United States
Consumer Product Safety Commission

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CPSC Staff Statement[1] on Jensen Hughes "Odorants for use with Flammable Refrigerants ASHRAE 97 Compatibility Tests Final Report"

The report, "Odorants for use with Flammable Refrigerants ASHRAE 97 Compatibility Tests Final Report," presents the findings of research conducted by Jensen Hughes under Contract Order No. 20346020P0004. CPSC sponsored this work to address safety concerns that have been raised by stakeholders regarding the near-term, wide-scale integration of flammable refrigerants in household appliances. CPSC does not require the use of these flammable refrigerants but is aware that manufacturers are replacing current refrigerants in their consumer products, which have a high global warming potential (GWP), with flammable refrigerants that have a low GWP.

<u>Background:</u> The refrigerants currently used in heating, ventilation, air-conditioning, and refrigeration (HVAC&R) appliances are being phased out by several U.S. states based on their high GWP, which is much greater than carbon dioxide. These changes are resulting in moves by firms to use new low-GWP refrigerants. However, the low-GWP refrigerants that would be used in household appliances are flammable, whereas previous refrigerants used were not. Flammable refrigerants could pose fire and explosion hazards if leaked from an appliance. One potential method to address these hazards would be to odorize the refrigerants, much like the fuel gas industry does with natural gas and liquid petroleum gas. The odor could alert a consumer to refrigerant leaking from an appliance. However, the compatibility of odorants with the substances used in HVAC&R appliances has not been previously studied. The goal of Contract Order No. 20346020P0004 was to help learn if low-GWP refrigerants could be compatible with the components within HVAC&R systems.

<u>Study:</u> For the study, CPSC contracted with Jensen Hughes to assess material compatibility of candidate odorants in combination with the low GWP refrigerants, lubricants, and metals. Jensen Hughes utilized the ASHRAE Standard 97-2007 methodology. The evaluated odorants were chosen based on previous work performed for ASHRAE[2] and included hydrogen sulfide (H_2S), carbonyl sulfide (COS), trimethylamine (TMA, $(CH_3)_3N$), ethyl mercaptan (C_2H_5SH), dimethyl sulfide (DMS, $(CH_3)_2S$), and methyl ethyl sulfide (MES, $(C_2H_5)S(CH_3)$). These were used to odorize the following low-GWP refrigerants, which are expected to be used in future

[1] This statement was prepared by the CPSC staff, and the attached report was prepared by Jensen Hughes for CPSC staff. The statement and report have not been reviewed or approved by, and do not necessarily represent the views of, the Commission.
[2] Forssell, E.W., "1794-TRP, White Paper Investigation Relating to the Use of Odorants in Flammable Refrigerants", RP-1794, Final Report, ASHRAE, Atlanta, GA, 2019.

HVAC&R appliances: difluoromethane (R-32[3], A2L[4], CH_2F_2), 2,3,3,3 tetrafluoropropene (R-1234yf[2], A2L, $C_3H_2F_4$), and propane (R-290[2], A3, C_3H_8). The classes of lubricants chosen were polyolester oil (POE), polyalkylene glycol oil (PAG), and polyvinylether oil (PVE), all of which are common in HVAC&R appliance compressors. The metals chosen were copper, steel, and aluminum because they are all common in HVAC&R refrigerant systems.

Results: Testing of each of the candidate odorants resulted in at least one combination of the odorant, refrigerant, and lubricant that indicated material incompatibility. However, most of the combinations of odorant, refrigerant, and lubricant suggested possible compatibility. Additional work is needed to further assess the possibility of odorizing low-GWP refrigerants in HVAC&R systems.

[3] ASHRAE Refrigerant Number
[4] ASHRAE Standard 34 Classification, A2L refrigerants have a lower toxicity and some but lower flammability, A3 refrigerants have lower toxicity and higher flammability

Odorants for use with Flammable Refrigerants

ASHRAE 97 Compatibility Tests

Final Report

Order No. 20346020P0004

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Executive Summary

This work performed a series of material compatibility tests involving candidate odorants for use with flammable refrigerants in the Heating, Ventilation, Air Conditioning, and Refrigeration (HVAC&R) industry applications. The candidate odorants involved were previously identified during the ASHRAE white paper on this topic as well as three additional odorants that are in use with natural gas. The performed tests evaluated the compatibility of odorants with common materials of construction (steel, copper, and aluminum) and with the lubricants and refrigerants being pursued as low global warming potential alternatives. These tests were a second step in the development of odorants for use in this application. Additional evaluation of these odorants is needed to fully determine the suitability of the candidate odorants and to facilitate their successful application. An outline of the recommended additional evaluations was prepared.

The three of the four candidate odorants from the ASHRAE white paper study: hydrogen sulfide (H_2S), carbonyl sulfide (COS), and trimethylamine ($(CH_3)_3N$) as well as three candidate odorants from the natural gas industry: ethyl mercaptan (C_2H_5SH), dimethyl sulfide - DMS ($(CH_3)_2S$), and methyl ethyl sulfide - MES ($(C_2H_5)S(CH_3)$), were evaluated during these tests. These candidate odorants were paired with three low GWP refrigerants: difluoromethane (R-32, classified by ASHRAE 34 as an A2L refrigerant), 2,3,3,3 tetrafluoropropene (R-1234yf, classified by ASHRAE 34 as an A2L refrigerant) and propane (R-290, classified by ASHRAE 34 as an A3 refrigerant) in combinations with three lubricants: polyolester oil (POE), polyalkylene glycol oil (PAG) and polyvinylether oil (PVE). 31 combinations and 9 control sets (without odorants) were sealed in glass tubes with copper, steel, and aluminum coupons. The glass tubes were heated and stored for 14 days to simulate aging. The tubes were then observed for changes in color or appearance and the lubricant was analyzed utilizing a modified ASTM D644 method, Ion Chromatography (IC) and Inductively Coupled Plasma (ICP) for changes during the simulated aging and compared to the control tubes that did not have the odorants present in the combination.

The hydrogen sulfide (H_2S) candidate odorant had the lowest boiling point of the candidate odorants and was evaluated in combination with R-32 which had the lowest boiling point of the three refrigerants. During the evaluation, the exposed steel and copper coupons were discolored which is an indication of a reaction between the odorant and these metals. The total organic acid anions (TOA) as determined by IC analysis and total acid number (TAN) as determined by a modified ASTM D644 analysis were elevated during these tests. H_2S was not evaluated with the other refrigerants.

The carbonyl sulfide (COS) candidate odorant was only tested in combination with the R-32 refrigerant. A light cloudiness in appearance of the liquid developed over the exposure, especially in combination with the PAG lubricant, and as a slight darkening of the exposed steel coupons was observed.

The ethyl mercaptan (C_2H_5SH) candidate odorant was tested with the R-290 refrigerant and PAG lubricant. This combination resulted in the formation of a precipitate during the exposure as well as the discoloration of copper coupon. The steel coupon was also discolored, but not to the extent that the copper coupon was. This test also had an elevated TAN value relative to the control tests without an added odorant. This was the only combination evaluated with the ethyl mercaptan. The methyl mercaptan originally identified as a candidate odorant in the ASHRAE White Paper Investigation would be expected to have performed similarly during these tests.

The other two added candidates, DMS and MES, were the only candidates evaluated with all three refrigerants and lubricants. The evaluations with the POE and PVE lubricants in combination with the R-1234yf and R-290 refrigerants resulted in slight discoloration of the steel and copper coupons. The discoloration of the copper coupon was more pronounced for the DMS odorant, R-290 refrigerant and POE lubricant combination. The combinations with these two odorants and the PVE lubricant and R-1234yf refrigerant resulted in elevated TOA values. The combination of MES odorant, R-290 Refrigerant and PVE lubricant had an elevated TOA value as well.

Trimethylamine ($(CH_3)_3N$) was evaluated with R-1234yf and R-290. The exposed metal coupons were unchanged with the exception of the R-290 refrigerant, PVE lubricant combination where the steel coupon was slightly darkened. The TAN values for the trimethylamine odorant, R-290 refrigerant, and PAG or PVE lubricant combinations were elevated.

