

VOLATILE ORGANIC COMPOUND (VOC) CONTENT TEST METHODOLOGY: PAST, PRESENT AND FUTURE

March 8, 2012

Uyên-Uyên T. Võ

Rule 1144: Metalworking Fluids and Direct-Contact Lubricants

Determination of VOC Content
by ASTM E 1868 - 10

ASTM E 1868-10

Loss-On-Drying by Thermogravimetry (TGA)



Parameter		Method A
Specimen Size		10 ± 1 µL
Specimen Holder	<i>Dimensions</i>	Shallow
	<i>Composition</i>	Platinum
Temperature Sensor Location (Sample vs. Furnace)		Sample
Atmosphere Control System	<i>Gas Type</i>	Nitrogen
	<i>Sample Purge Flow</i>	30 or 40 mL/min
	<i>Balance Protection Flow</i>	20 or 10 mL/min
	<i>Total Flow</i>	50 mL/min
Temperature Program		25 ± 2°C to 81°C @ 25°C/min Isothermal @ 81°C for 110 min
Experiment Termination		110 minutes from t ₀
Baseline Correction		Yes
Auto-sampler Use		No

Additional Requirements to ASTM E 1868 – 10

- Equipment
- Standards and Reagents
- Sampling, Sample Handling and Storage
- Calibration
- Sample Holder Preparation
- Additional Analyses
- Procedure
- Calculations
- Quality Control

Test Method Development

Test Method Development

U.S. EPA Method 24

- Gravimetric analysis of VOCs in coatings and inks
- Imprecise for lubricants and metalworking fluids, especially those containing semi-volatile compounds

Sample	VOC (g/L) by M24	Number of Runs
40 SUS Naphthenic Oil	815 - 854	5
60 SUS Naphthenic Oil	374 - 465	5
100 SUS Naphthenic Oil	207 - 266	2
200 SUS Naphthenic Oil	119 - 119	2
Vegetable Based MWF	100 - 121	2
Vegetable Based MWF	104 - 171	3

