



South Coast

Air Quality Management District

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Non-Volatile, Semi-Volatile, or Volatile: Redefining Volatile for Volatile Organic Compounds

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ABSTRACT

The term volatile organic compound (VOC) is poorly defined because measuring volatility is subjective. There are numerous standardized tests designed to determine VOC content, each with an implied method to determine volatility. The parameters (time, temperature, reference material, column polarity, etc.) used in the definitions and the associated test methods were created without a significant evaluation of volatilization characteristics in real world settings. Not only do these differences lead to varying VOC content results, but occasionally they conflict with one another. An ambient evaporation study of selected analytes and a few formulated products was conducted and the results were compared to several current VOC test methodologies, as follows: SCAQMD Method 313 (M313), ASTM Standard Test Method E 1868-10 (E1868) and U.S. EPA Reference Method 24 (M24). The ambient evaporation study showed a definite distinction between non-volatile, semi-volatile and volatile compounds. Some low vapor pressure (LVP) solvents, currently considered exempt as a VOC by some methods, volatilize at ambient conditions nearly as rapidly as the traditional high volatility solvents they are meant to replace. Conversely, bio-based and heavy hydrocarbons did not readily volatilize, though they often are calculated as VOCs in some traditional test methods. The study suggests that regulatory standards should be reevaluated to better reflect these findings to more accurately reflect real world emission from the use of VOC containing products.

INTRODUCTION

Volatile organic compounds are among the key precursors involved in the chemical reactions that form tropospheric ozone. The federal air quality standard for ozone is 0.075 parts per million (ppm)¹ and the California state air quality standard for ozone is 0.070 ppm averaged over eight hours², with consideration for further lowering the national standard³. Accurately defining VOC and volatility is critically important because multiple metropolitan areas and states are developing low VOC (≤ 50 g/L) regulations and implementing programs that reduce VOC emissions in order to attain the federal and state ambient air quality standards for ozone.

Test methods are often incorporated into these regulations and programs that define volatility by specifying analytical procedures and parameters (time, temperature, reference material, column polarity, etc.) for determining VOC content. Consequently, each test method implies its own definition for volatility. These differences lead to varying VOC content results which may conflict with one another, resulting in regulations that can limit the environmental benefits anticipated or unnecessarily exclude potential alternative formulations.

ASTM Standard Test Method D 2369 (D2369) is the original test method for determining VOC content of coatings. D2369 initially required specimens to be heated at 110°C for twenty minutes in a forced-draft oven, which limited the definition of volatility to the relatively low boiling point solvents that evaporated under these conditions. Coatings at that time were predominantly formulated with high vapor pressure solvents such as methyl ethyl ketone and toluene. With the adoption of D2369, manufacturers seeking to lower VOC content altered their formulations to include lower vapor pressure solvents, water, higher solids content and multi-component coatings. The original test method parameters did not yield accurate or precise results for the newer waterborne and high-solids coatings; therefore, the test time was extended to sixty minutes⁴. This time extension not only resolved the accuracy and precision issues, but also redefined which organic compounds were considered volatile. In October 1980, U.S. EPA (EPA) published M24⁵ which incorporated D2369 with the extended test time. Generally, M24 is the accepted standard for VOC testing for all surface coatings, lubricants, cleaning materials and some inks.

M24 determines the VOC content of a coating by measuring the water, exempt compound, and non-volatile fractions, with the remainder calculated as VOCs. For low VOC coatings, as the water, exempt compound and non-volatile fractions of the coating approach 100%, the precision of M24 becomes unreliable. Another inherent issue with M24 for low VOC coatings is the development of regulatory VOC calculation. To address a shift from solvent to waterborne and exempt solvent-based technologies, EPA derived the calculation for regulatory VOC. Regulatory VOC, also referred to as the VOC of coating, mathematically removes the water and exempt solvents when determining VOC content⁶. This calculation was intended to prevent manufacturers from adding water or exempt solvents to a coating to meet the VOC limit, only requiring additional coats of paint to achieve the same coverage and hiding power, therefore eliminating the VOC reduction benefit. However, calculation of the regulatory VOC magnifies any error in the water or exempt compound measurement, making the value especially unreliable for low-VOC and low-solids coatings. Therefore, gas chromatograph (GC) methods, such as ASTM Standard Test Method D 6886 (D6886) and M313, have been developed⁷. GC methods reduce these uncertainties by directly measuring the VOC present in the coating. Implementation of M313 includes methyl palmitate as an endpoint, primarily to reproduce VOC results from M24⁸.

South Coast Air Quality Management District (SCAQMD) found that for semi-volatile metalworking fluids, M24 was unable to yield reproducible VOC content results and GC methods were difficult to implement⁹. In an effort to more accurately and precisely measure VOC, SCAQMD evaluated alternative approaches, including thermogravimetric analysis (TGA), to measure VOCs in semi-volatile fluids. The time and temperature parameters for the TGA approach were selected to simulate the results of W.S. Dodge Oil's (Maywood, CA) six month evaporation study conducted on naphthenic base oils¹⁰. Subsequently, these TGA parameters were incorporated into E1868 and approved by SCAQMD for VOC determination of metalworking fluids and direct-contact lubricants. While TGA was an innovative approach to measuring the VOC content of non-film forming metal working fluids, it may have limited applicability for paint and coatings due to the presence of water and exempt compounds

Many regulatory agencies and third party certification agencies have attempted to define VOC by establishing endpoints based on physical properties to exclude chemicals that do not evaporate in a reasonable time under ambient conditions. The EPA exempts solvents in consumer products with a vapor pressure of 0.1 mm Hg or less at 20°C, concluding that those compounds have little or no volatility and that an exemption will not result in significant VOC emissions and contribute to ozone formation¹¹. However, the measurement for vapor pressure becomes difficult at values below 7.5 mm Hg¹² and most vapor pressure endpoints are ten to a hundred times lower. In efforts to develop a more easily measured surrogate to vapor pressure, boiling point and number of carbon atoms have been substituted. The EPA, California Air Resources Board (CARB) and Ozone Transport Commission (OTC) exempt LVP solvents in consumer products with a vapor pressure less than 0.1 mm Hg, a boiling point greater than 216°C or 12 or more carbon atoms^{13,14}. The European Union (EU) and Canada exempt solvents with a boiling point greater than 250°C^{15,16}. Green Seal exempts solvents with a boiling point greater than 280°C¹⁷. Some regulatory agencies utilize maximum incremental reactivity (MIR) values to determine a compound's contribution to ozone formation, as well as a parameter to define what is considered an exempt solvent. MIR measures the relative photochemical reactivity of chemicals on a common, continuous scale. MIR values are typically expressed in mass of additional ozone formed per mass of VOC added to the emissions¹⁸.

A study was conducted to examine volatility of several analytes and a few formulated products under various VOC test methodologies – M313, E1868, and M24 – and ambient evaporation. The results of the test methods were compared to the ambient evaporation results. Ambient evaporation results were also compared to VOC endpoints used by various regulatory agencies and third party certifiers. This study provides a comparative review of analytes and may not reflect analyte behavior in more complex blends or mixtures. This paper discusses the strengths and weaknesses of each test method and regulation; the information gained from this study may be useful to refine each test method and regulation to more accurately reflect real world emissions of VOC containing products.

MATERIALS AND METHODS

Manufacturer, purity, number of carbons, boiling point, vapor pressure and MIR values of compounds used in this study are listed according to ambient evaporation rate in Table 1. Preconditioned (at 110°C for a minimum of 24 hours) aluminum weighing dishes were obtained from Fisher Scientific, measuring 64 mm in diameter and 19 mm in height. Petri dishes were obtained from Gelman Sciences, measuring 9 mm in diameter.