Each of the candidate odorants had at least one combination of refrigerant and lubricant that had an adverse result. However, the majority of the combinations without an observed difference between the combinations with the odorants present and the controls without the odorant present. The observed differences were, in general, mild in nature, with the exception of the combinations involving the hydrogen sulfide or the ethyl mercaptan candidate odorants.

In order to fully evaluate these candidates, additional analysis would be necessary. This analysis would include:

- Confirmation of the Odorant Amount Required. The odorant concentration in the mixtures tested were estimated to result in odorant concentrations that would be higher than twice the lower detection threshold for the odorant when the refrigerant was at 25% of its lower flammable limit. Research should be conducted to determine if the margins above the lower detection threshold is sufficiently noticeable to provide the intended warning.

- Chemical Stability Testing. The stability of the added odorant in the refrigerant lubricant mixture should be evaluated. If the odorant is reacting with the refrigerant, lubricant or the materials of construction to form compounds that are not as easily detected (higher odor detection threshold), then the ability of the odorant to provide the desired warning would fade over time.

- Impact of odorant addition on refrigerant loop performance: This effort would include measuring the loop efficiency and design compensations (larger coils, higher/lower pressure) due to addition of odorant in the refrigeration loop.

- Additional Material Compatibility tests: This effort would include performing the material compatibility tests for standard materials such as brass, copper, rubber, nylon etc. These tests would address issues related to solvation, crazing, and any reactions due to addition of odorant in the refrigerant.

- Refrigerant and odorant dispersion modeling and testing: This effort would include performing both testing and computer modeling to assess performance of odorant for different leak scenarios. These scenarios can include vapor/liquid leaks with conditions corresponding to different refrigeration components such as compressor, evaporator etc.

- Toxicity evaluation: This effort would include evaluation of toxicity levels due to exposure of odorant to appliance manufacturers, technicians, and owners.

- Odorant distribution measurement: This effort would include measurement of odorant in different locations within the refrigeration systems such as compressor, condenser, evaporator etc. As the odorants concentration may be non-uniform throughout the loop, the task would help to evaluate the quantity of odorant to be added to a particular refrigerant.

Disclaimer: The evaluation of the identified odorants presented in this report is preliminary in nature. Further, in depth evaluation is required to assess the suitability of these candidates in this application.

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Background

The desire to reduce the global warming impact associated with refrigerant use is leading to increased use of low global warming potential (GWP) refrigerants, which are flammable. Currently, the use of these refrigerants is limited to residential type refrigerators and other small appliances based on the amount of the refrigerant present in the appliance due to the risk associated with the flammability of these refrigerants. These limitations are expected to be relaxed to allow for increased use in larger systems and appliances in order to reduce the global warming impact associated with Heating, Ventilation, Air-Conditioning, or Refrigeration (HVAC&R) equipment, while accepting an increased safety risk. The low GWP refrigerants are odorless and colorless providing no warning of their presence following a leak from a HVAC&R appliance. One potential method for providing a warning of developing dangerous conditions would be to add an odorant to the refrigerant that alert personnel/residents to its presence.

Odorants are added to natural gas supplies for use in household appliances to provide warning of supply line leaks that could lead to dangerous conditions. The odorant added, commonly ethyl mercaptan, flows with the natural gas through the pipeline and is ultimately consumed in the natural gas flames of the appliance. It has a relatively short residence time in the supply piping, on the order of a few hours. The odorants added have a higher boiling point than the natural gas it flows with and will plate the walls of the system piping. As the natural gas and odorant is constantly flowing through the piping, an equilibrium is established between the odorant lining the walls of the piping and that dispersed within the flowing the natural gas. In this application the odorant needs to be compatible with the natural gas and the piping materials, commonly steel, be flammable so that it is completely consumed in the appliance flames and not present a toxicity hazard either prior to combustion or after combustion.

For an odorant applied to a HVAC&R appliance, the residence time in the refrigerant loop would be the 10 to 15 year lifespan of the appliance. This would emphasize the need to be compatible with the materials of construction and with the lubricant and refrigerant with which it would be exposed. The attributes of an odorant for use in this application would be as follows:

- Non-toxic, at least at the concentrations that residents would be exposed to.
- Easily detected, limiting the amount of the odorant that needs to be added in order to be effective.
- Compatible with the refrigerants and lubricants that it would be teamed with and with the materials of construction utilized in the HVAC&R Industry (Copper, Aluminum and Steel).
- Have only a limited impact of the appliance efficiency. Plating of the odorant on the tubing or piping walls, that is common for the odorants utilized in the natural gas industry applications, could have a negative impact on the appliance performance.

A white paper study was conducted by The American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE) that reviewed the potential application of an odorant with low GWP flammable refrigerants [1]. A few potential candidate odorants were identified that could provide an indication of the presence of the refrigerant. The study pointed out several issues that needed further investigation in order to apply the potential candidate odorants in the HVAC&R industry. One of these identified issues for further evaluation was the compatibility of the candidate odorants with the refrigerant, compressor lubricant, and metals used in system components to which it would be exposed.

Acknowledgement

This project was conducted under the auspices of the Consumer Product Safety Commission (CPSC). A volunteer project advisory committee was assembled and provided invaluable assistance and advice in the conduct of this project. The members of the committee are gratefully acknowledged and listed below:

Marc Scancarello	Emerson
Julie Majurin	AHRI
Jessica Demott	Arkema
Xudong Wang	AHRI
Elyse Sorenson	Trane Technologies
Valerie Baish Lisi	Carrier
Randy Cooper	AHAM
Chris Seeton	Shrieve Chemical Products
Scott Ayers	CPSC COR

Objective

The objective of this project is to evaluate the material compatibility of the identified odorants in combination with the low GWP refrigerants, lubricants and metals utilizing the ASHRAE Standard 97-2007 methodology [2].

Approach

The ASHRAE Standard 97-2007 method involves sealing mixtures of the refrigerant and lubricant in a glass tube with metal coupons representing the materials of construction that the mixture would be exposed to during HVAC&R applications. The sealed tube is heated to an elevated temperature, typically 175 °C (347 °F), to represent accelerated aging and observed for changes over a 14-day exposure period. The refrigerant, lubricant and metal coupons are then examined and analyzed for signs of adverse effects.

During this project, the gaseous candidate odorants were added to the refrigerant prior to its introduction to the glass tubes, while the liquid candidate odorants were added to the lubricant prior to the addition of the refrigerant. The impact of the odorant presence was determined by comparison of the glass tubes that had the odorant present in the mixture to a set of glass tubes that contained the refrigerant and lubricant mixtures that did not contain the odorant (controls).

Candidate Odorants

The three of the four candidate odorants that were identified during the ASHRAE study [1] will be included in this project. These odorants are: Hydrogen Sulfide (H_2S), Carbonyl Sulfide (COS) and

Trimethylamine ($(CH_3)_3N$). They were selected based on their similar boiling points to the flammable, low GWP refrigerants that were the target of the study. Methyl Mercaptan (CH_4S) was not included due to material acquisition issues. Selected properties of these candidate odorants are given in Table 1.

In addition to the previously identified candidate odorants, three additional odorants that are used for natural gas or LPG, were included in this study. These odorants are Ethyl Mercaptan (C_2H_6S), Dimethyl Sulfide ($(CH_3)_2S$), and Methyl Ethyl Sulfide ($CH_3SC_2H_5$). These odorants have higher boiling points than the low GWP refrigerants but have high enough vapor pressures to allow them to be well above the detection threshold based on the refrigerant – odorant - air vapor mixture resulting from a leak in the refrigerant loop when the refrigerant is at 25% of the refrigerant's LFL. Selected properties of these candidate odorants are given in Table 1.

The trimethylamine and carbonyl sulfide were acquired from SynQuest Laboratories. The hydrogen sulfide, ethyl mercaptan, dimethyl sulfide, and methyl ethyl sulfide were acquired from Sigma Aldrich. Certificates of Conformity are given in Appendix A.