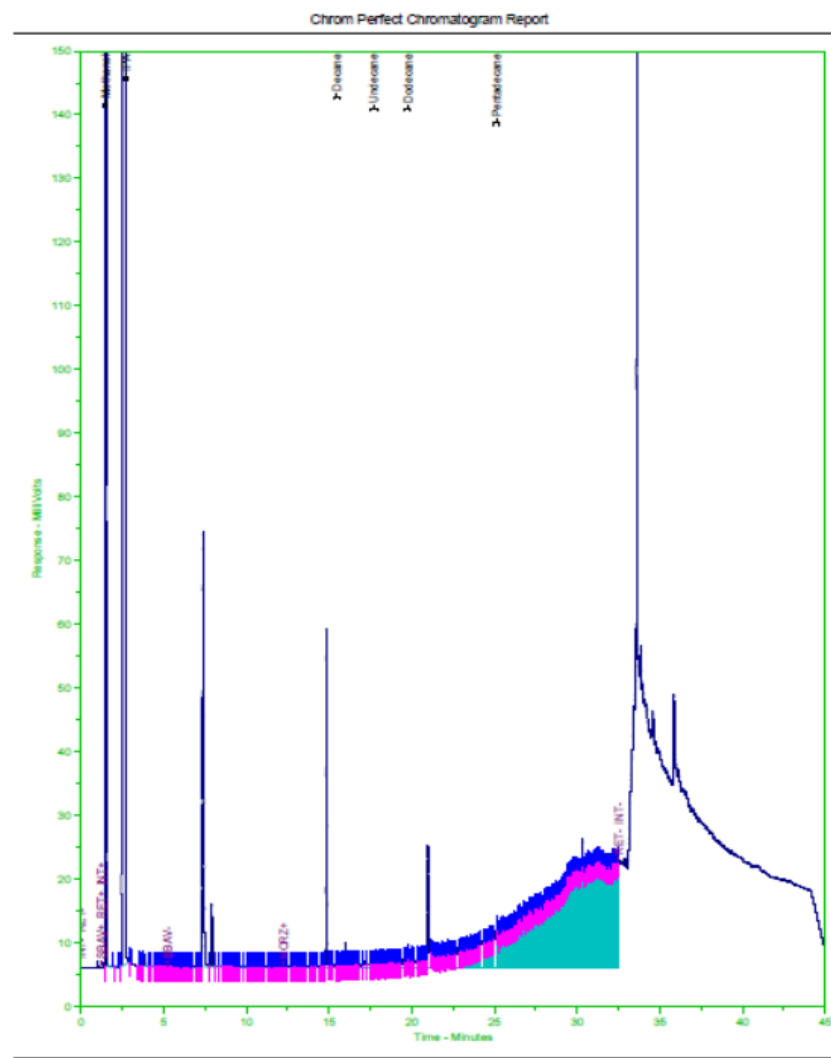
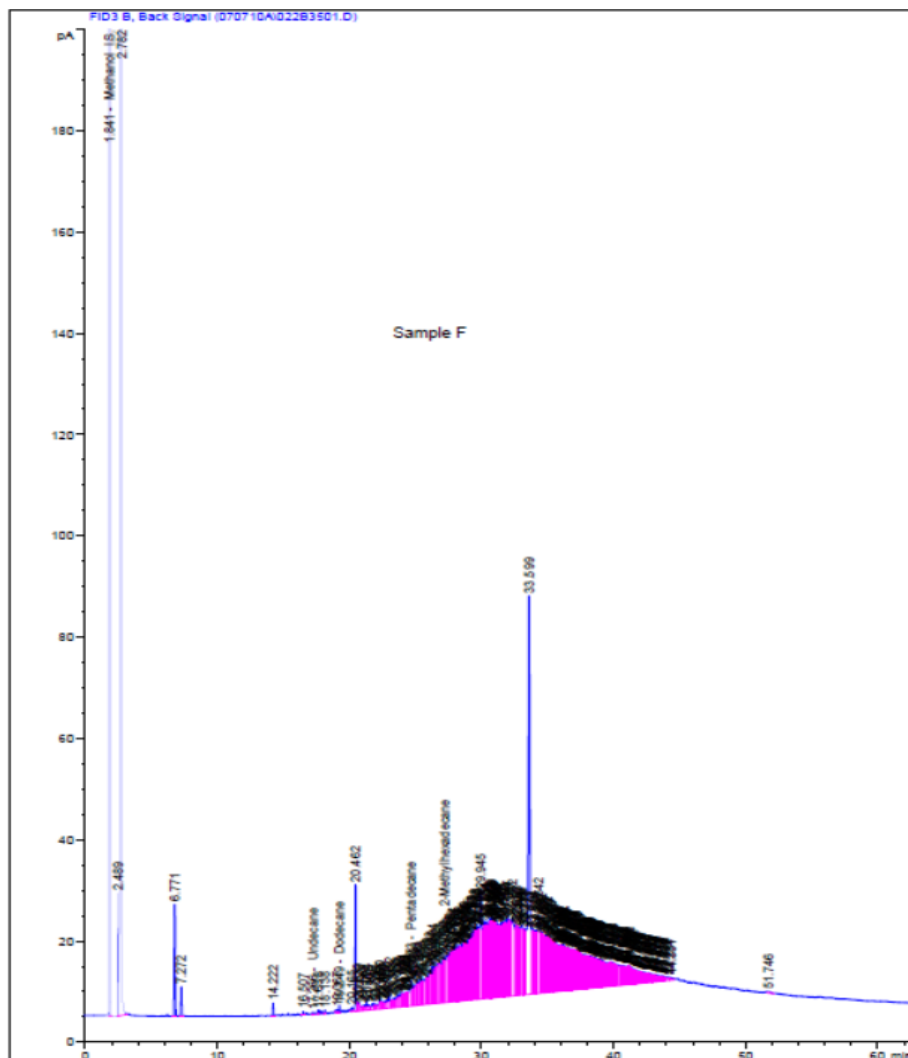
Test Method Development

GC SCAQMD Method 313-L

- Determination of VOCs in lubricants, oils and other metalworking fluids using direct injection gas chromatography/flame ionization detector method (GC/FID)
 - Modified from SCAQMD Method 313
- Complicated method
 - Integration parameters
 - Baseline placement
 - Endpoint retention time marker compound
- Not validated via ASTM E 691 – 05
- Expensive

Test Method Development

SCAQMD Method 313-L (cont.)



