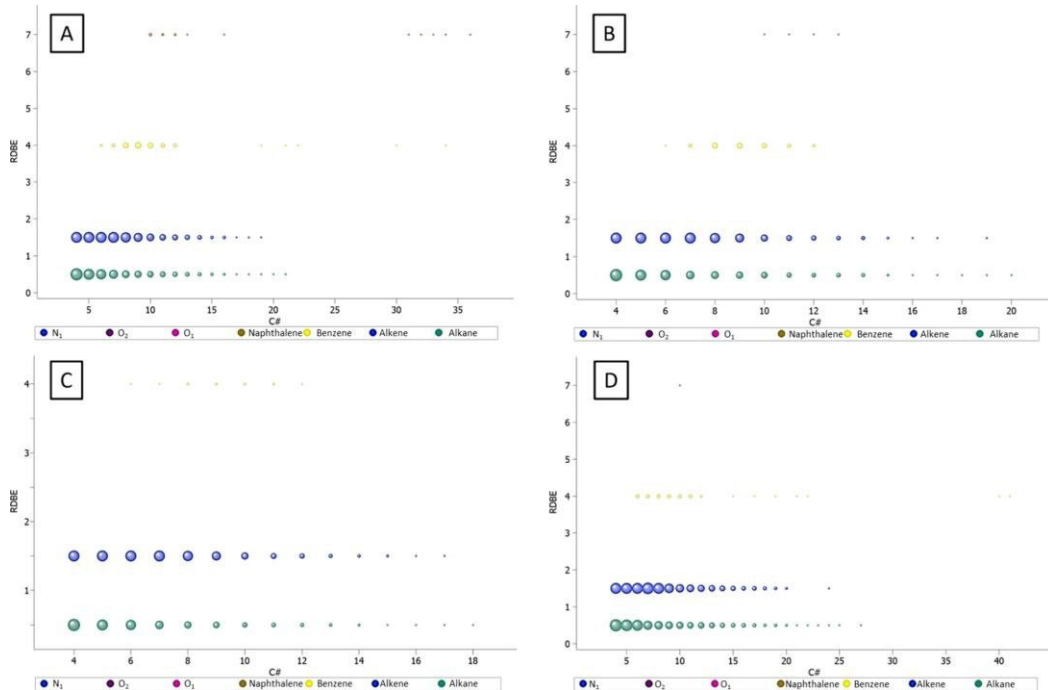


HyVac oil is chemically more complicated than diesel fuel!

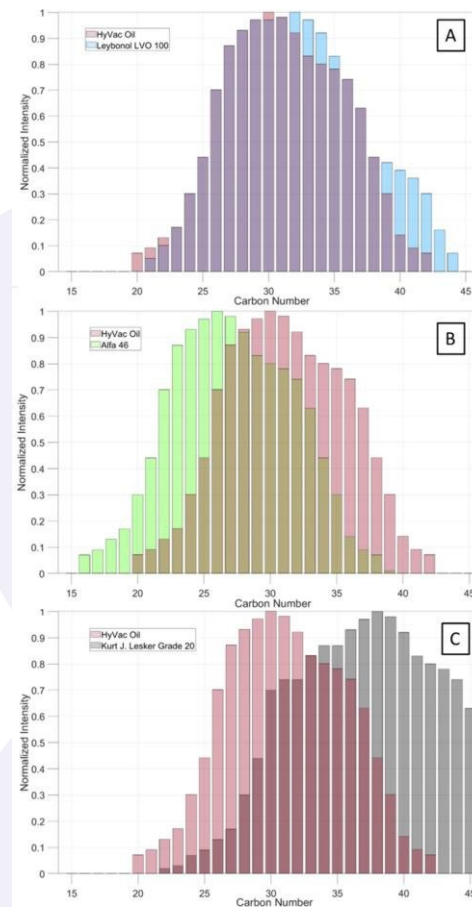
Methodology

- Samples diluted in hexane and injected onto a PTV that ramped from 40°C to 400°C at a rate of 360°C/min
- Special high-temperature columns (Zebron ZB-1HT connected to a Zebron ZB-35HT) were used to prevent column bleed above 320°C
- Mass spectrally analyzed using electron impact ionization (EI), positive chemical ionization (PCI), and negative chemical ionization (NCI) between m/z 50 and m/z 600
 - Downloaded data too large for chemometric analysis, so HRMS data binned to unit resolution