Ambient Evaporation (Ambient Evap): Ambient evaporation experiments were carried out in a non-climate-controlled interior storage space with negligible air flow. Approximately one gram of neat compounds was added to Petri dishes. For compounds that reacted with the Petri dish, the experiment was repeated using aluminum weighing dishes. Compound weights, time, temperature and humidity were recorded. Data is reported in days to complete compound evaporation or weight percent non-volatile at six months.

Table 1. Compound Information Listed by Evaporation Rate

Compound	Manufacturer	Purity	Carbon Atoms	Boiling Point (°C)	Vapor Pressure (mm Hg @ 25°C)	MIR ¹⁹
Isopropyl Alcohol (IPA)	EMD Millipore	≥99.99%	3	83	33	0.61
C9-C16 Hydrotreated Light Distillate (Light Distillate)	Calumet Specialty Products	UNK	9 - 16	216 - 278	<0.1 - 0.3	0.70
Ethyl Lactate	JT Baker	99%	5	154	1.2	2.67
N-Methylpyrrolidinone (NMP)	Sigma-Aldrich	99%	5	202	0.5	2.41
Benzyl Alcohol	Sigma-Aldrich	≥99%	6	205	0.14	5.11
Dodecane (C12)	Sigma-Aldrich	≥99%	12	216	0.3	0.55
Propylene Glycol	SAFC Global	≥99.5%	3	187	0.13	2.58
Ethylene Glycol	Aldrich	99.8%	2	198	0.09	3.13
2,2,4-Trimethylpentanediol Diisobutyrate	Aldrich	98.5%	16	280	0.004	0.38
2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate	Aldrich	99%	12	255	0.01	0.81
Pentadecane (C15)	Sigma-Aldrich	99+%	15	270	0.01	0.50
Dipropylene Glycol	Aldrich	99%	6	232	<0.01	1.83
2-Methyl Hexadecane	MP Biomedicals	90-100%	17	291	<0.01	UNK
Hexadecane (C16)	Sigma-Aldrich	99%	16	287	0.005	0.45
Naphthenic Oil (Hynap N60HT)	San Joaquin Refinery	UNK	16 - 20	279	<0.001	UNK
Heptadecane (C17)	Aldrich	99%	17	302	<0.001	0.42
Naphthenic Based Metal Working Fluid (MWF)	W.S. Dodge Oil	UNK	UNK	UNK	UNK	UNK
Alkyl Alkanolamine	Taminco Higher Amines, Inc.	>99%	8	283	<0.01	UNK
Methyl Palmitate	Fluka	≥99.0%	17	332	<0.001	0.44
Soy Oil	W.R. Meadows	UNK	14 - 18	>250	<0.001	1.58
Glycerol	EM Science	99.5+%	3	290	<0.001	3.15

UNK = Information not known.

SCAQMD Method 313 (M313): M313 experiments were carried out on a Finnigan Trace GC with a Finnigan Trace Mass Spectrometer (MS) equipped with a Thermo Finnigan AS 2000 liquid autosampler (Thermo Fisher Scientific Inc, Waltham, MA) and an Agilent DB-624, 30 m x 0.32 mm x 0.25 μ m column (Agilent Technologies, Inc., Santa Clara, CA). The initial oven program was held at 40°C for 5.5 min, then ramped to 95°C at 3°C/min, then ramped to 225°C at 25°C/min and held for 10.97 min. Inlet temperature was set at 190°C with helium carrier gas flow set at 4.5 mL/min operated in constant flow mode. A 1 μ L split injection with a split flow of 36 mL/min was made. The transfer line temperature was set at 250°C. The detector temperature was set at 200°C. Compounds were qualitatively diluted in tetrahydrofuran and analyzed by GC/MS/FID for their retention times.

ASTM Standard Test Method E 1868-10 (E1868): E1868 experiments were carried out according to SCAQMD Rule 1144 specifications on a STA 449 F1-Jupiter (NETZSCH Instruments, Inc. Burlington, MA) equipped with: a silicon carbide furnace with a type S thermocouple and a thermogravimetric (TG) sample carrier with a radiation shield, a 10 mm aluminum oxide slip-on plate, a Q5000 100 μ L platinum pan (TA Instruments, New Castle DE), and a type S thermocouple. Neat compounds were analyzed and volatilization was reported as weight percent non-volatile.

U.S. EPA Reference Method 24 (M24): M24 experiments were carried out according to D2369 in a Thermolyne Mechanical Oven (Thermo Fisher Scientific Inc, Waltham, MA). Neat compounds were analyzed and volatilization was reported as weight percent non-volatile.

RESULTS AND DISCUSSION

Ambient Evaporation

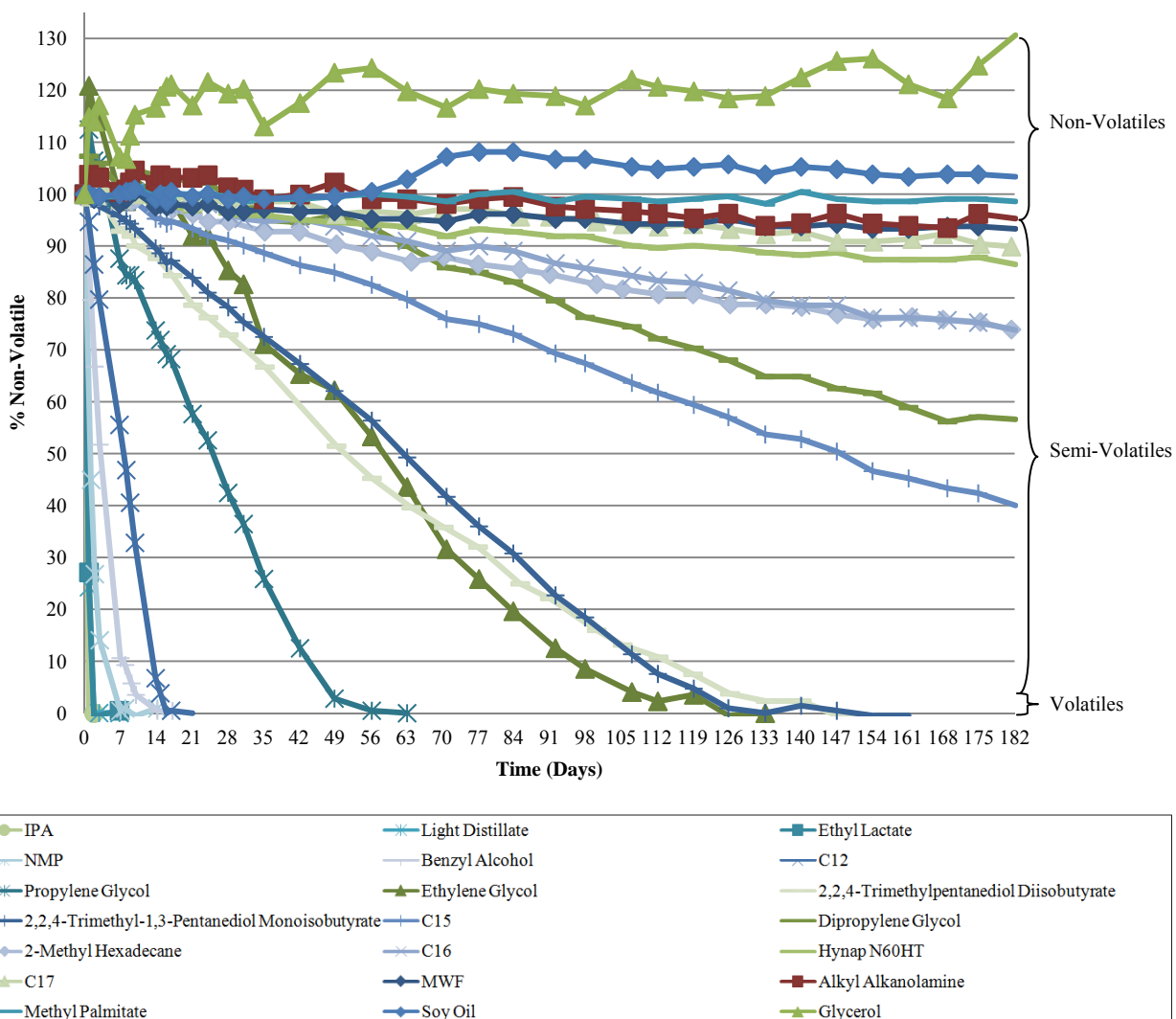
The temperature and humidity of the non-climate-controlled interior storage space is summarized in Table 2.