Test Method Development

TGA - California Dept of Pesticide Regulation (DPR)

- “Estimation of Volatile Emission Potential of Pesticides by Thermogravimetry”
 - ▣ 115°C until sample mass-loss rate is stabilized at 0.5% or less
 - ▣ If sample mass-loss rate is not reached after 80 minutes, then retest at 55°C for 11 hours
- Naphthenic oils
 - ▣ Failed to reach a stable endpoint at 115°C
 - ▣ Discrepancies between results at 115°C and 55°C
 - ▣ 55°C for 11 hours infeasible

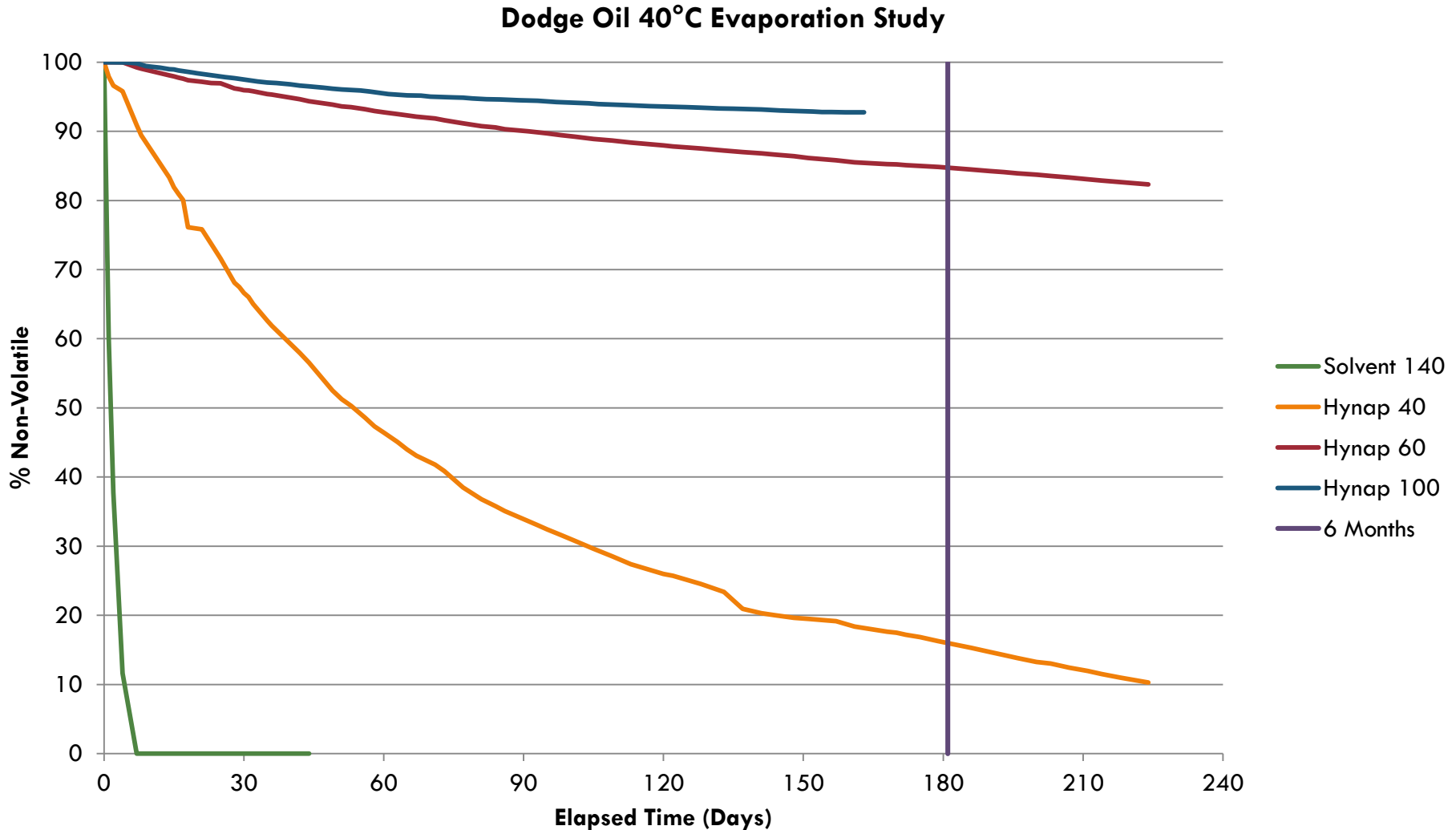
Test Method Development

W.S. Dodge Oil Six Month Evaporation Study

- W.S. Dodge Oil
- Blue-M Lab Oven
 - $40 \pm 5^{\circ}\text{C}$
- 4 samples
 - ~20 g
 - 90 mm Petri Dish

Test Method Development

W.S. Dodge Oil Six Month Evaporation Study (cont.)



