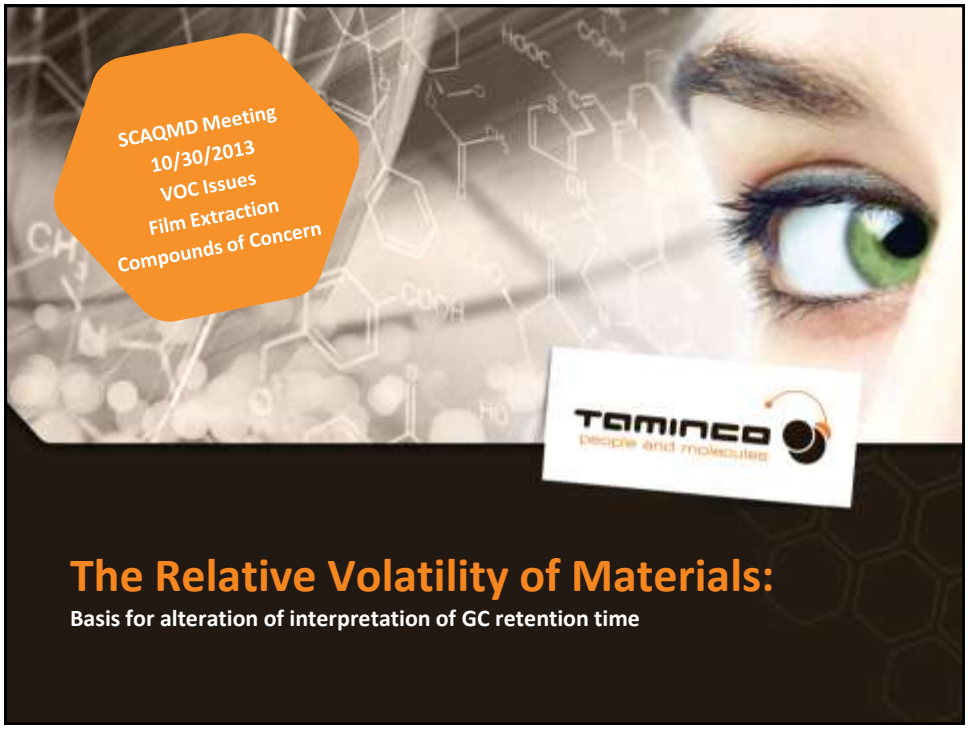


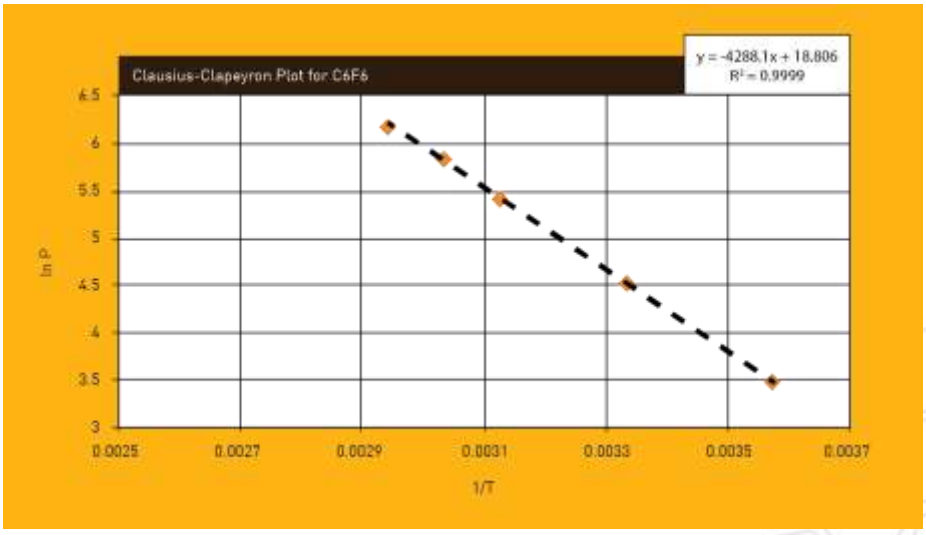
The Relative Volatility of Materials:

Basis for alteration of interpretation of GC retention time

Presentation Outline

- **Relative Volatility as a function of Temperature**
- **Thermal Results clearly show relative volatility changes**
- **GC Rt exhibits all the discrepancies of high T methods + more**