Table 2. Ambient Evaporation Temperature and Humidity Summary

	Temperature (°C)	Humidity (%)
Low	20	16
Average	24	41
High	30	54

The results from the ambient evaporation study are shown in Figure 1, which illustrates the evaporation profiles of the compounds.

Figure 1. Overall Ambient Evaporation Results



For the purpose of this study, the compounds are evaluated at six months. Using this as the reference point, the results from the ambient evaporation study delineated the compounds into three categories: volatile, non-volatile, and semi-volatile.

Volatile Compounds: Figure 2 isolates the volatile compounds from Figure 1. A volatile compound is defined as a compound that evaporates more than 95% by weight within six months under ambient evaporation testing conditions. IPA, light distillate, and ethyl lactate all evaporate completely within two days (Figure 3). It takes ten days for complete evaporation of NMP, two weeks for benzyl alcohol to fully evaporate and C12 takes 16 days to completely evaporate. The remainder of the volatile compounds – propylene glycol, ethylene glycol, 2,2,4-trimethylpentanediol diisobutyrate, and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate – are fully evaporated by six months.

Figure 2. Ambient Evaporation Results – Volatiles

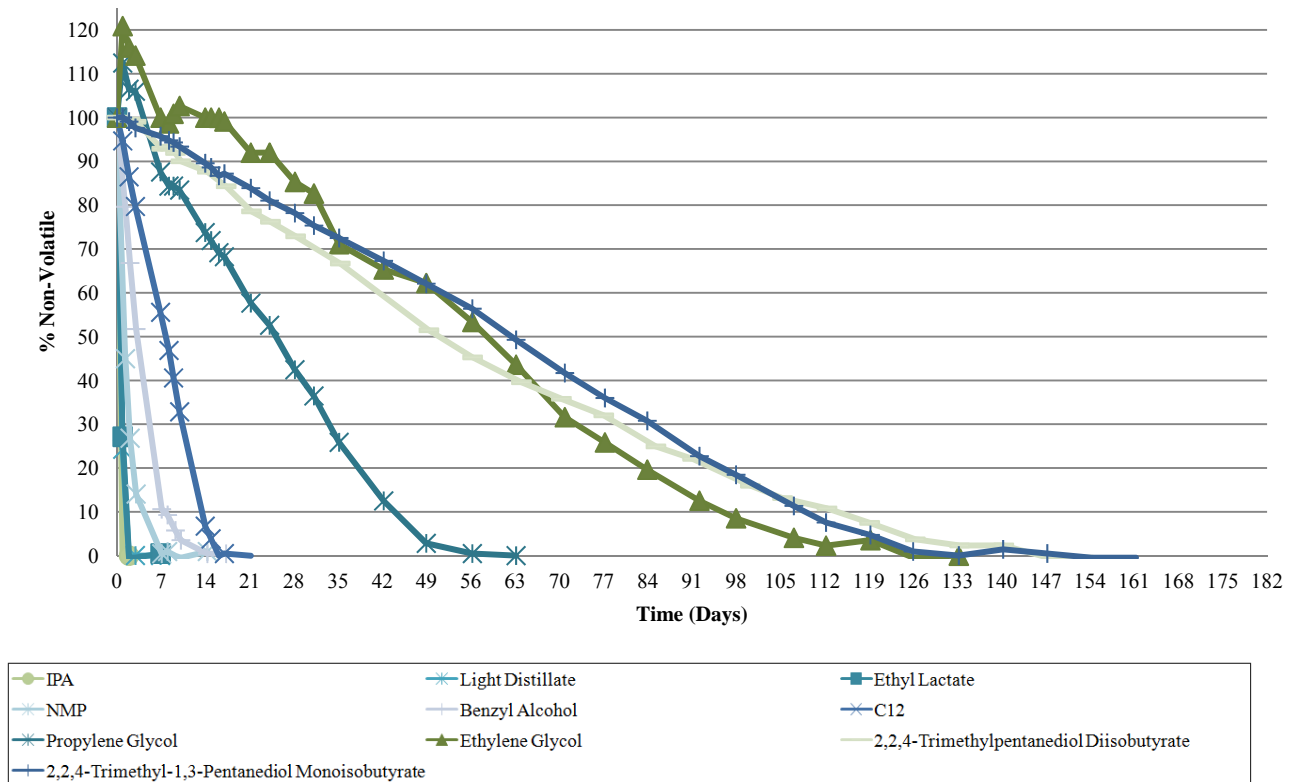
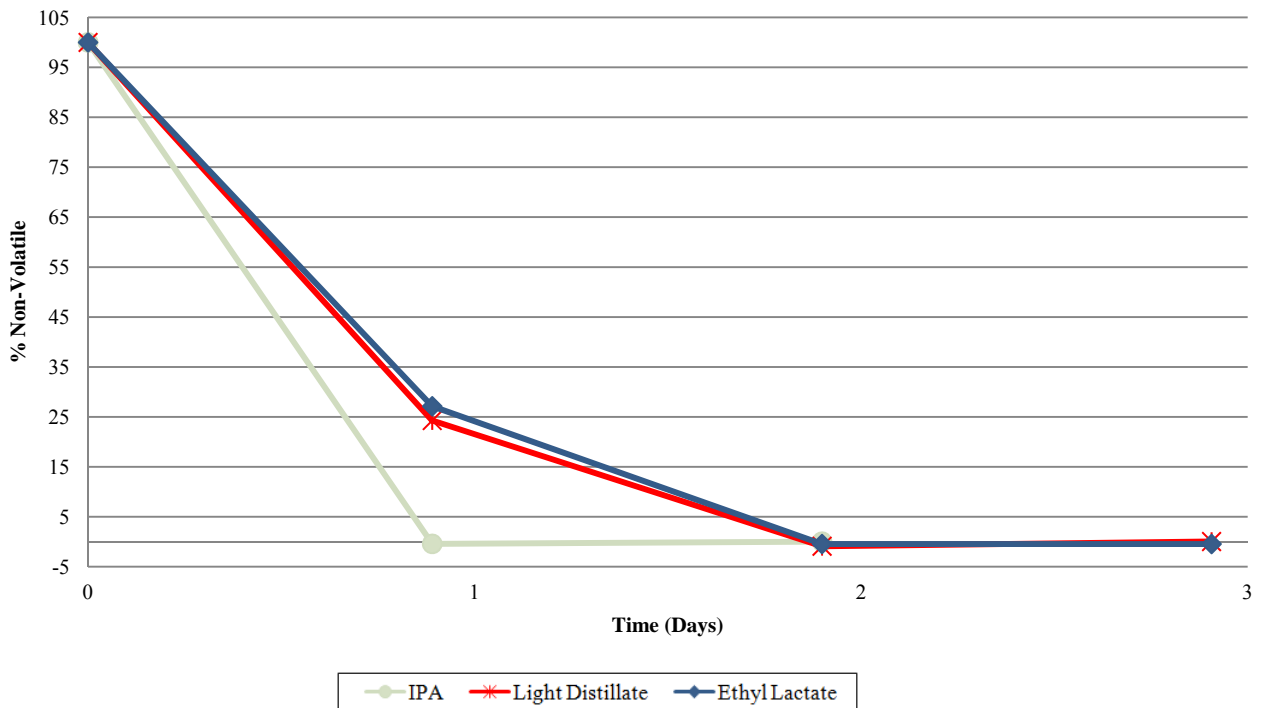


Figure 3. Ambient Evaporation Results –IPA, Light Distillate and Ethyl Lactate



Non-Volatile Compounds: Figure 4 isolates the non-volatile compounds from Figure 1. A non-volatile compound is defined as a compound that evaporates less than five percent by weight in six months under ambient evaporation testing conditions. Alkyl alkanolamine, methyl palmitate, soy oil and glycerol all fall under this category. Several compounds had minor weight gain during the study. In the case of glycerol, significant weight gain was noticed, particularly during periods of higher humidity (Figure 5). This weight gain can potentially be attributed to glycerol's hygroscopic properties²⁰. Further evaluation of this issue is planned in subsequent studies, including speciation of the remaining analyte and testing analyte in a moisture-free environment.