Test Method Development

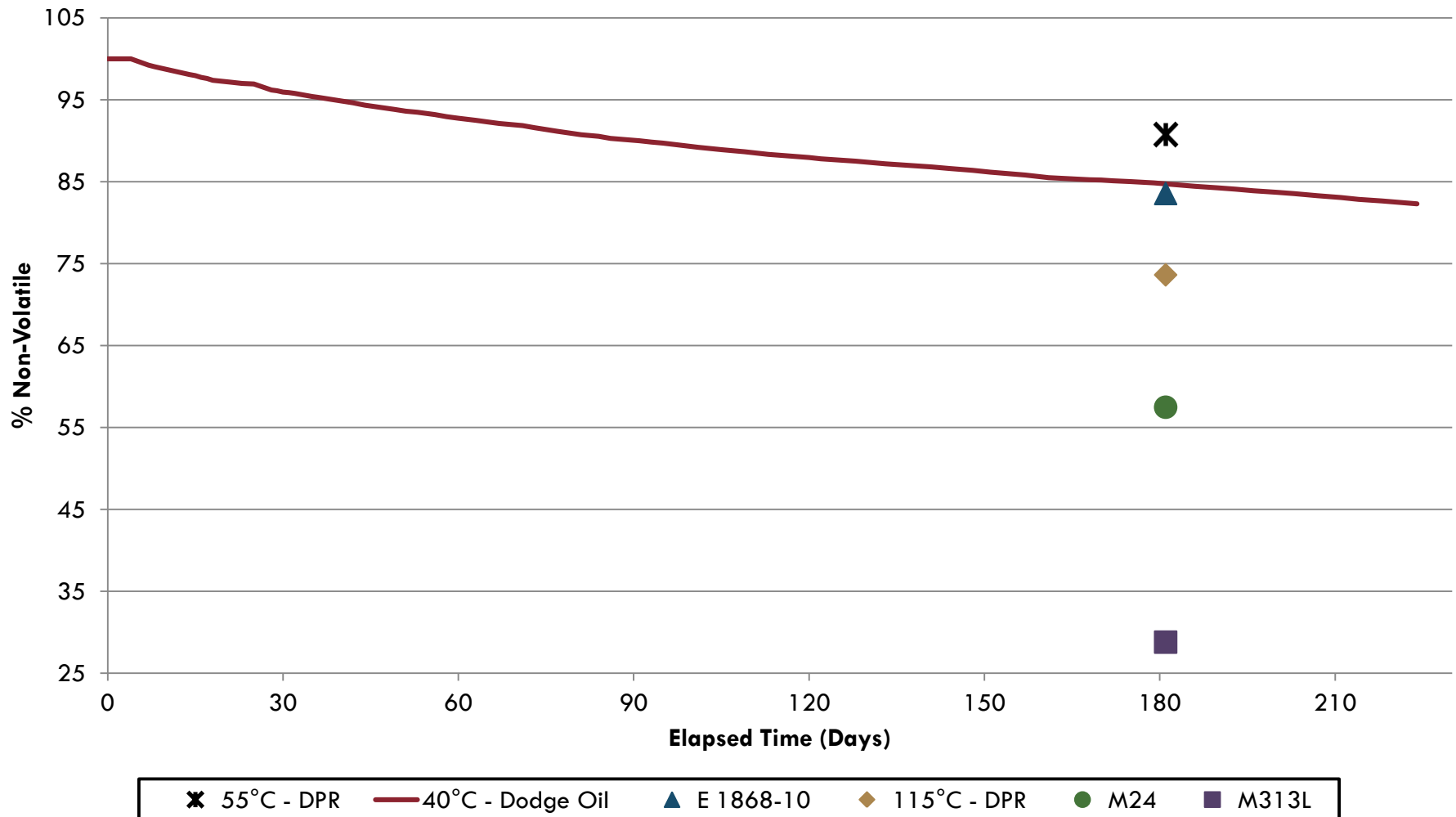
TGA Parameters

- Houghton International
- Developed TGA parameters to simulate results from W.S. Dodge Oil Evaporation Study
 - 81°C for 110 minutes

Test Method Development

TGA Parameters (cont.)