Table 1 – Odorant Properties [1,3-11]

Property		Units	Carbonyl Sulfide	Hydrogen Sulfide	Methyl Mercaptan	Trimethyl amine	Ethyl mercaptan	Dimethyl Sulfide	Methyl Ethyl Sulfide
Formula			COS	H_2S	CH_4S	$(CH_3)_3N$	C_2H_5SH	$(CH_3)_2S$	$(CH_3)S(C_2H_5)$
Molecular Weight			60.07	34.08	48.11	59.112	62.134	62.135	76.162
Normal Melting Point		[°C]	-139	-82	-123	-117	-144	-98	-106
		[°F]	-217.8	-115.6	-189.4	-178.6	-227.9	-144.4	-158.8
Normal Boiling Point		[°C]	-50.2	-60.0	6.0	2.85	35	37.35	66.65
		[°F]	-58.4	-76.0	42.7	37.1	95.0	99.2	152.0
Vapor Pressure @ 25 °C (77 °F)		[kPa]	906	1,839	205	193	71	64	22
		[psia]	131	267	30	28	10	9	3
Lower Flammability Limit		[% Vol]	11.9	4	3.9	2	2.8	2.2	8.6
NFPA Diamond Label	Fire Hazard		4	4	4	4	4	4	3
	Health Hazard		3	4	4	3	1	2	1
	Reactivity		1	0	1	0	0	0	0
Odor Detection Limit		[ppm]	0.055	0.00047	0.0021	0.0021	0.001	0.001	0.002
Toxicity Assessment	TWA	[ppm]	5	1	1	5	1	10	
	STEL	[ppm]		5		15	10		

NFPA Diamond Label – Relative hazard rating for a chemical compound ranging from 0 – no or minimal hazard to 4 – severe hazard relative to flammability, toxicity, stability or special hazards in accordance with NFPA Standard 704 [11].

TWA – Maximum permissible time weighted average concentration over an 8-hour period

STEL – Short term exposure limit, 15-minute duration unless specified.

Low Global Warming Potential (GWP) Refrigerants

The three refrigerants included in this project are: difluoromethane (R-32); 2,3,3,3 tetrafluoropropene (R-1234yf); and propane (R-290). R-32 and R-1234yf, are classified by ASHRAE Standard 34 as A2L refrigerants while R-290 is classified by ASHRAE Standard 34 as an A3 refrigerant. They were included in the previous ASHRAE study [1].

Refrigerants in commercial applications are classified by safety groups in accordance with ASHRAE Standard 34 [12]. The classification is designated by a capital letter based on toxicity followed by a number designating flammability. Refrigerants in toxicity group A are non-toxic up to a concentration of 400 ppm(vol). Toxicity group B refrigerants exhibit toxic effects at concentrations of less than 400 ppm (vol). Flammability group 1 refrigerants are non-flammable. Flammability group 2 refrigerants have a lower flammability limit of greater than 0.1 kg/m^3 and have a heat of combustion of less than 19 kJ/kg. Flammability group 3 refrigerants have flammability limits below 0.1 kg/m^3 or have a heat of combustion of greater than 19 kJ/kg. Flammability group 2 is further divided with a sub-group designated as 2L refrigerants with a burning velocity of less than 10 cm/sec.

Selected properties of these refrigerants are given in Table 2 and a comparison of the vapor pressures of the candidate odorants and these refrigerants is given in Figure 1. Riedel's vapor pressure correlation [3] was used to compare the vapor pressures of the refrigerants and the potential odorants. This correlation is as follows:

$$\ln\left(P_{vpr}\right) = A - \frac{B}{T_r} + C\ln(T_r) + D\,T_r^6$$

$$A = -35\,Q$$

$$B = -36\,Q$$

$$C = 42Q + \propto_c$$

$$D = -Q$$

$$Q = 0.0838(3.758 - \propto_c)$$

$$\propto_c = \frac{0.315\,\varphi_b + \ln\,(P_c)}{0.0838\,\varphi_b - \ln\,(T_{br})}$$

$$\varphi_b = -35 + \frac{36}{T_{br}} + 42\ln(T_{br}) - T_{br}^6$$

Where P_{vpr} is the reduced vapor pressure (P_{vp}/P_c), T_r is the reduced temperature (T/T_c), T_{br} is the reduced boiling point (T_b/T_c), T_c is the critical temperature, P_c is the critical pressure, P_{vp} is the vapor pressure, T is the temperature, T_b is the normal boiling point and A, B, C, D, Q, φ_b and α_c are correlation constants.

Table 2 – Refrigerant properties [3,12,13]

Property	Units	HFC-32	HFO-1234yf	R-290
Formula		CH_2F_2	$CF_3CF{=}CH_2$	C_3H_8
ASHRAE 34 Classification		A2L	A2L	A3
Molecular Weight		52.00	114.00	44.10
Critical Temperature	[°C]	78.5	94.8	96.7
	[°F]	173.2	202.6	206.0
Critical Pressure	[kPa]	5,830	3,382	4,266
	[psia]	846	491	619
Normal Melting Point	[°C]	-136	-150	-188
	[°F]	-212.8	-238.0	-306.4
Normal Boiling Point	[°C]	-53.2	-29.2	-42.1
	[°F]	-63.8	-20.6	-43.7
Liquid Density @ Ambient Temp	[kg/m^3]	960	1,094	501
	[lb/ft^3]	59.9	68.3	59.9
Vapor Density @ Ambient Temp and Press	[kg/m^3]	2.13	4.66	1.80
	[lb/ft^3]	0.133	0.291	0.113
Vapor Pressure @ 25 °C (77 °F)	[kPa]	1,700	673	853
	[psia]	247	98	124
Ozone Depletion Potential (ODP)	R-12=1.0	0	0	0
Global Warming Potential (GWP)	CO_2=1.0	675	4	3.3
Lower Flammability Limit @ 23 °C (73 °F)	[% Vol]	14	6.2	2.1
	[kg/m^3]	0.30	0.29	0.038
	[lb/ft^3]	0.019	0.018	0.0024
Upper Flammability Limit @ 23 °C (73 °F)	[% Vol]	31	12.3	9.5
	[kg/m^3]	0.66	0.57	0.17
	[lb/ft^3]	0.041	0.036	0.011
Heat of Combustion	[MJ/kg]	9.55	10.7	50.35
	[Btu/lb]	22,213	24,888	117,114
Burning Velocity	[cm/s]	6.7	1.5	39
	[ft/s]	0.22	0.05	1.28