Figure 4. Ambient Evaporation Results – Non-Volatile

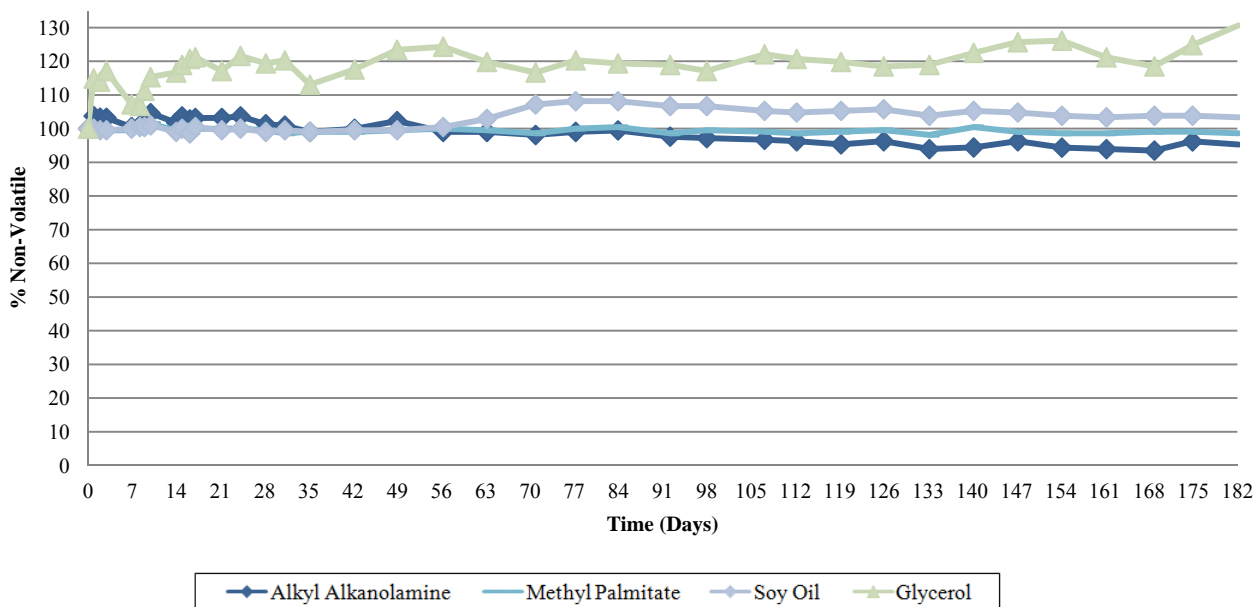
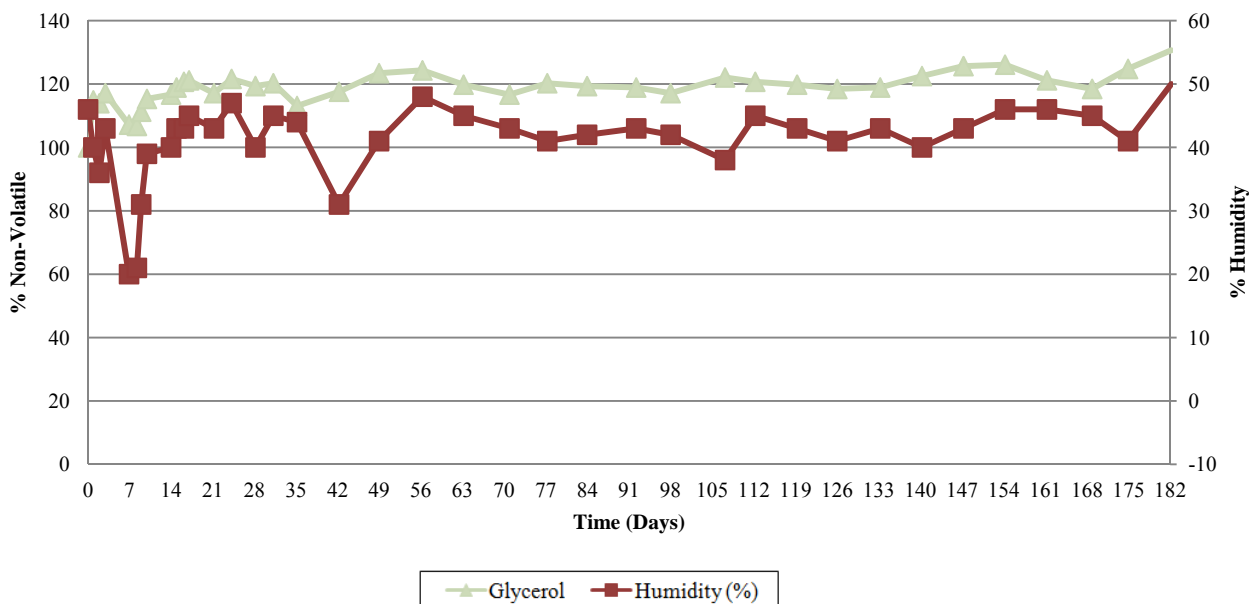
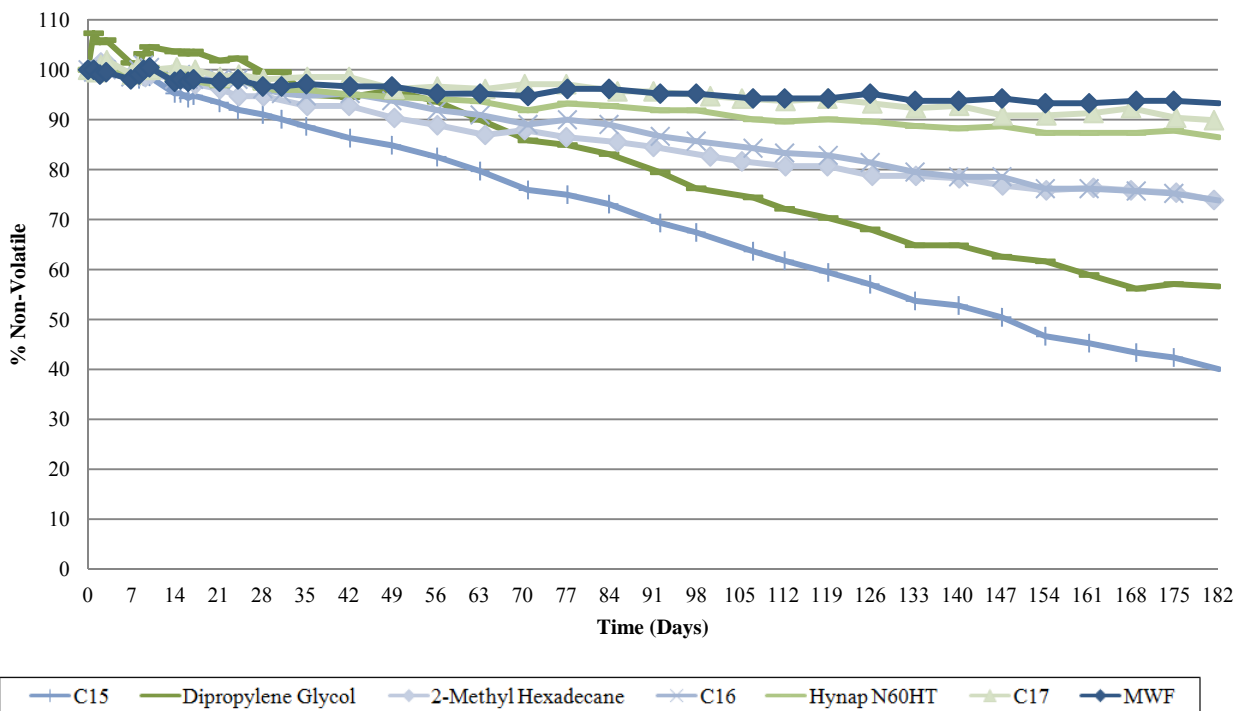