Volatility Profile of Hynap N60HT



Test Method Development

ASTM E 691 - 05

- E 691 – 05: Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
 - Relative Standard Deviation (RSD)
 - <10% or 20 g/L
- ILMA
 - 8 laboratories
 - 4 samples, 5 runs/sample
- Research Report E37-1039

Test Method Development

ASTM E 1868 - 10

- ASTM E 1868 – 10: Standard Test Method for Loss-On-Drying by Thermogravimetry
- ILMA
- Incorporate
 - ▣ Test temperature and time parameters
 - ▣ Requirements specific to SCAQMD Rule 1144
 - ▣ Interlaboratory study results

Final Outcome

- A VOC test method for metalworking fluids and direct-contact lubricants
 - Repeatable
 - Simple
 - Efficient
 - Cost effective

ASTM E 1868 - 10

For Metalworking Fluids and Direct-Contact
Lubricants

ASTM E 1868 – 10

AQMD's Experiences

- Overall
 - Reproducible
 - Uncomplicated
- Instrument / Equipment
 - Sensitivity
 - Specimen Holders
 - Cool down time
- Samples
 - Viscous
 - Highly volatile

ASTM E 1868 – 10

Other Laboratories' Experiences

- Lack of standard
 - ▣ Round Robin Samples
- Specimen holders
 - ▣ Emphasize importance of parameters
- Temperature ramp
 - ▣ 25°C/min overshoots 81°C
- Water content
 - ▣ Always an issue with evaporative methods
- Relative standard deviation (RSD)
 - ▣ Why RSD for VOC Content

ASTM E 1868 – 10

Future Work

- Find a suitable standard
- Water content
 - Karl Fischer
 - GC/TCD
 - M313L
- Additional Requirements
- Other Studies

Relative Volatility of Pure Compounds

By Various Test Methods

Relative Volatility of Pure Compounds

Why was this study conducted?

- Expand on W.S. Dodge Oil's Evaporation Study
- Study behavior under ambient settings
- Investigate VOC reference material
- Explore semi-volatiles used in other VOC containing products

Relative Volatility of Pure Compounds

Methods Explored

- Gas Chromatography (GC) by SCAQMD M313
- TGA by ASMT E 1868-10
- U.S. EPA Method 24
- Ambient Evaporation