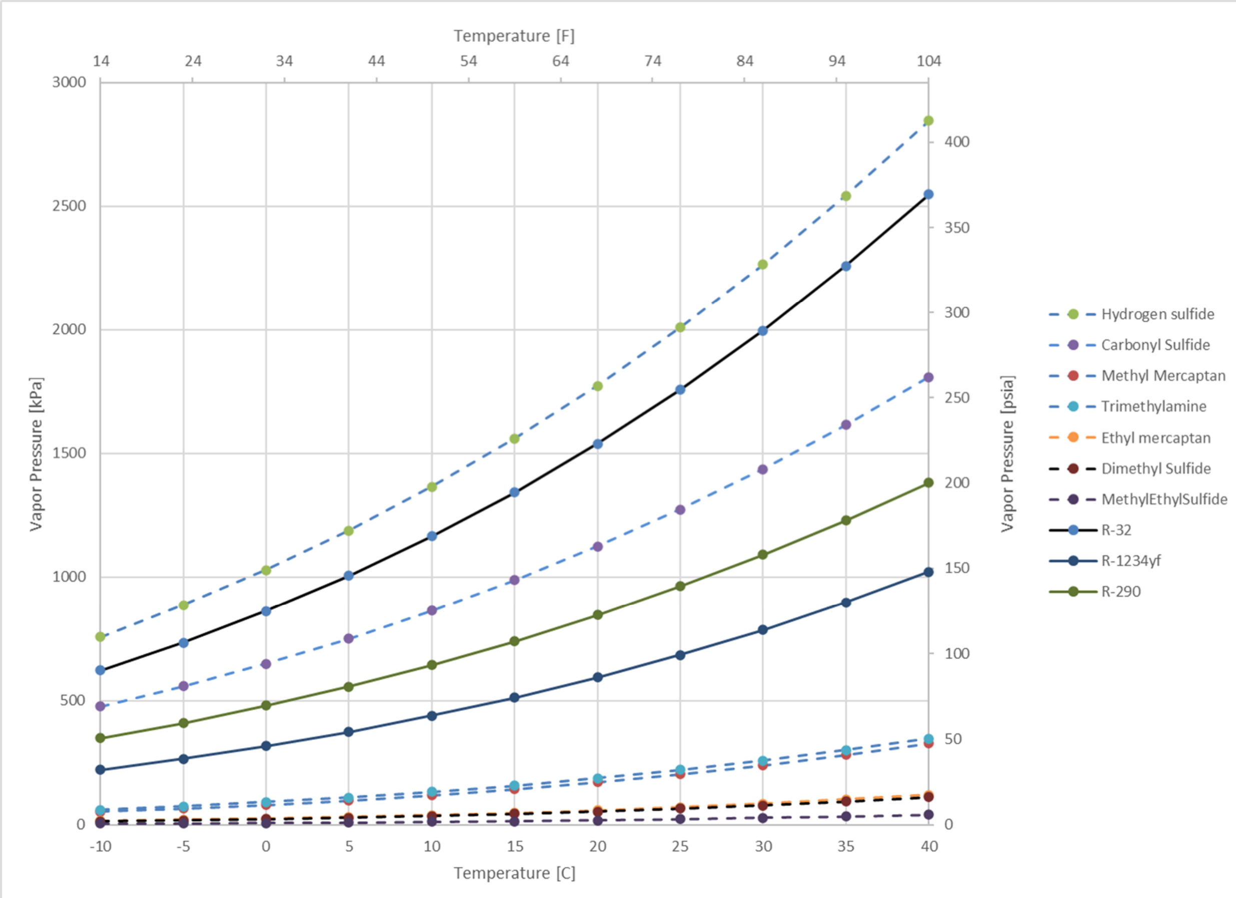


Figure 1 – Vapor pressures of candidate odorants and low GWP refrigerants

Lubricants

The three lubricants are: a polyalkylene glycol (PAG) oil (double capped 46 cS viscosity grade with 0.1% BHT additive), a polyolester (POE) oil (mixed acid 32 cS viscosity grade with 0.1% BHT additive) and a polyvinylether (PVE) oil (68 cS viscosity grade). The lubricants were provided without their normal additives that are used to increase their service life in the appliances. The lubricants utilized were provided by Emerson and Shrieve Chemical Products

Odorant Minimum Use Requirements

The amount of odorant required would depend on the detection limit relative to the lower flammable limit of the refrigerant. With the assumption that the refrigerant and the odorant would not separate after leaking from a refrigerant loop (no condensation of either odorant or refrigerant), the mass of odorant required, M_{odor}, could be estimated as follows [1]:

$$M_{odor} = M_{Ref}\left(\frac{F_{Safety}Thr_{odor}\rho_{odor}}{F_{LFL}LFL_{Ref}\rho_{Ref}}\right)$$

$$Y_{odor} = \frac{\left(\frac{F_{Safety}Thr_{odor}}{F_{LFL}LFL_{Ref}}\right)}{1+\left(\frac{F_{Safety}Thr_{odor}}{F_{LFL}LFL_{Ref}}\right)}$$

Where M_{odor} is the mass of the odorant, Y_{odor} is the minimum odorant concentration in the mixture at the leak, M_{ref} is the mass of refrigerant, F_{Safety} is the factor of safety applied to the odorant detection threshold, Thr_{odor} is the detection threshold of the odorant (by vol), ρ_{odor} is the vapor density of the odorant, F_{LFL} is the safety factor applied the lower flammability limit of the refrigerant, LFL_{Ref} is the lower flammable limit of the refrigerant and ρ_{Ref} is the vapor density of the refrigerant. For example, carbonyl sulfide, which has a detection threshold of 0.055 ppm and a vapor density of 2.46 kg/m3 (0.153 lb/ft3), would require 0.0036 g per kg of R-32 (3.6×10^{-5} lb/lb of R-32) to be detectable with a safety factor of 2 at 25% of the LFL of 14% by volume for R-32.

The above equations for the odorant requirements are based on the assumption that the phase composition of the odorant-refrigerant-lubricant mixture does not vary significantly from the overall composition of the mixture other than the absence of the lubricant in the vapor phase. For the higher boiling point odorants, this assumption may be challenged. As a check on this, the odorant composition was estimated utilizing the Peng Robinson Equation of State with geometric mixing rules and the Rachford Rice procedure [3,14]. The estimated vapor phase composition was then compared to the minimum odorant composition at the leak site. This comparison is shown in Tables 3 through 5 with the vapor phase composition estimated when 50% of the mixture had been vaporized/condensed at -12^{o}C (10^{o}F) and 32^{o}C (90^{o}F). The estimated odorant composition for these mixtures is given in Figures 2 through 12 as a function of the fraction of the refrigerant odorant lubricant mixture. The overall composition of the odorant in the mixture was 50 ppm (wt) relative to the refrigerant and the lubricant was 5% of the refrigerant mass. The odorant composition was increased to 150 ppm (wt) relative to the refrigerant composition for dimethyl sulfide (DMS), methyl ethyl sulfide (MES) and ethyl mercaptan (EMC) in an attempt to compensate for the higher boiling point of these odorants relative to the three refrigerants. Details of the estimated phase compositions are given in Appendix B.

During a leak from a refrigerant loop, the flow through the leak would be expected to consist of both the vapor phase and the liquid phase with the amount of each consistent with the location of the leak in the loop, leak size and whether the compressor is operating or not.

Table 3 – Odorant Mass and Vapor Composition Comparison for R-32 {BP: -53.2 °C (-63.8°F) LFL: 14%}

		Boiling Point		Odor Threshold	Odorant Mass Required*	Min Required Odorant Composition at leak	Overall Composition (Used for Estimate)		Estimated Odorant Vapor Composition at -12°C (10°F)			Estimated Odorant Vapor Composition at 32°C (90°F)		
									At Leak	At 25% Ref. LFL		At Leak	At 25% Ref. LFL	
Odorant	Formula	[°C]	[°F]	[ppm]	[ppm wt]	[ppm]	[ppm wt]	Rel. to Mass Req.	[ppm]	[ppm]	Rel. to Threshold	[ppm]	[ppm]	Rel. to Threshold
Hydrogen Sulfide	H_2S	-60	-76	0.00047	0.018	0.027	50.0	2841	87.9	3.08	6546	82	2.87	6107
Carbonyl Sulfide	COS	-50.2	-58.36	0.055	3.631	3.143	50.0	14	39.3	1.38	25	38.5	1.35	25
Dimethyl Sulfide	$(CH_3)_2S$	37.35	99.2	0.001	0.068	0.057	150.0	2197	8.6	0.301	301	22.7	0.795	795
Methyl Ethyl Sulfide	$(CH_3)S(C_2H_5)$	66.65	151.94	0.002	0.167	0.114	150.0	896	2.1	0.074	37	8.1	0.284	142