Statistical Methods



RDBE compared vs carbon number



Carbon range distribution

Pearson's correlation coefficient

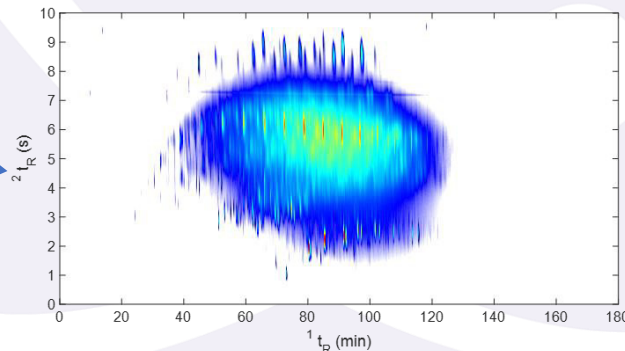
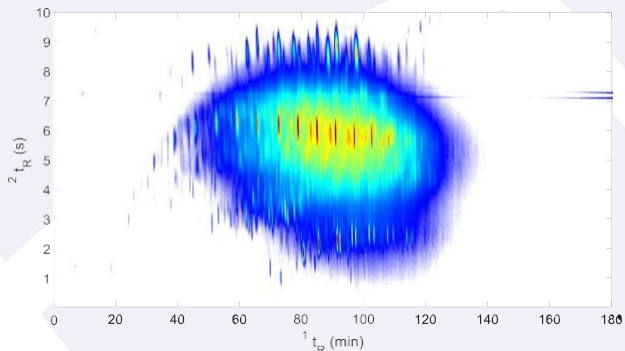
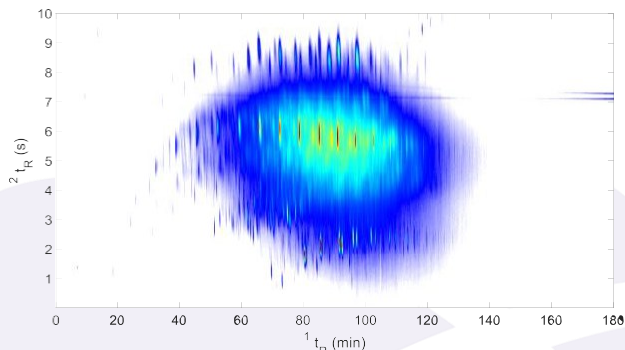
- A measure of linear correlation between two sets of data
 - A normalized measure of covariance

$$\rho_{X,Y} = \frac{\text{cov}(X, Y)}{\sigma_X \sigma_Y} \quad \rho=0.99$$

- Pearson's correlation coefficient values between all 3 lots of HyVac oil were between 0.93 and 0.99