Relative Volatility of Pure Compounds

Results

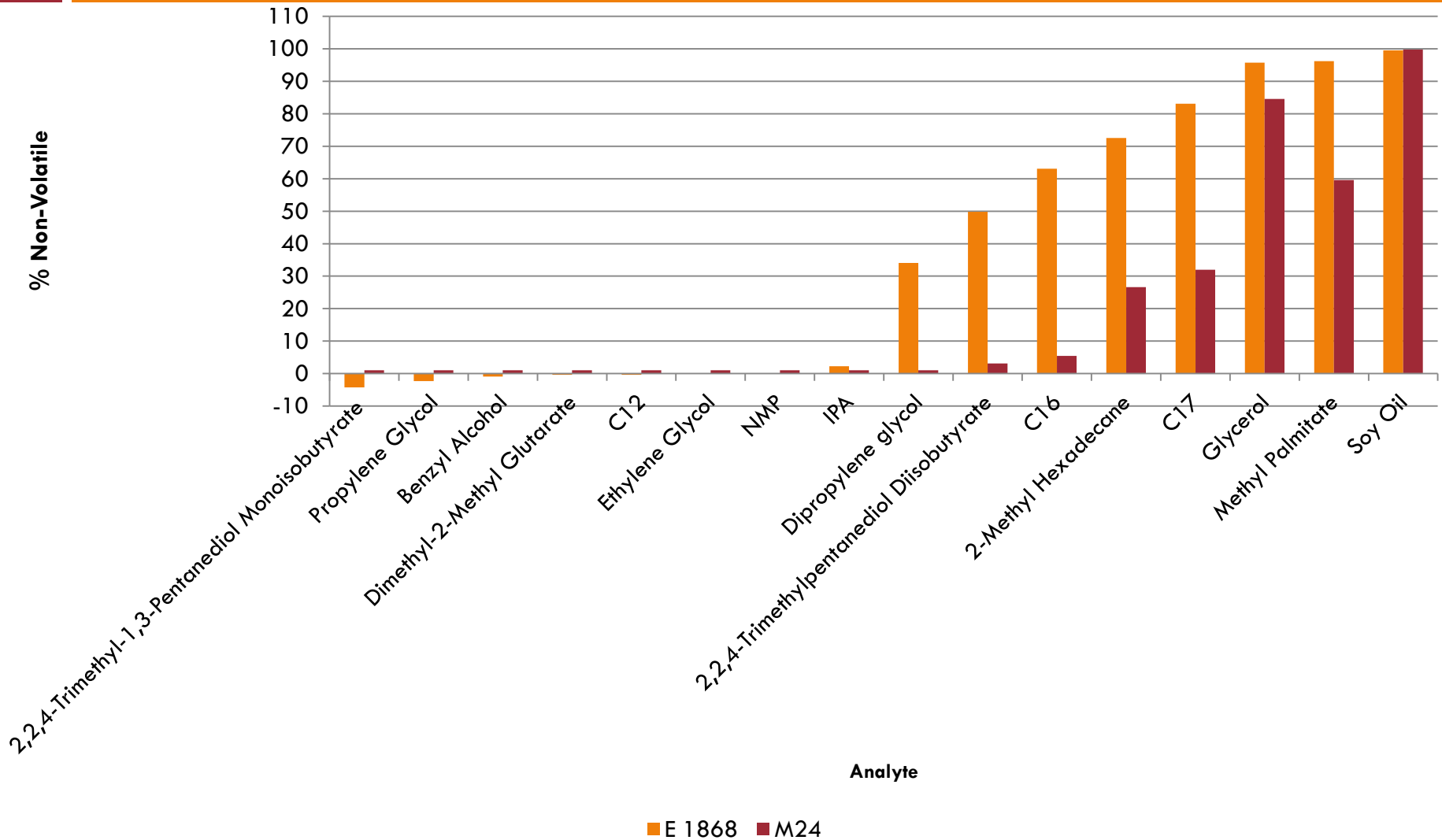
G

C

Analyte	Retention Time (minutes)
IPA	2:16
C6	2:97
MEK	3:87
Ethylene Glycol	11:73
Propylene Glycol	13:92
Glycerol	26:00
Benzyl Alcohol	26:04
NMP	26:21
Dipropylene Glycol	26:77
C12	26:97
Dimethyl-2-Methyl Glutarate	27:22
2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate	28:73, 28:82
C16	29:69
2,2,4-Trimethylpentanediol Diisobutyrate	30:18
2-Methyl Hexadecane	30:18
Diethyl Phthalate	30:44
C17	30:48
C18	31:48
C19	32:81
Methyl Palmitate	33:76
C20	34:59
Dibutyl Phthalate	35:86
Soy Oil	∞

Relative Volatility of Pure Compounds

Results (cont.)



Relative Volatility of Pure Compounds

Results (cont.)

A M B I E N T	Analyte	Time to 100% Evaporation (Days)
	IPA	1.9
	Hydrotreated Light Distillate (C9-C16)	1.9
	Ethyl Lactate	1.9
	NMP	10
	Benzyl Alcohol	14
	C12	16
	Propylene Glycol	63
	Ethylene Glycol	126
	2,2,4-Trimethylpentanediol Diisobutyrate	147
2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate	154	