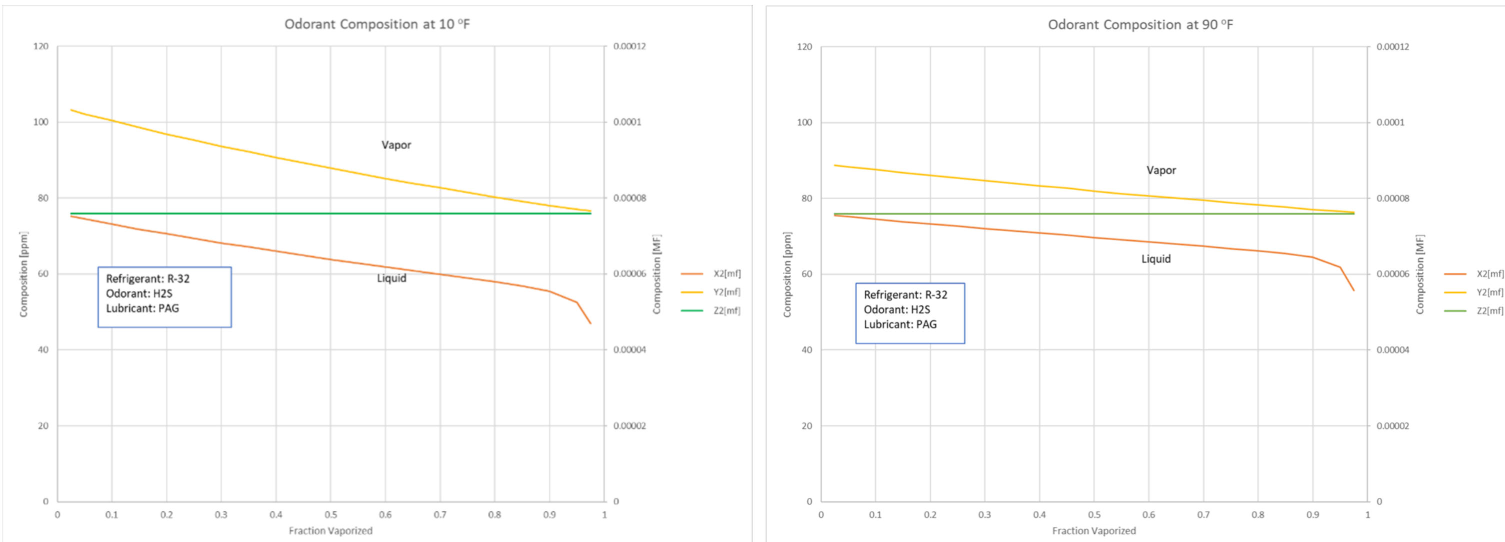
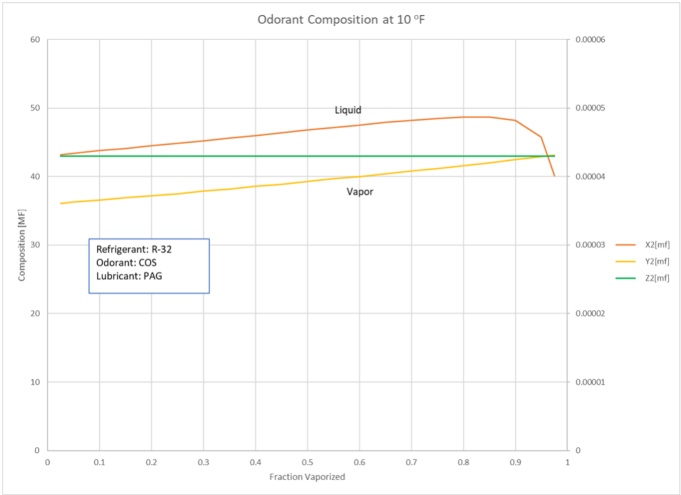


Figure 2 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-32, hydrogen sulfide and PAG lubricant as a function of vaporization fraction



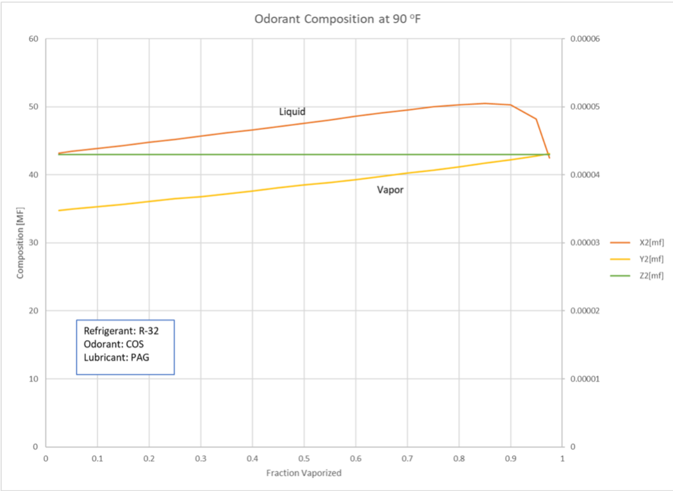
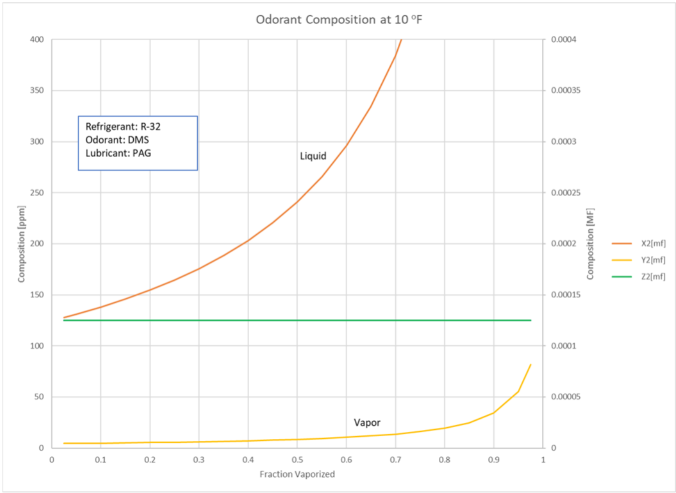


Figure 3 – Odorant Composition in the vapor and liquid phases at -12ºC (10ºF) and 32ºC (90ºF) for R-32, carbonyl sulfide and PAG lubricant as a function of vaporization fraction



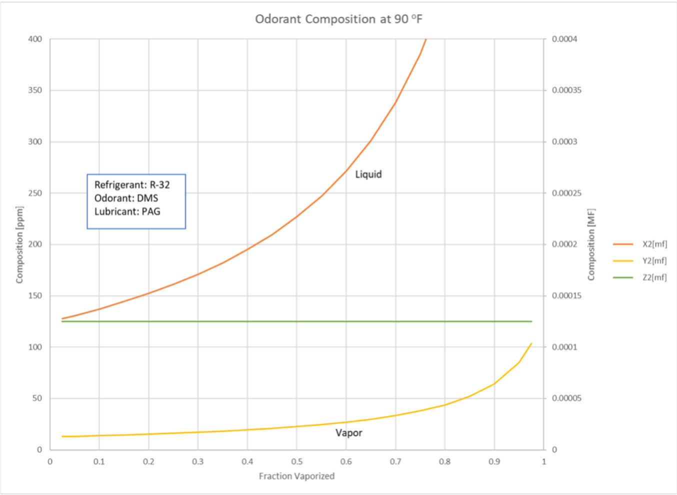


Figure 4 – Odorant Composition in the vapor and liquid phases at -12ºC (10ºF) and 32ºC (90ºF) for R-32, dimethyl sulfide and PAG lubricant as a function of vaporization fraction