University of Maine



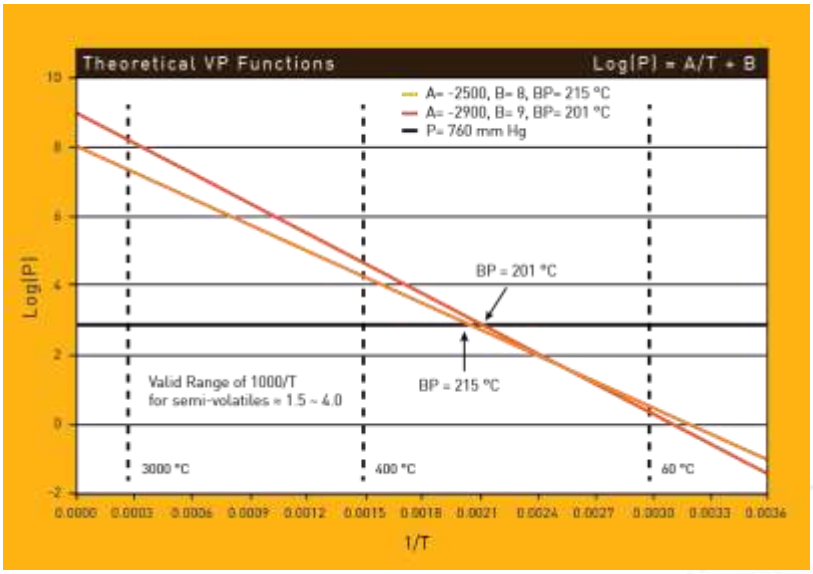
Hexafluorobenzene: Normal BP = 82 °C

http://chemistry.umeche.maine.edu/~amar/spring2010/clausiusclapeyron.html

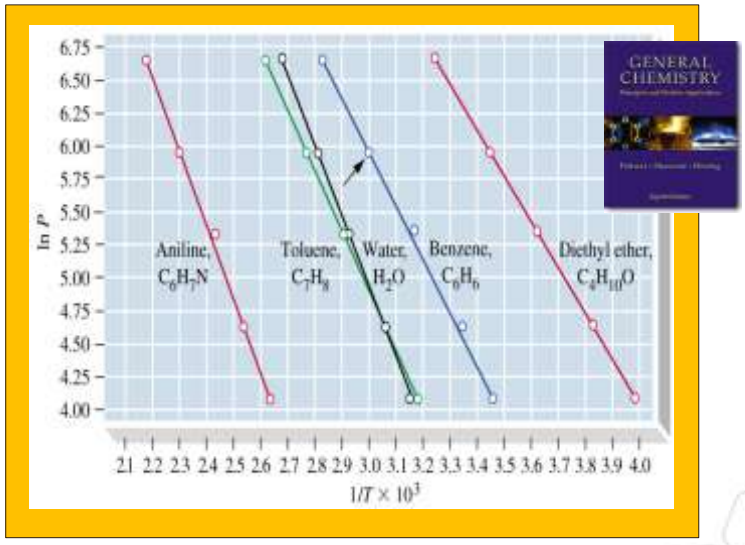
Relative Volatility

“Relative Volatility” Changes with Temperature

Theoretical VP Functions



VP Functions



VOC-or Not?

Surface Coatings International 1997 (10)

VOC – or Not?
Determination of an Important Environmental Parameter
C Nielsen, B Hogh and E Walistrom

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VOC or not: boiling point limits

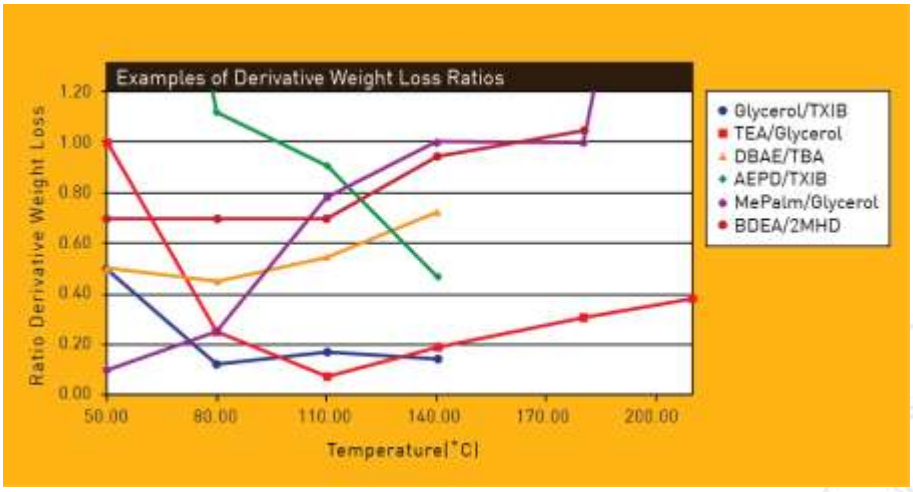
A screening of the literature for experimental values of the boiling point temperatures and vapor pressures at 23°C gave the following:

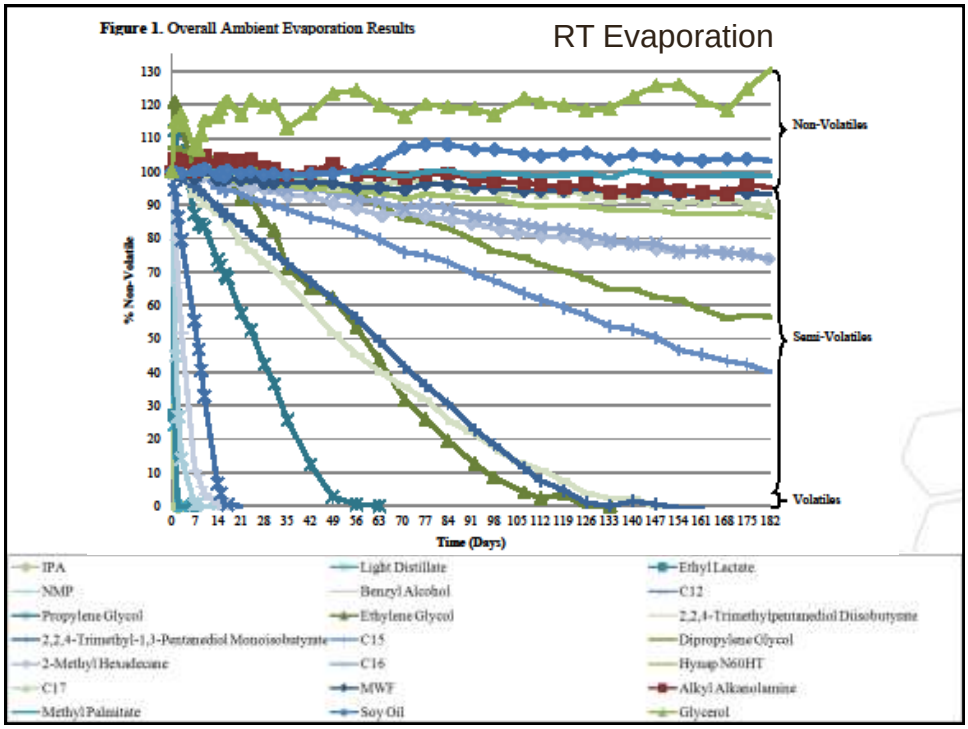
- no organic solvents boiling below 170°C have a vapor pressure below 10 Pa at 23°C
- all solvents boiling above 260°C have a vapor pressure which is below 10 Pa at 23°C
- only three solvents, two ethers and a chlorinated compound, were found to have a vapor pressure above 10 Pa in the boiling point range 235-260°C
- for common organic solvents such as linear hydrocarbons, alcohols and polyols the boiling point is below 220°C before the solvents become a VOC according to their vapor pressure at room temperature.

$$T = \frac{\Delta\Delta H}{R\ln\left(\frac{P_2}{P_1}\right) + \Delta\Delta S} = \frac{\Delta A}{\ln\left(\frac{P_2}{P_1}\right) + \Delta B}$$

ΔΔH (J/mol)	ΔΔS (J/mol-K)	VP Ratio (P_2/P_1)	T(°C)
1000	3	1.1	180
1000	3	1.0	60
1000	3	$(1.1)^{-1}$	-116
4000	10	1.3	238
4000	10	1.0	127
4000	10	$(1.3)^{-1}$	55

Examples of Derivative Weight Loss Ratios





ASTM E1868-10

(81°C, 110 minutes)