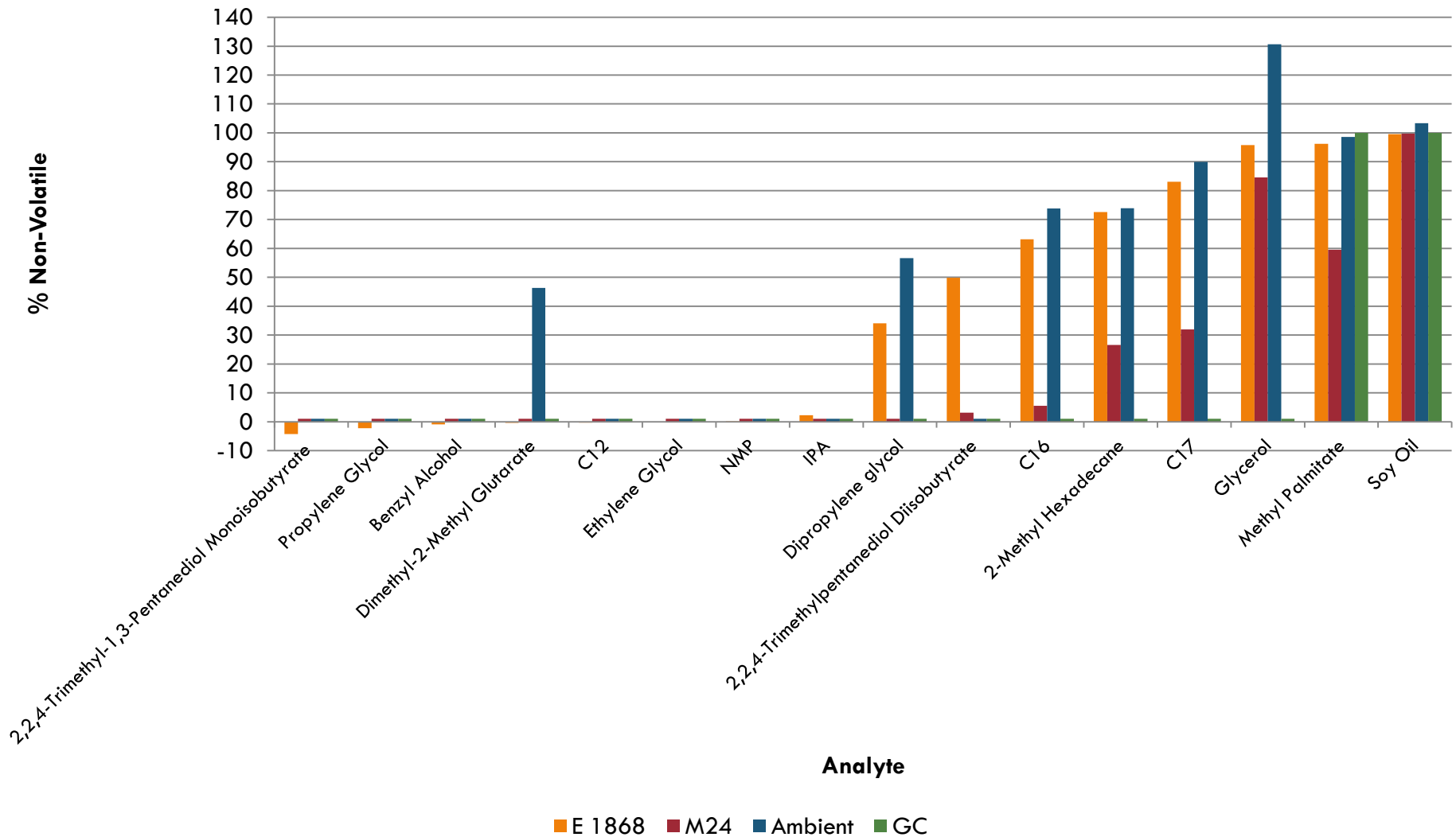
Relative Volatility of Pure Compounds

Results (cont.)

A M B I E N T	Analyte	Percent Non-Volatile @ 6 Months (%)
	C15	40.0
	Dimethyl-2-Methyl Glutarate	46.3
	Dipropylene Glycol	56.6
	2-Methyl Hexadecane	73.9
	C16	73.8
	Naphthenic Oil (Hynap N60HT)	86.5
	C17	89.9
	Methyl Palmitate	98.6
	Soy Oil	103
Glycerol	131	