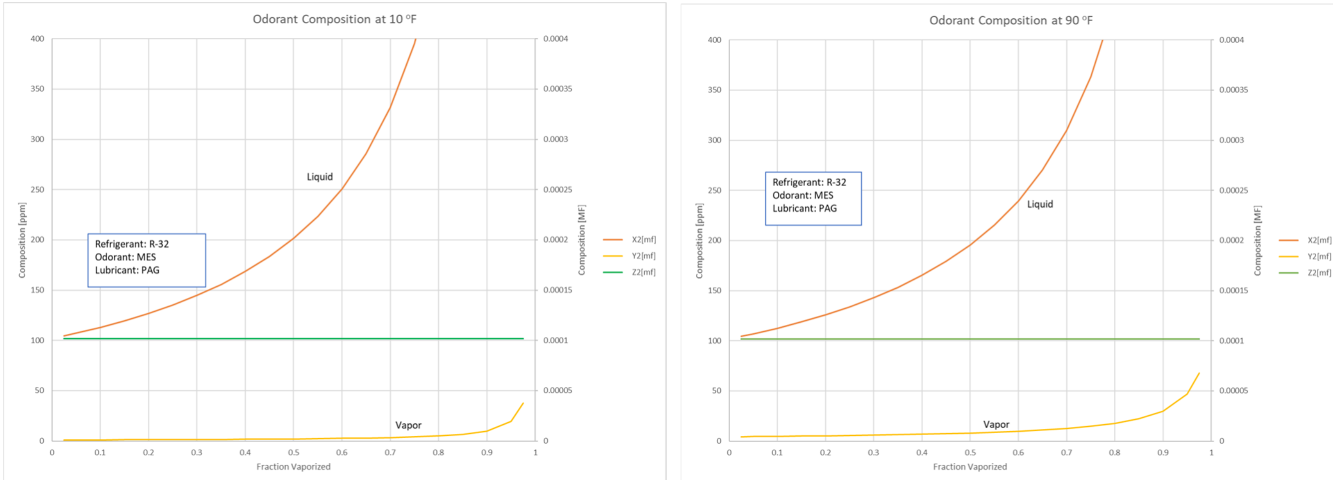


Figure 5 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-32, methyl ethyl sulfide and PAG lubricant as a function of vaporization fraction

Table 4 – Odorant Mass and Vapor Composition Comparison for R-1234yf {BP: -29.2°C (-20.6°F) LFL: 6.2%)

Odorant	Formula	Boiling Point		Odor Threshold	Odorant Mass Required*	Min Required Odorant Composition at leak	Overall Composition (Used for Estimate)		Estimated Odorant Vapor Composition at -12°C (10°F)			Estimated Odorant Vapor Composition at 32°C (90°F)		
									At Leak	At 25% Ref. LFL		At Leak	At 25% Ref. LFL	
		[°C]	[°F]	[ppm]	[ppm wt]	[ppm]	[ppm wt]	Rel. to Mass Req.	[ppm]	[ppm]	Rel. to Threshold	[ppm]	[ppm]	Rel. to Threshold
Trimethylamine	$(CH_3)_3N$	2.85	37.1	0.0021	0.141	0.271	50.0	356	47.5	0.74	351	63.3	0.98	467
Dimethyl Sulfide	$(CH_3)_2S$	37.35	99.2	0.001	0.070	0.129	150.0	2133	62.2	0.964	964	116.2	1.801	1801
Methyl Ethyl Sulfide	$(CH_3)S(C_2H_5)$	66.65	151.94	0.002	0.172	0.258	150.0	870	14.1	0.219	109	42.1	0.653	326

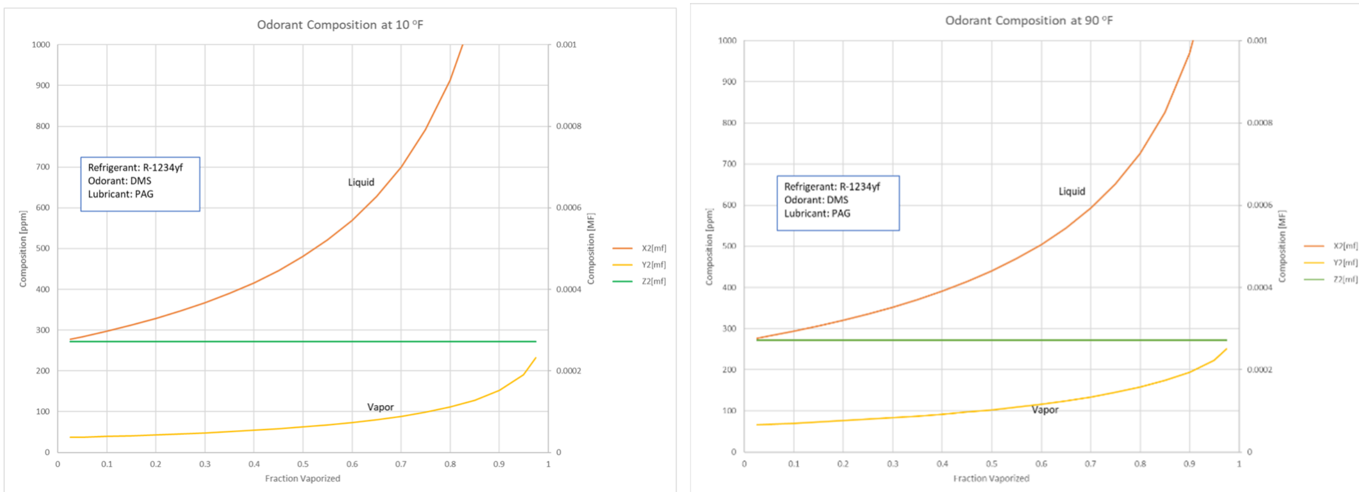


Figure 6 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-1234yf, dimethyl sulfide and PAG lubricant as a function of vaporization

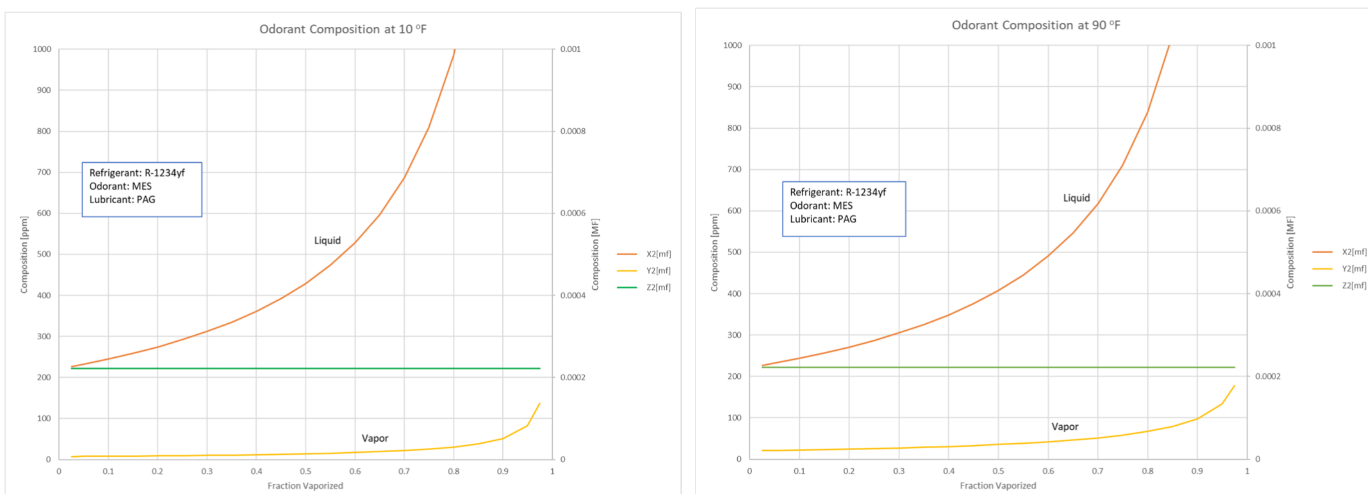


Figure 7 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-1234yf, methyl ethyl sulfide and PAG lubricant as a function of vaporization