Figure 5. Effects of Humidity on Glycerol



Semi-Volatile Compounds: Figure 6 isolates the semi-volatile compounds from Figure 1. A semi-volatile compound is defined as a compound that evaporates between five and 95% by weight, during the six months under ambient evaporation testing conditions. The following compounds exhibit semi-volatile behavior: C15, dipropylene glycol, 2-methyl hexadecane, C16, Hynap N60HT, C17, and MWF.

Figure 6: Ambient Evaporation Results – Semi-Volatile



Comparing Ambient Evaporation Results to Various Test Methods

- Figure 7 and Table 3 compare ambient evaporation results to the VOC test methods results. Several observations can be made about current test methods when comparing them to the results of the ambient evaporation study. For the purpose of this discussion, E1868 and M24 will have the same definition for volatile (evaporates more than 95%), non-volatile (evaporates less than five percent) and semi-volatile (evaporates between five and 95%) as used for ambient evaporation. All methods agree on most of the volatile compounds –IPA, light distillate, ethyl lactate, NMP, benzyl alcohol, C12, propylene glycol, ethylene glycol and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate.
- Soy oil is non-volatile by every test method.
- When compared to ambient evaporation results, M24 shows higher volatility. Of the eighteen compounds where M24 and ambient evaporation data is available, at six months, the average difference is 24%, with the largest discrepancy being 74% for alkyl alkanolamine.
- Of the three test methods, M313 differs the most with ambient evaporation results in the semi-volatiles region.
- M313 is the only test method that categorizes glycerol as a volatile. Ambient evaporation and TGA show glycerol as a non-volatile. Glycerol is a semi-volatile by M24.

- E1868 is not exactly representative of ambient evaporation, but its results are the closest to ambient evaporation results of the three test methods, particularly for the semi-volatiles. Of the twenty-one compounds where E1868 and ambient evaporation data is available, the average difference is 6.6% at six months, with the largest discrepancy being 50% for 2,2,4-trimethylpentanediol diisobutyrate.

Figure 7. Comparison of Compound Volatility by Ambient Evaporation, GC, TGA, and M24

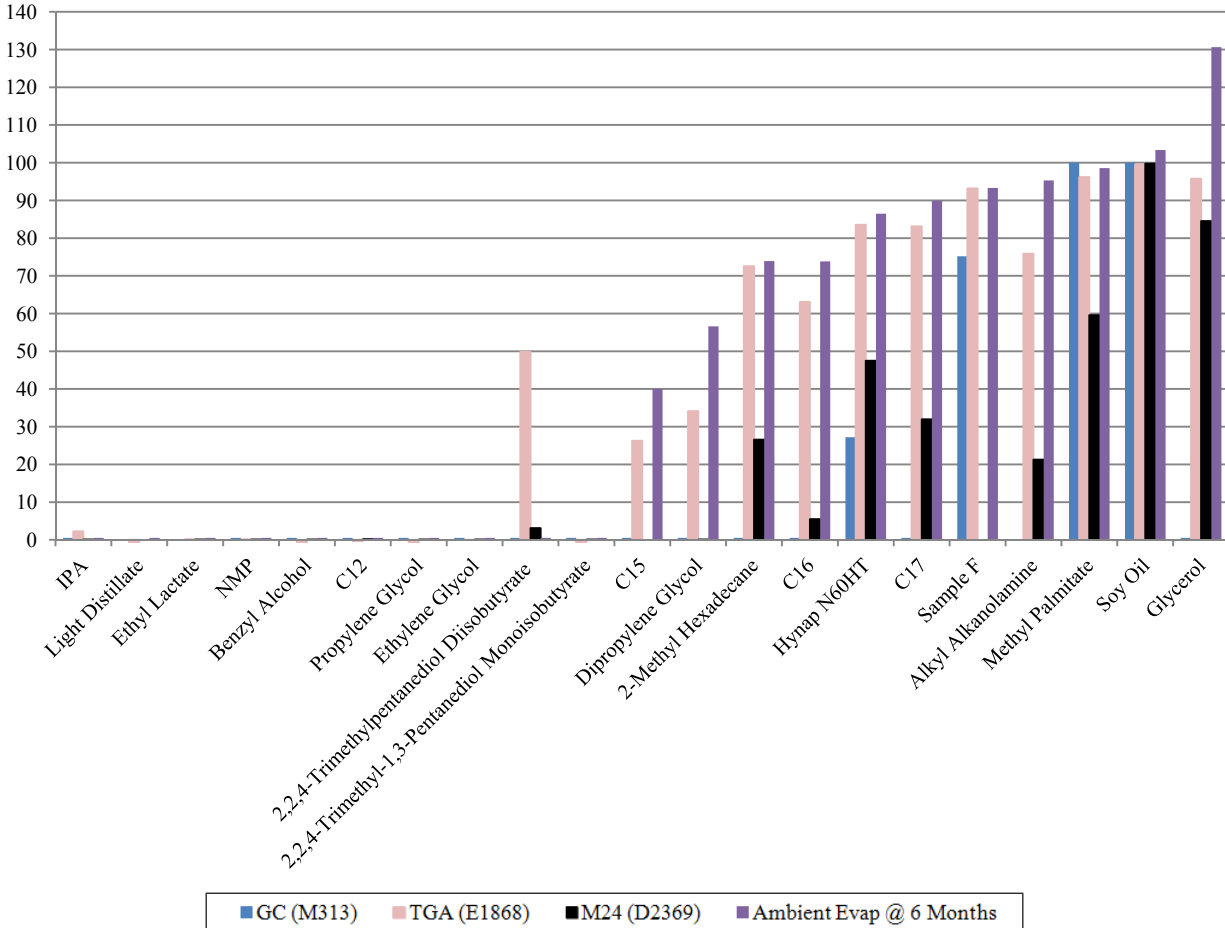


Table 3. Combined Results – Ambient Evaporation, GC, TGA, and M24

Compound	Retention Time (minutes)	Percent Non-Volatile (%)			Time to 100% Evaporation (Days)
	GC (M313)	TGA (E1868)	M24 (D2369)	Ambient Evap @ 6 Months	Ambient Evap
IPA	02:10	2.25	0.04	0.0	0.9
Light Distillate	N/T	-1.25	N/T	0.0	1.9
Ethyl Lactate	N/T	0.16	0.01	0.0	1.9
NMP ^a	26:13	0.10	0.07	0.0	9.2
Benzyl Alcohol ^a	26:02	-0.89	0.03	0.0	14
C12	26:58	-0.34	0.12	0.0	16
Propylene Glycol	13:55	-2.27	0.03	0.0	63
Ethylene Glycol	11:44	-0.01	0.03	0.0	126
2,2,4-Trimethylpentanediol Diisobutyrate ^a	30:11	50	3.1	0.0	147
2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate	28:44, 28:49	-4.2	0.05	0.0	154
C15	N/T	26	N/T	40	>180 Days
Dipropylene Glycol	26:46	34	0.06	57	>180 Days
2-Methyl Hexadecane	30:11	73	27	74	>180 Days
C16	29:41	63	5.5	74	>180 Days
Hynap N60HT	N/A	84	47	86	>180 Days
C17	30:29	83	32	90	>180 Days
MWF	N/A	93	N/T	93	>180 Days
Alkyl Alkanolamine	N/T	76	21	95	>180 Days
Methyl Palmitate	33:46	96	60	99	>180 Days
Soy Oil	∞	100	100	103	>180 Days
Glycerol	26:00	96	85	131	>180 Days

N/T denotes that compound was not tested.