Relative Volatility of Pure Compounds

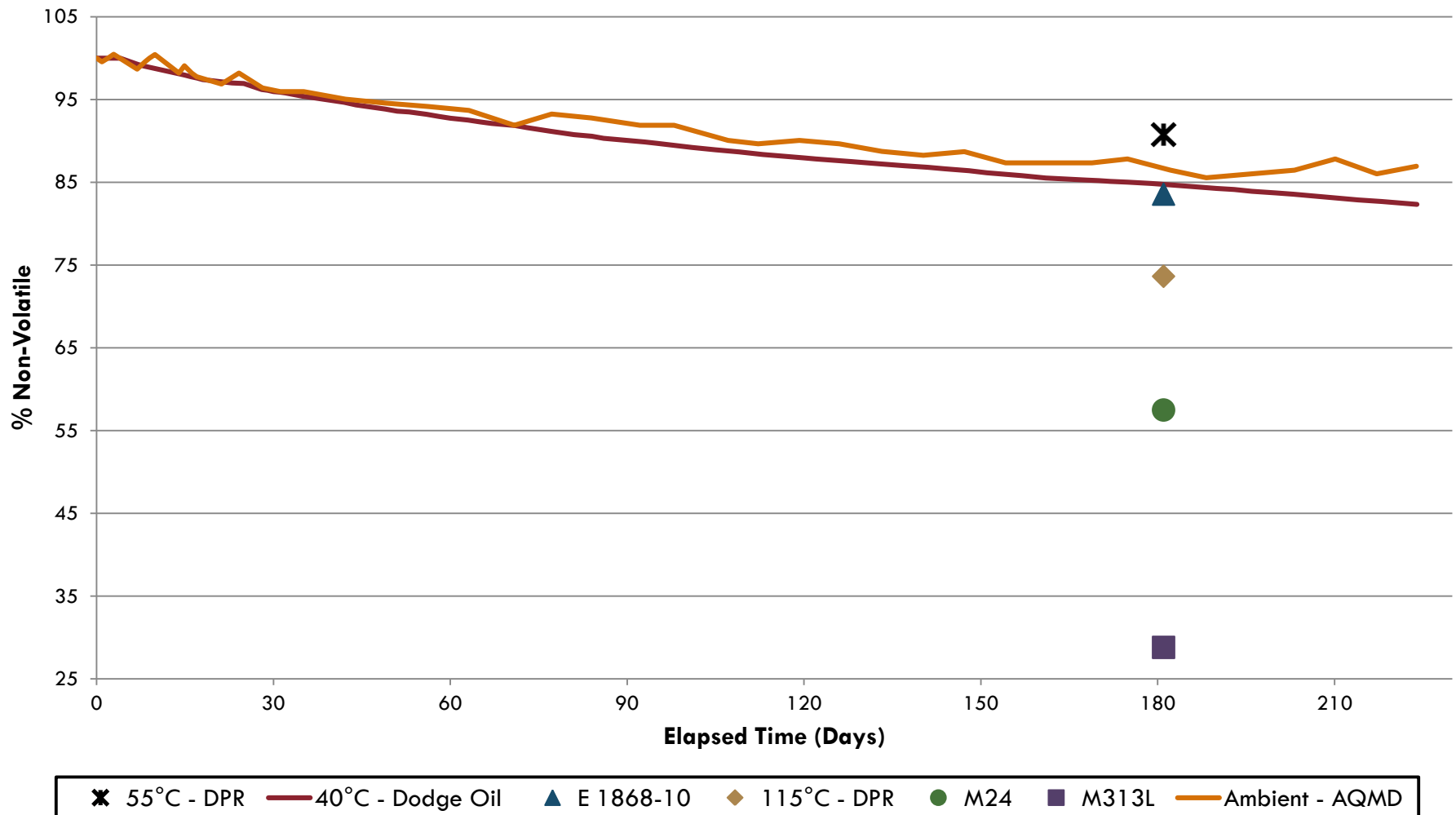
Method Comparisons



Relative Volatility of Pure Compounds

Method Comparisons

Volatility Profile of Hynap N60HT



Relative Volatility of Pure Compounds

Future Work

- Additional studies – under consideration
 - ▣ Formulated products
 - ▣ Spiked samples
- Encourage others to duplicate efforts
- Correlate to other VOC test methods
 - ▣ GC endpoint marker
 - ▣ Semi-volatiles
 - ▣ Anomalous compounds
 - glycerol

Questions? Comments?

Uyên-Uyên T. Võ

Air Quality Chemist

South Coast Air Quality Management District

(909) 396-2238

uvo@aqmd.gov