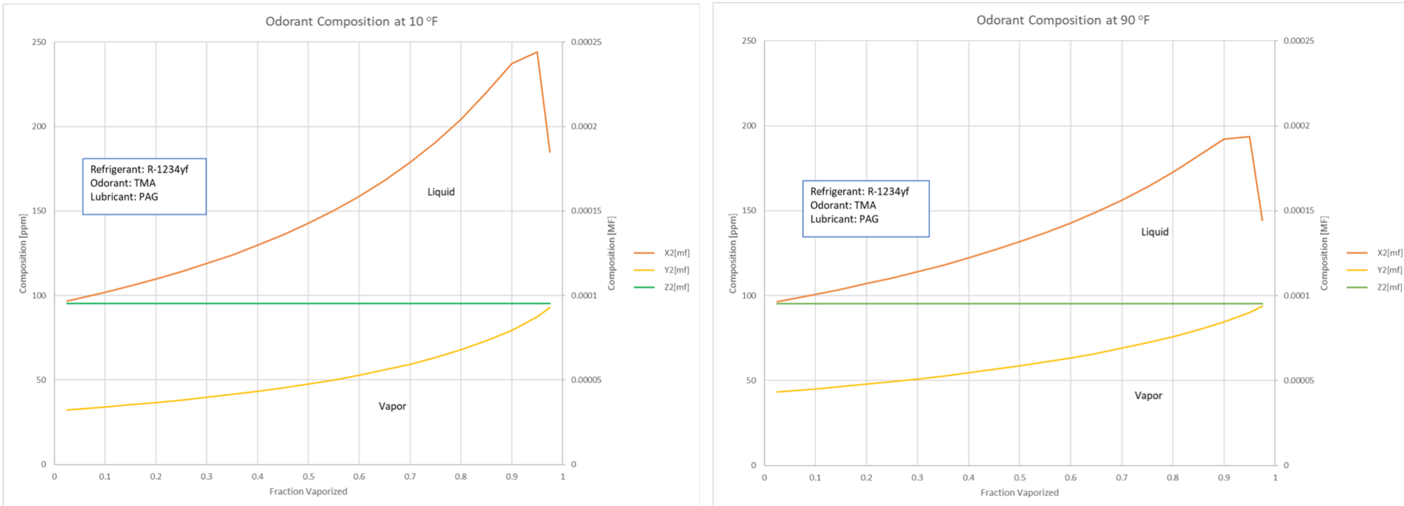


Figure 8 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-1234yf, trimethylamine and PAG lubricant as a function of vaporization

Table 5 – Odorant Mass and Vapor Composition Comparison for R-290 {BP: -42.1°C (-43.7°F) LFL: 2.1%}

Odorant	Formula	Boiling Point		Odor Threshold	Odorant Mass Required*	Min Required Odorant Composition at leak	Overall Composition (Used for Estimate)		Estimated Odorant Vapor Composition at -12°C (10°F)			Estimated Odorant Vapor Composition at 32°C (90°F)		
									At Leak	At 25% Ref. LFL		At Leak	At 25% Ref. LFL	
		[°C]	[°F]	[ppm]	[ppm wt]	[ppm]	[ppm wt]	Rel. to Mass Req.	[ppm]	[ppm]	Rel. to Threshold	[ppm]	[ppm]	Rel. to Threshold
Trimethylamine	$(CH_3)_3N$	2.85	37.1	0.0021	1.072	0.800	50.0	47	12.7	0.07	32	20.7	0.11	52
Dimethyl Sulfide	$(CH_3)_2S$	37.35	99.2	0.001	0.537	0.381	150.0	279	14.3	0.075	75	30	0.158	158
Methyl Ethyl Sulfide	$(CH_3)S(C_2H_5)$	66.65	151.94	0.002	1.316	0.762	150.0	114	3.2	0.017	8	12.3	0.065	32
Ethyl Mercaptan	C_2H_5SH	35	95.0	0.001	0.537	0.381	60.0	112	5.7	0.030	30	13.9	0.073	73

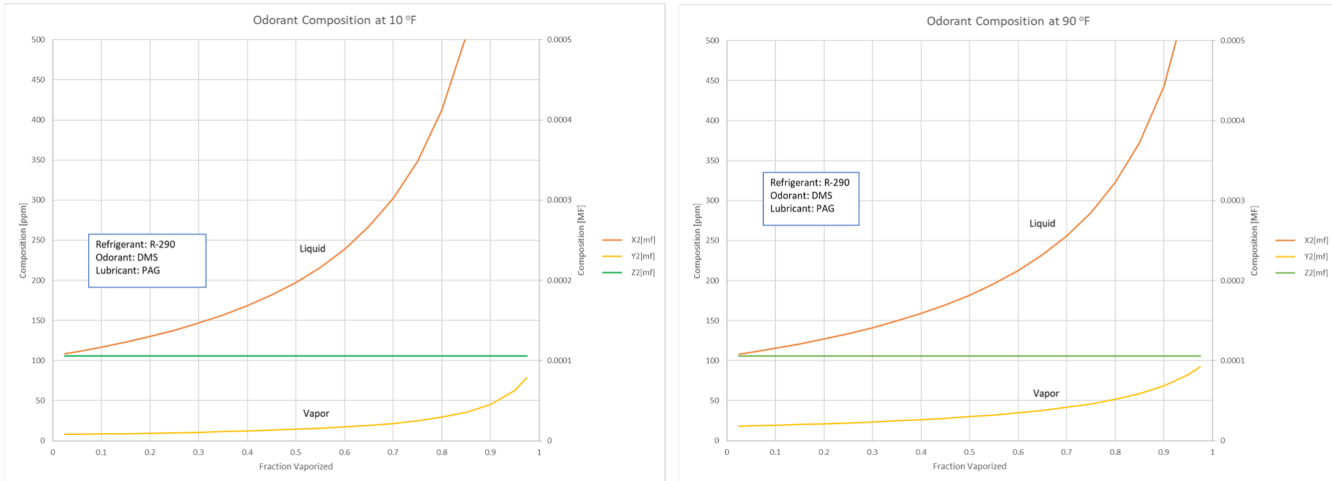


Figure 9 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-290, dimethyl sulfide and PAG lubricant as a function of vaporization

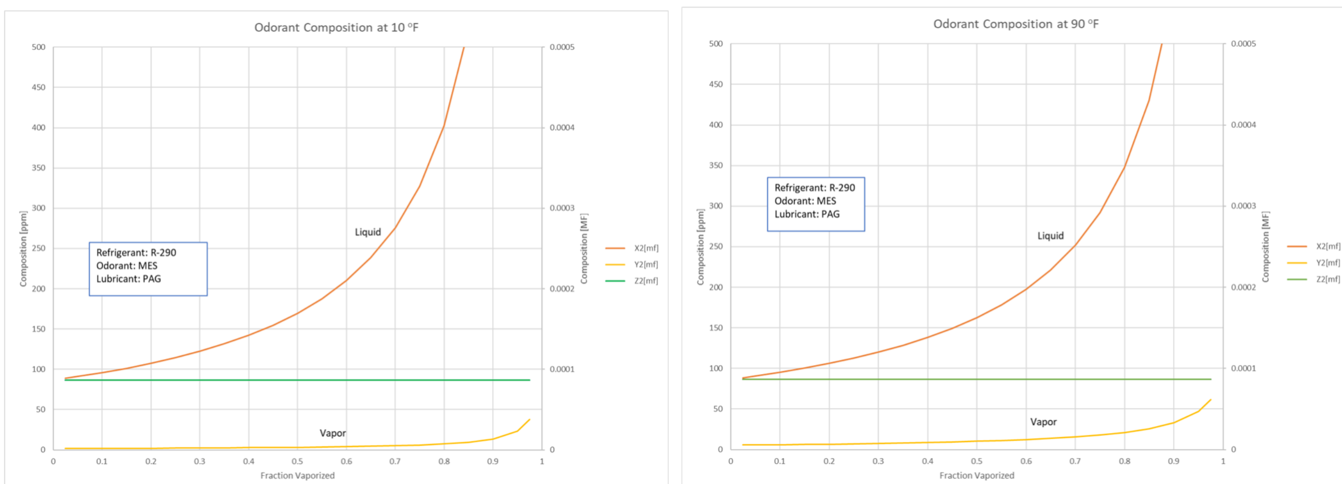


Figure 10 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-290, methyl ethyl sulfide and PAG lubricant as a function of vaporization