∞ denotes compound did not elute from the column.

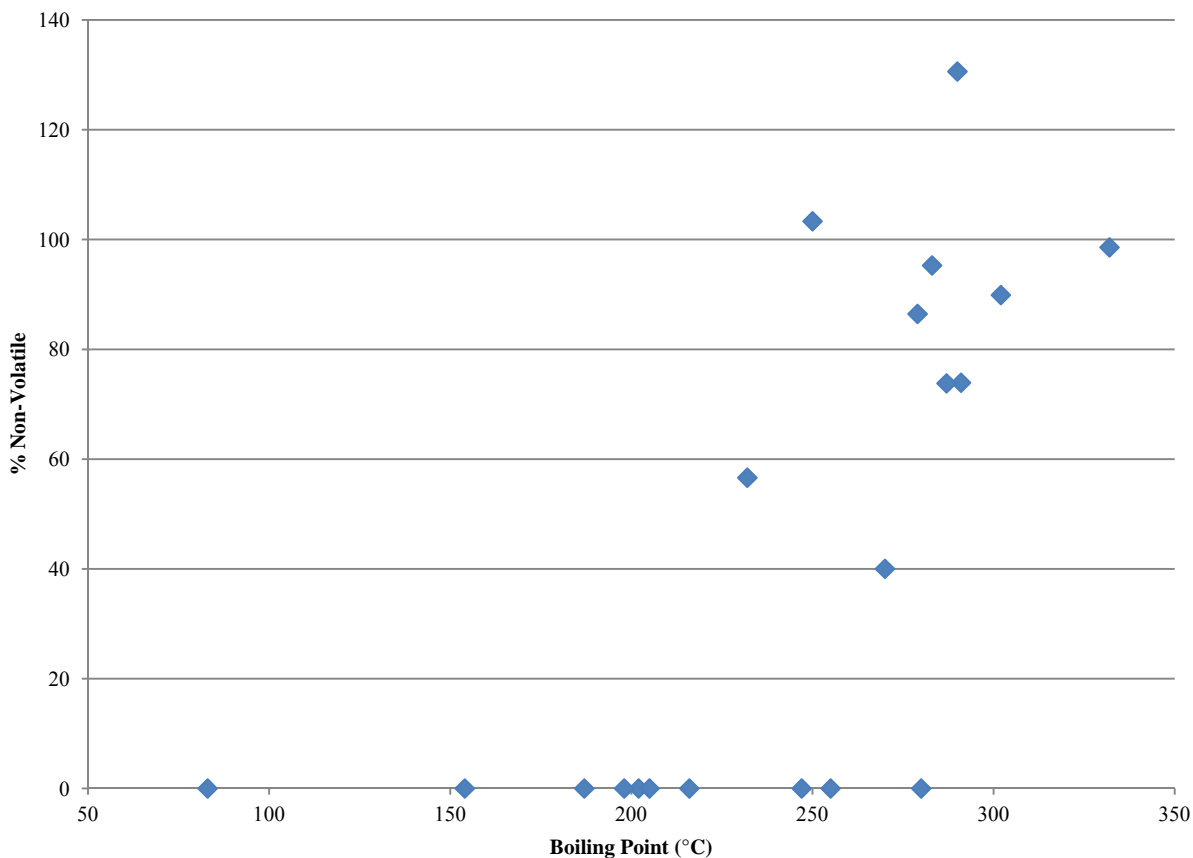
^a denotes that experiment was carried in aluminum weighing dish and not Petri dish.

N/A denotes that compound has multiple peaks.

Comparing Ambient Evaporation Results to Physical Properties

Boiling Point: Figure 8 shows the correlation between a compound's ambient evaporation and its boiling point. Compounds with a boiling point of less than 220°C – IPA, ethyl lactate, propylene glycol, ethylene glycol, NMP, benzyl alcohol, and C12 – are volatile. The four non-volatile compounds – soy oil, alkyl alkanolamine, glycerol, and methyl palmitate – have boiling points of 250°C, 283°C, 290°C, and 332°C, respectively. Compounds with boiling points between 220°C and 280°C fall under all three volatility categories: non-volatile (soy oil), volatile (light distillate, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, and 2,2,4-trimethylpentanediol diisobutyrate) and semi-volatile (dipropylene glycol, C15, and Hynap N60HT). There are no volatile compounds with a boiling point greater than 280°C, only semi-volatile (C16, 2-methyl hexadecane, C17, and MWF) and non-volatile (alkyl alkanolamine, glycerol, and methyl palmitate) compounds.

Figure 8. Correlation of Boiling Point and Ambient Evaporation Results

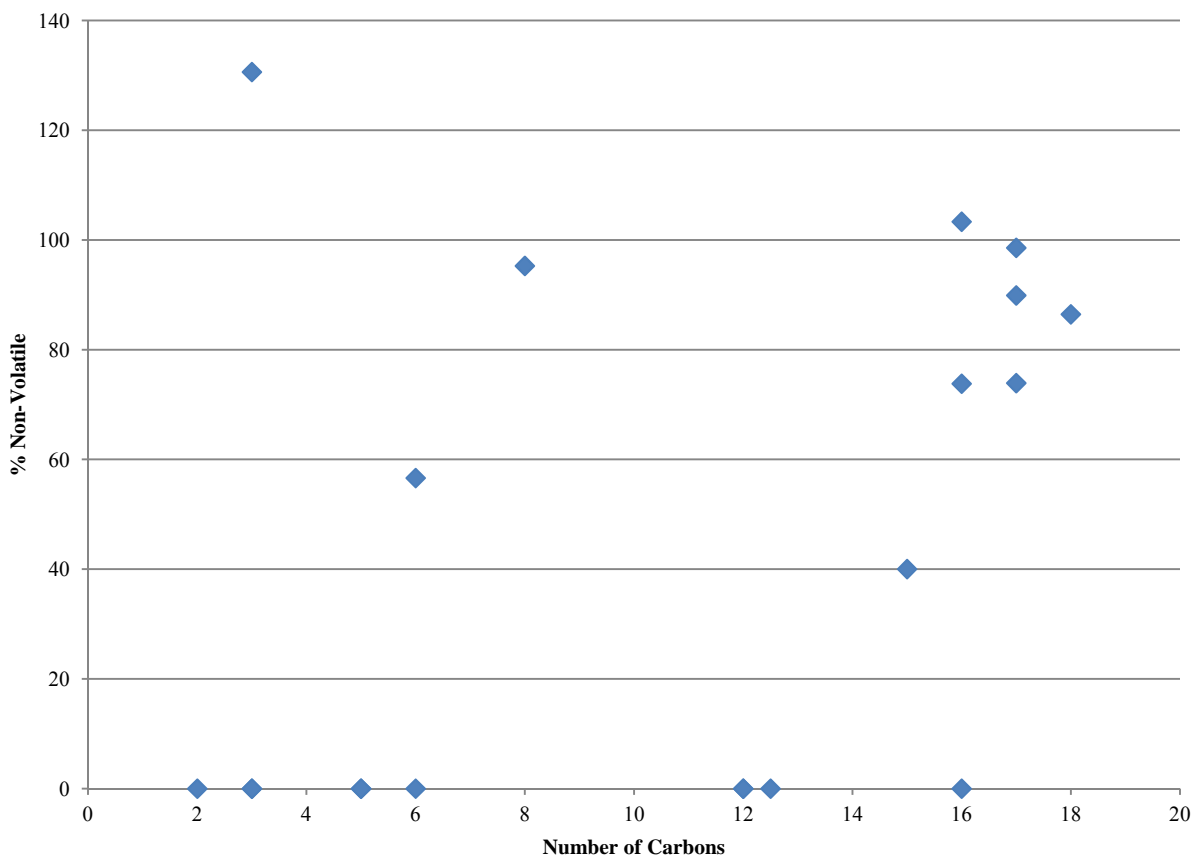


Note 1: Boiling point for light distillate is an average of its boiling point range.