AAA	VOC (g/l)	% Evaporated	Normal BP (C)
DCHA	911 g/l	99.7%	256
BAE	883 g/l	98.9%	199
DBAE	860 g/l	99.8%	230
3-amino-4-octanol	620 g/l	78.2%	218
≈50% MDEA (aq)	197 g/l	68.3%	-
MDEA	**171 g/l**	**16.5%**	**247**
HBHEBA	151 g/l	18.1%	≈295
≈50% BDEA (aq)	**87 g/l**	**58.4%**	**-**
BDEA	69 g/l	7.5%	285
ODEA	<10 g/l (considered zero VOC)	0%	≈350

Loss-On-Drying by Thermogravimetry ASTME1868-10

LOD, Loss-On-Drying 110 min @ 81° CASTME1868-10	58.4%
Volatile Material Content ASTME1868-10	588.6g/L
VOC, Volatile Organic Compounds Content ASTME 1868-10	16.5%
Density @ 15C ASTM(D4052)	1.0075 g/ml
Water by Karl Fischer (ASTME D6304)	49.780 wt%

LOC, Loss-On-Drying 110 min @81° CASTME1868-10	16.5%
Volatile Material Content ASTME1868-10	171.8g/L
VOC, Volatile Organic Compounds Content ASTME1868-10	171.4g/L
Density @ 15oC (ASTM D4052)	1.0428 g/ml
Water by Karl Fischer (ASTM D6304)	0.040wt%

Assessment of Volatility

GC Rt as an assessment of volatility?

- **High T Volatility Assessment + ….**
- **Stationary Phase Polarity Issues**
- **Relative volatility and the T ramp Program**
- **Entropy of Vaporization has an influence**

GC1/Rt and Volatility

GC 1/Rt does not strongly correlate to volatility

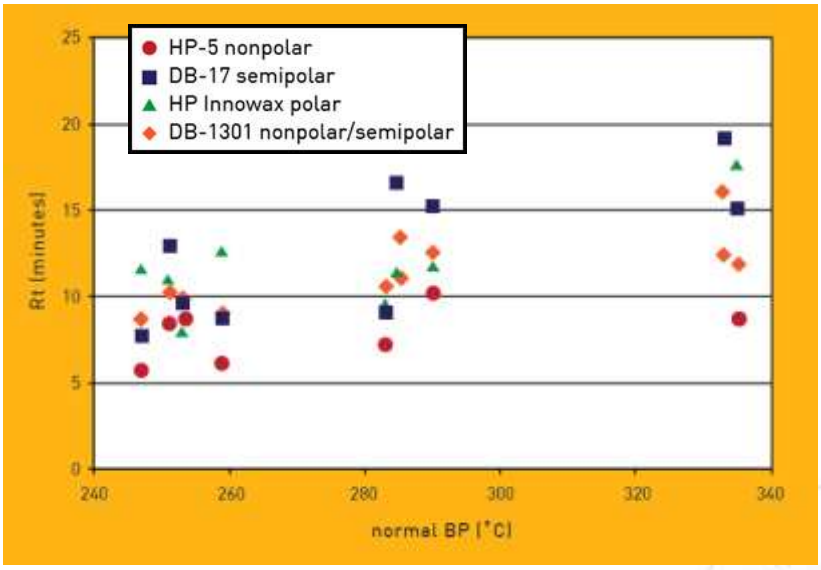
HP-5 (apolar)		
Compound	**Boiling point °C**	**RT min**
Methyldiethanolarnine	247	5.70
2-amino 2-ethyl 1, 3 propaandiol	259	6.20
Butyldiethanolarnine	283	7.30
Diethyladipate	**251**	**8.50**
Tetradecane	**253**	**8.53**
Triethanolarnine	335	8.60
BisDMAPA-PO	290	10.30
Tris-DMAPA	285	11.10

DB-1301 (apolar)		
Compound	**Boiling point °C**	**RT min**
Methyldiethanolarnine	247	8.58
2-amino 2-ethyl 1, 3 propaandiol	259	9.04
Tetradecane	**253**	**10.00**
Diethyladipate	**251**	**10.40**
Butyldiethanolarnine	**283**	**10.52**
Triethanolarnine	335	11.91
BisDMAPA-PO	290	12.55
Tris-DMAPA	285	13.42
Methylpalmitate	333	16.10