$\rho=0.95$

$\rho=0.93$



Pearson Correlation Coefficients

Electron Ionization

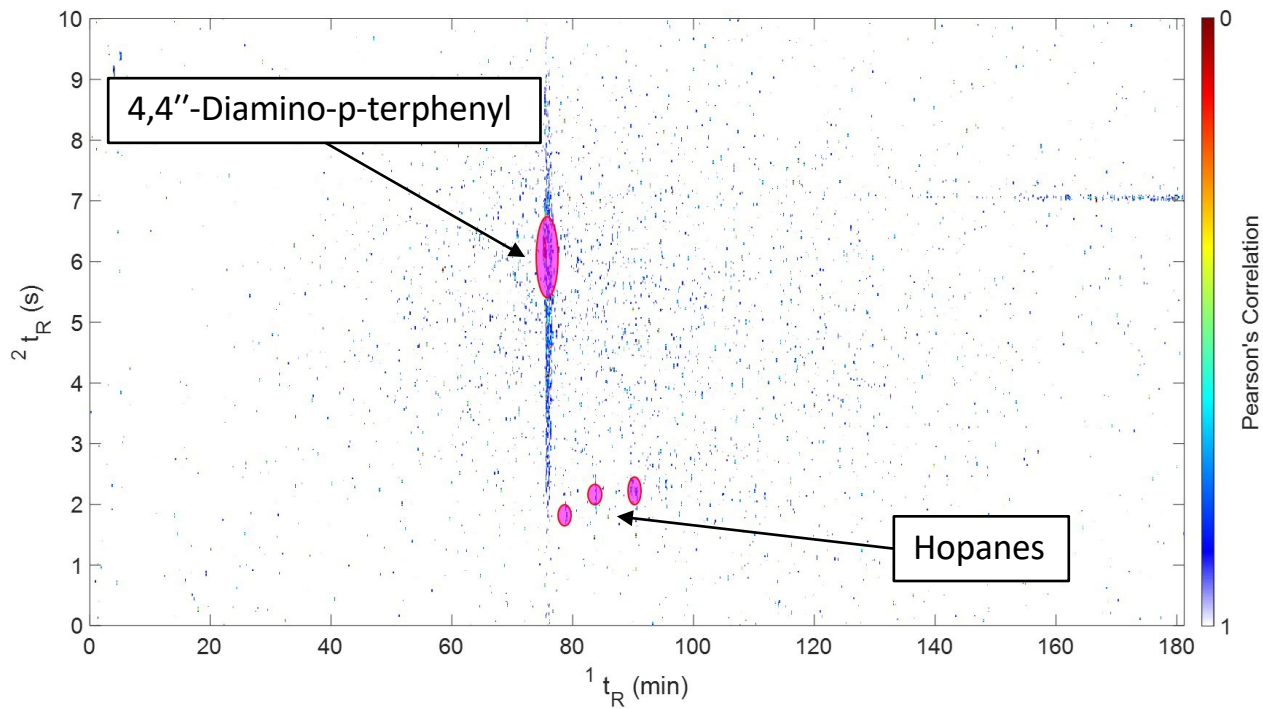
	1	2	3	4	5	6	7	8	9	10	11
1	1.00							1. HyVac® Oil 2. Edwards 70 3. Kurt J. Lesker 70 4. Leybonol LVO 710 5. Leybonol LVO 100 6. Leybonol LVO 130 7. Duratex 68 8. Edwards 19 9. Kurt J. Lesker 19 10. VWR 19 11. Edwards 20			
2	0.91	1.00									
3	0.86	0.92	1.00								
4	0.14	0.13	0.14	1.00							
5	0.94	0.92	0.88	0.14	1.00						
6	0.91	0.99	0.92	0.14	0.91	1.00					
7	0.93	0.90	0.85	0.11	0.91	0.90	1.00				
8	0.88	0.90	0.96	0.13	0.83	0.92	0.85	1.00			
9	0.87	0.90	0.96	0.13	0.83	0.91	0.85	0.99	1.00		
10	0.93	0.98	0.91	0.13	0.90	0.98	0.91	0.93	0.93	1.00	
11	0.70	0.84	0.87	0.13	0.83	0.82	0.71	0.74	0.74	0.75	1.00

Chemical Ionization

<u>PCI</u>	1	2	3	4	
1	1.00		1. HyVac® Oil 2. Leybonol LVO 100 3. Duratex 68 4. VWR 19		
2	0.98	1.00			
3	0.97	0.95			1.00
4	0.95	0.93			0.90

<u>NCI</u>	1	2	3	4	
1	1.00		1. HyVac® Oil 2. Leybonol LVO 100 3. Duratex 68 4. VWR 19		
2	0.96	1.00			
3	0.92	0.89			1.00
4	0.95	0.92			0.88

Discovery-based Pearson Correlation Coefficient



Conclusions

- High vacuum pump oils are highly variable in their composition
 - Requires the use of a two-dimensional separations for complete chemical understanding
- The most similar sample to HyVac oil found using all three ionization techniques were Leybonol LVO 100
- Duratex 68 was statistically similar to HyVac oil using electron ionization, but was found to be chemically different using chemical ionization
- Pearson correlation can be transformed to be used as a discovery-based technique

Acknowledgements

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