Note 2: Boiling point for soy oil is its minimum boiling point.

Number of Carbon Atoms: The correlation between a compound's ambient evaporation with its number of carbon atoms is shown in Figure 9. With the exception of glycerol, dipropylene glycol and alkyl alkanolamine all compounds with 12 carbon atoms or less are volatile. Compounds with more than 12 carbon atoms fall under all three volatility categories: non-volatile (soy oil and methyl palmitate), volatile (light distillate and 2,2,4-trimethylpentanediol diisobutyrate), and semi-volatile (C15, C16, 2-methyl hexadecane, C17 and Hynap N60HT).

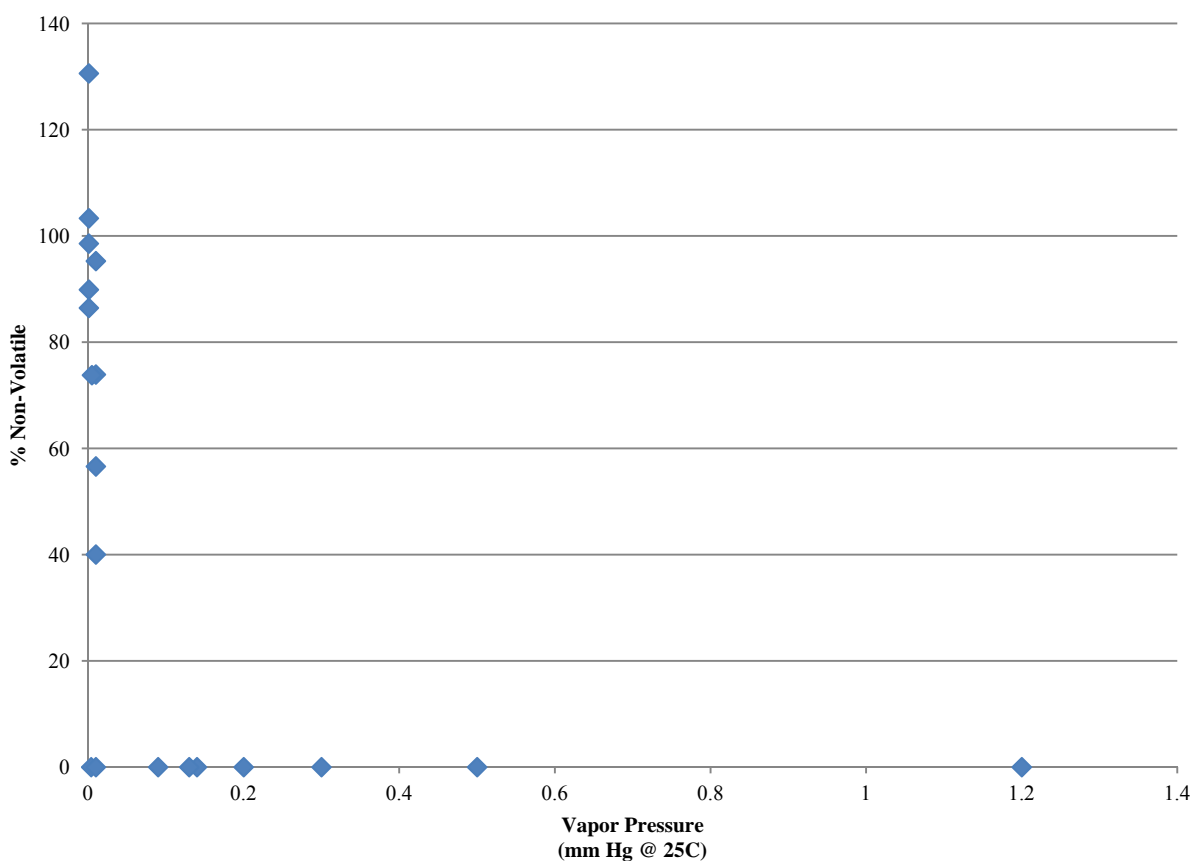
Figure 9. Correlation of Number of Carbons and Ambient Evaporation Results



Note: Number of carbons for Light Distillate and Hynap N60HT is an average of their carbon number ranges.

Vapor Pressure: Figure 10 (excluding IPA) shows the correlation between a compound's ambient evaporation with its vapor pressure. Nearly all of the compounds tested have vapor pressures below 7.5 mm Hg at 25°C, at which point the vapor pressure becomes difficult to measure. Compounds with a vapor pressure greater than 0.1 mm Hg at 25°C – propylene glycol, benzyl alcohol, light distillate, C12, NMP, ethyl lactate, and IPA, light distillate, ethyl lactate, NMP, benzyl alcohol, C12 and propylene glycol – are volatile. Compounds with a vapor pressure less than 0.1 mm Hg at 25°C fall under all three categories: non volatile (methyl palmitate, soy oil, glycerol and alkyl alkanolamine), volatile (ethylene glycol, 2,2,4-trimethylpentanediol diisobutyrate and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) and semi-volatile (C15, dipropylene glycol, 2-methyl hexadecane, C16, Hynap N60HT, C17 and MWF).

Figure 10. Correlation of Vapor Pressure and Ambient Evaporation Results



Note: IPA data omitted from Figure 10.

Summary of Results

Table 4 summarizes each compound's volatility by ambient evaporation, test method and regulatory standard.

Ambient Evaporation versus M313: M313 uses methyl palmitate as a retention time standard. All compounds that elute before methyl palmitate are calculated as volatile and those that elute

with or after are calculated as non-volatile. Ambient evaporation and M313 both agree on the volatile compounds: IPA, light distillate, ethyl lactate, NMP, benzyl alcohol, C12, propylene glycol, ethylene glycol, 2,2,4-trimethylpentanediol diisobutyrate and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate. Of the four compounds listed as non-volatile – alkyl alkanolamine, methyl palmitate, soy oil and glycerol – M313 calculates alkyl alkanolamine and glycerol as volatiles because they elute before methyl palmitate. All but one of the semi-volatile compounds – C15, dipropylene glycol, 2-methyl hexadecane, C16 and C17 – are the compounds in which ambient evaporation and M313 are not completely in agreement; these semi-volatile compounds by ambient evaporation are considered volatile by M313. The reason for this discrepancy is that M313 does not have a semi-volatile parameter for individual analytes, only volatile or non-volatile depending on the analytes' elution time relative to methyl palmitate. The formulated products, HyNap N60HT and MWF, are semi-volatile under M313 because they are formulated with a mixture of volatile and non-volatile analytes.