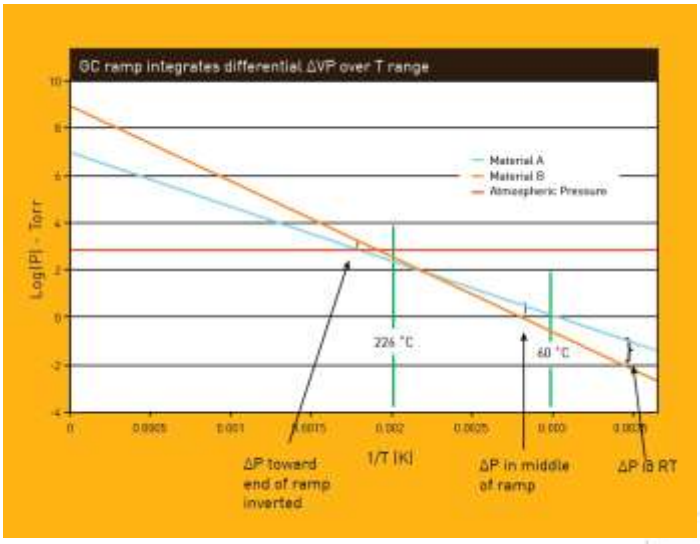
HP-Innowax (polar)		
Compound	**Boiling point °C**	**RT min**
Tretradecane	**253**	**7.94**
Butyldiethanolarnine	283	9.45
Diethyladipate	**251**	**11.05**
Tris-DMAPA	285	11.35
Methyldiethanolarnine	247	11.50
BisDMAPA-PO	290	11.70
2-amino 2-ethyl 1, 3 propaandiol	259	12.5
Triethanolarnine	335	17.70

DB-17 (semi-polar)		
Compound	**Boiling point °C**	**RT min**
Methyldiethanolarnine	247	**7.80**
2-amino 2-ethyl 1, 3 propaandiol	259	8.65
Butyldiethanolarnine	**283**	**9.05**
Tetradecane	**253**	**9.55**
Diethyladipate	**251**	**12.95**
Triethanolarnine	335	15.15
BisDMAPA-PO	290	15.25
Tris-DMAPA	285	15.50

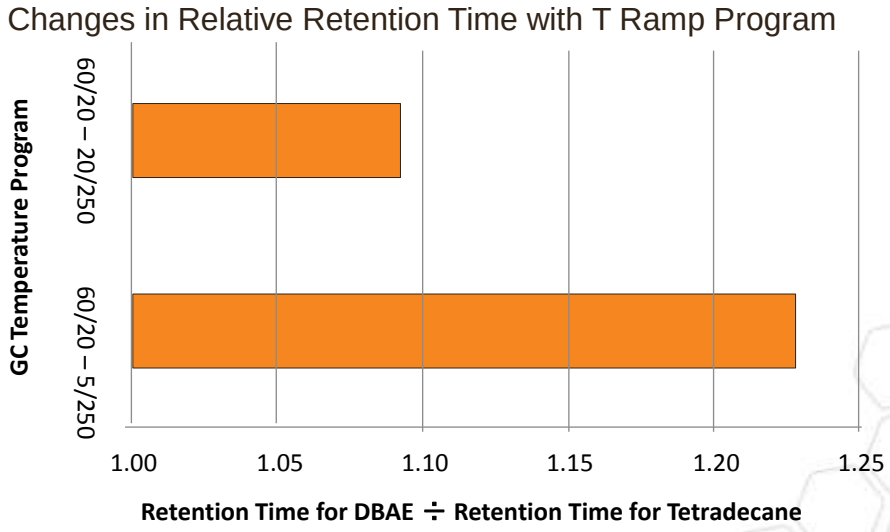
Comparisons



GC ramp - ΔVP over T range



Relative Retention Time



Film Extraction Techniques

1) Theoretically Good Idea
2) Technical Difficulties Exist
3) Need to account for reactivity

e.g., formation of esters during film drying process

Compound Breakdown on/in Injector/Detector

1) Mechanisms too numerous to comprehensively list
2) For Example; Alkylhydroxylamines need $T_{inj} < 125\ ^oC$
3) Ester pyrolysis type reactions start to occur at $\approx 225\ ^oC$
4) Cyclic etherification of diols
5) These “degradations” are usually compensated for by detector sensitivity calibrations; requires authentic sample of known purity

Does the threshold need to be adjusted empirically?

Both the VOC limit and definition could be continuously improved as a means of giving industry time to adjust.

Have VOC threshold issues been ignored while focus was on precision and methodology?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