Ambient Evaporation versus E1868: E1868 calculates volatility by converting weight percent loss at the end of 110 minutes at 81°C in a TGA into VOC content. Two compounds are categorized differently between ambient evaporation and E1868: 2,2,4-trimethylpentanediol diisobutyrate and alkyl alkanolamine. 2,2,4-trimethylpentanediol diisobutyrate is a volatile compound according to ambient evaporation but is a semi-volatile according to E1868. Alkyl alkanolamine is non-volatile under ambient evaporation but semi-volatile according to E1868.

Ambient Evaporation versus M24: M24 calculates volatility by converting weight percent loss at the end of 60 minutes at 110°C in a forced draft oven into VOC content. M24 categorizes C15 and dipropylene glycol as volatiles, whereas they are semi-volatiles by ambient evaporation. Alkyl alkanolamine, methyl palmitate and glycerol are considered semi-volatiles by M24 and non-volatile by ambient evaporation.

Ambient Evaporation versus EPA, CARB & OTC: EPA, CARB and OTC exempt LVP solvents with a vapor pressure less than 0.1 mm Hg, a boiling point of 216°C or 12 or more carbon atoms. Only IPA, ethyl lactate, NMP and C12 are volatiles according to EPA, CARB and OTC; other compounds tested are treated as non-volatile whereas ambient evaporation testing showed otherwise.

Ambient Evaporation versus EU & Canada: The EU and Canada exempt solvents with a boiling point greater than 250°C. Two compounds – 2,2,4-trimethylpentanediol diisobutyrate and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate – are treated as non-volatile by the EU and Canada, but they are volatile by ambient evaporation. Dipropylene glycol is considered a volatile by the EU and Canada, but is a semi-volatile by ambient evaporation. C15, 2-methyl hexadecane, C16, Hynap N60HT, C17 and MWF are semi-volatile by ambient evaporation but considered non-volatile by the EU and Canada.

Ambient Evaporation versus Green Seal: Green Seal exempts solvents with a boiling point greater than 280°C. Green Seal treats 2,2,4-trimethylpentanediol diisobutyrate as non-volatile while it is measured as a volatile by ambient evaporation. Three compounds – C15, dipropylene glycol and Hynap N60HT – are volatile by Green Seal but semi-volatile by ambient evaporation. Four compounds – 2-methyl hexadecane, C16, C17 and MWF – are non-volatile by Green Seal

but semi-volatile by ambient evaporation. Soy oil is considered a volatile by Green Seal but is non-volatile by ambient evaporation.

Table 4. Compound Volatility by Test Method and Regulatory Standard

Compound	Ambient Evap @ 6 Months	M313	E1868	M24 (D2369)	EPA, CARB & OTC	EU & Canada	Green Seal
IPA	V	V	V	V	V	V	V
Light Distillate	V	V	V	V	NV	V	V
Ethyl Lactate	V	V	V	V	V	V	V
NMP	V	V	V	V	V	V	V
Benzyl Alcohol	V	V	V	V	NV	V	V
C12	V	V	V	V	V	V	V
Propylene Glycol	V	V	V	V	NV	V	V
Ethylene Glycol	V	V	V	V	NV	V	V
2,2,4-Trimethylpentanediol Diisobutyrate	V	V	SV	V	NV	NV	NV
2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate	V	V	V	V	NV	NV	V
C15	SV	V	SV	V	NV	NV	V
Dipropylene Glycol	SV	V	SV	V	NV	V	V
2-Methyl Hexadecane	SV	V	SV	SV	NV	NV	NV
C16	SV	V	SV	SV	NV	NV	NV
Hynap N60HT	SV	SV	SV	SV	NV	NV	V
C17	SV	V	SV	SV	NV	NV	NV
MWF	SV	SV	SV	SV	NV	NV	NV
Alkyl Alkanolamine	NV	V	SV	SV	NV	NV	NV
Methyl Palmitate	NV	NV	NV	SV	NV	NV	NV
Soy Oil	NV	NV	NV	NV	NV	NV	V
Glycerol	NV	V	NV	SV	NV	NV	NV

V = Volatile
 NV = Non-Volatile
 SV = Semi-Volatile

CONCLUSIONS

The volatility of several analytes and a few formulated products is studied by M313, E1868, M24 and ambient evaporation. The study shows a definite distinction between non-volatile, semi-volatile and volatile compounds.

Volatile compounds, those that show more than 95% by weight evaporation under ambient conditions at six months, are completely available to form ozone commensurate to their individual reactivity rate. The study demonstrates that some LVP solvents being categorized as non-volatile clearly volatilized at ambient conditions, nearly as rapidly as the traditional high volatility solvents they are meant to replace. Light distillate evaporates at nearly an identical rate as IPA. Benzyl alcohol evaporates at nearly an identical rate as NMP. IPA and NMP are both commonly accepted as volatile solvents, while light distillate and benzyl alcohol would be likely respective LVP replacements. On a pound for pound conversion from commonly accepted volatile solvents to LVP solvents, there could be no change in emission generation or ozone formation.

Non-volatile compounds, those that show less than five percent by weight evaporation under ambient conditions at six months, are generally not available to contribute to ozone formation. Methyl palmitate and glycerol are clearly non-volatile, though they are often calculated as VOCs in traditional test methods. Due to its negligible evaporation rate, methyl palmitate is a suitable endpoint for GC VOC test methods; it elutes just after volatile and semi-volatile compounds. Alkyl alkanolamine, bio-based oils (i.e. soy oil) and glycerol are sometimes considered volatile despite their extremely low evaporation rates and thus may be unnecessarily excluded as possible alternative solvents.

Semi-volatile compounds, those that show between five and 95% by weight evaporation under ambient conditions at six months, are the most difficult category of compounds to calculate VOC content. Regulatory exemptions and GC test methods define a compound as either volatile or non-volatile. Semi-volatile compounds challenge the pass or fail nature of endpoints in regulatory exemptions and GC VOC methods. In these cases, the choice of an endpoint may exempt one compound allowing unrestricted use while prohibiting another, even though they have nearly identical evaporation profiles. As an example, 2,2,4-trimethylpentanediol diisobutyrate has a boiling point of 280°C, completely evaporates in 147 days in the ambient evaporation study, and is not considered a VOC solvent by Green Seal. On the other hand 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate has a boiling point of 255°C, is considered a VOC by Green Seal, but evaporates more slowly than 2,2,4-trimethylpentanediol diisobutyrate (154 days). A more equitable solution may be to assign partial VOC content values to semi-volatile materials in GC methods and to avoid pass or fail exemption criteria.

This study provides ample evidence and findings to warrant a reevaluation of regulatory standards. Current definitions may lead to regulations that exclude otherwise viable alternatives or allow substitutions of chemicals that may limit the environmental benefits sought in the regulation. Boiling point and number of carbon atoms do not appear to be a reliable indicator of volatility. Vapor pressure may correlate well with volatility but at a value much lower than 0.1 mm Hg at 20°C which is problematic to accurately measure. M24 results show higher volatility than any of the other test methods. E1868 results most closely replicated ambient evaporation

results. However, more work is necessary to refine TGA parameters that better align with ambient evaporation studies. GC methods for determining VOC should incorporate an endpoint, such as methyl palmitate, to avoid overestimating VOC content from clearly non-volatile compounds. Additionally, GC VOC methods should consider excluding compounds that elute early but do not evaporate in a reasonable time under ambient conditions, particularly glycerol. Further work is necessary to address semi-volatile materials in GC VOC methods to reflect their contributions to ozone formation. Finally, efforts to establish physical property endpoints, such as vapor pressure, carbon number or boiling point, should be carefully assessed to ensure that the exemption of LVP solvents is truly based on their lack of availability to participate in atmospheric photochemical reactions.

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KEYWORDS

VOC, volatility, measurement, LVP, test method, evaporation, EPA Method 24, non-volatile, coatings, consumer products, thermogravimetric, TGA, gas chromatography, GC, MIR