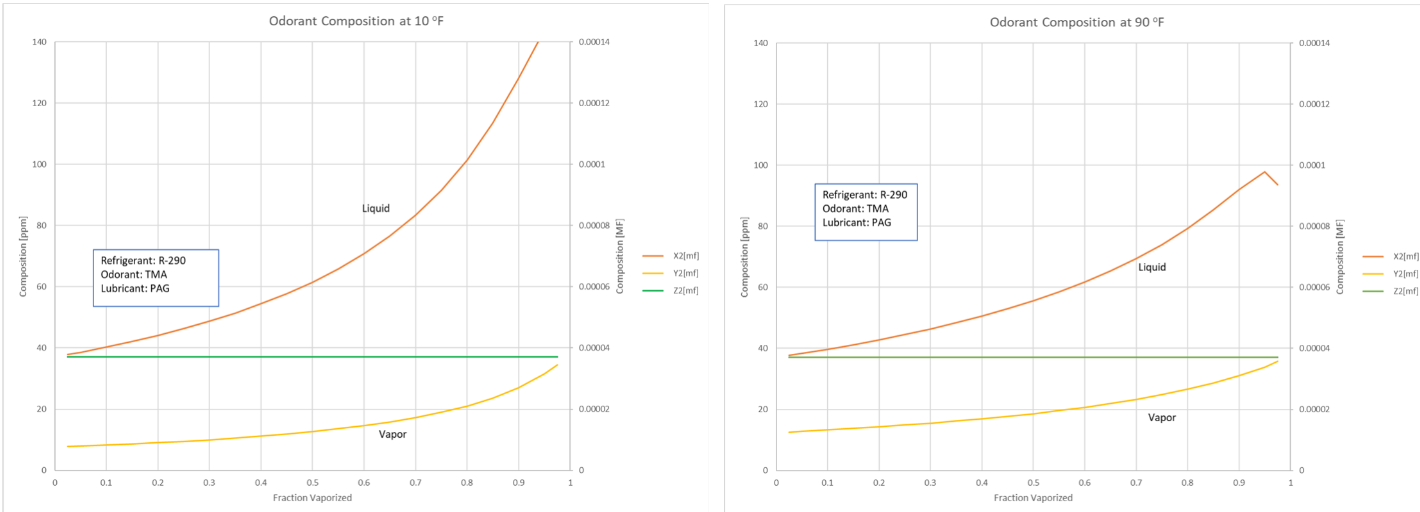


Figure 11 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-290, trimethylamine and PAG lubricant as a function of vaporization

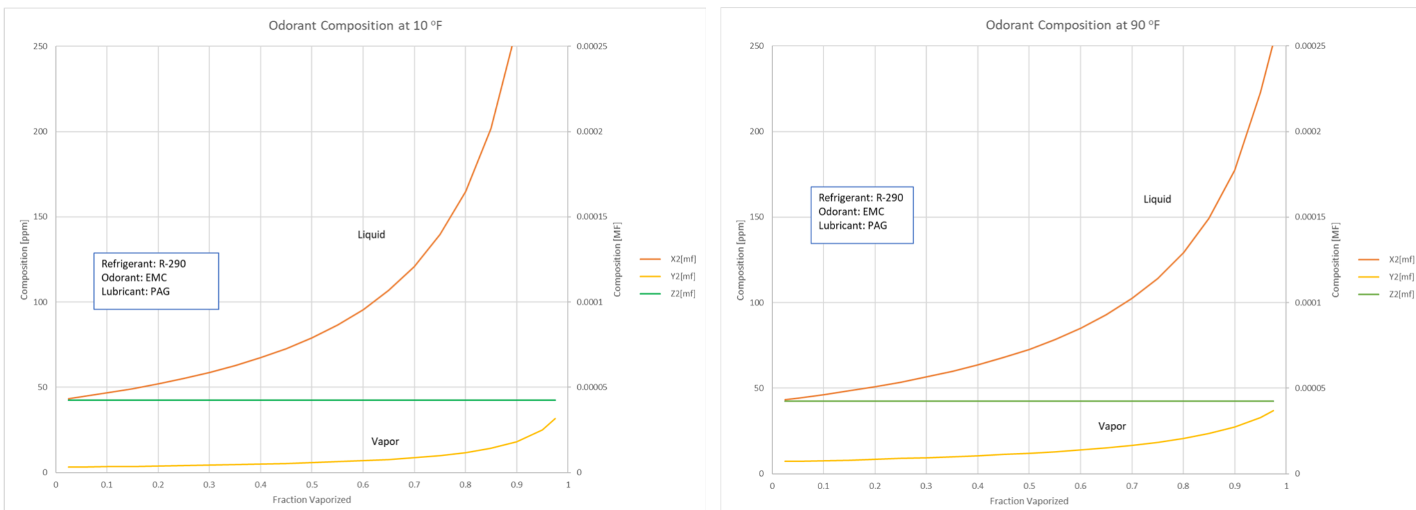


Figure 12 – Odorant Composition in the vapor and liquid phases at -12°C (10°F) and 32°C (90°F) for R-290, ethyl mercaptan and PAG lubricant as a function of vaporization

Test Odorant Refrigerant Lubricant Combinations and Test Matrix

The combinations of odorants, refrigerants, and lubricants to be tested are given in the test matrix presented in Table 3. The matrix has the two odorants with the lowest boiling points: Hydrogen Sulfide (H_2S) and Carbonyl Sulfide (COS); tested with R-32 (difluoromethane) which has the lowest boiling point of the three refrigerants to be included. Trimethylamine ($(CH_3)_3N$) was tested with the other two refrigerants with higher boiling points: R-1234yf and R-290 (propane). The boiling points for these refrigerants are lower than that of trimethylamine.

The added candidate odorants: dimethyl sulfide and methyl ethyl sulfide were tested with all three refrigerants. These candidate odorants have higher boiling points than the three refrigerants and trimethylamine.

The odorant minimum use concentration is based on being at twice its detection threshold when the refrigerant is at 25% of its lower flammability limit. Note that the odorant added at these low concentrations would not change the ASHRAE 34 classification of the refrigerant.

The test composition was set to a value of 50 ppm(wt) to ease the sample preparation. The increase over the minimum use composition represents a safety factor with regards to the use concentration of the odorant. The higher boiling point odorants: dimethyl sulfide, methyl ethyl sulfide, and ethyl mercaptan; were tested with a higher concentration of 150 ppm(wt) to allow for increased addition to offset the odorant that would reside with the lubricant in the compressor.

Methyl mercaptan was eliminated from the test matrix due to the difficulty in acquiring and safely handling this odorant in its pure form. Carbonyl sulfide was reduced to testing only with R-32 for similar reasons.

Ethyl mercaptan was tested only with R-290. The results obtained would be expected to be representative of what would be obtained for other mercaptan compounds, including the methyl mercaptan that was eliminated from the matrix. Ethyl mercaptan is commonly utilized to odorize natural gas and liquified petroleum gas (LPG).

Table 6 – Test Matrix for initial round of ASHRAE 97 compatibility tests

	Refrigerant					Lubricant		Odorant						
Test Number	Name	Formula	Class	MW []	LFL [%]	Name	Composition [%]	Name	Formula	MW []	Detection Threshold in Air [ppm(vol)]	Min Use Composition in Refrigerant* [ppm(wt)]	Test Composition in Refrigerant [ppm(wt)]	Test Composition in Refrigerant Ratio to Min Use
1	R-32	CH_2F_2	A2L	52.00	14.00	PAG	50.0	Hydrogen Sulfide	H_2S	34.08	0.00047	0.018	50.0	2841
2	R-32	CH_2F_2	A2L	52.00	14.00	PAG	50.0	Carbonyl Sulfide	COS	60.07	0.055	3.63	50.0	13.8
3	R-32	CH_2F_2	A2L	52.00	14.00	PAG	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.068	150.0	2196
4	R-32	CH_2F_2	A2L	52.00	14.00	PAG	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	0.17	150.0	882
5	R-32	CH_2F_2	A2L	52.00	14.00	PAG	50.0	None/Control						
6	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	PAG	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.070	150.0	2133
7	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	PAG	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	0.17	150.0	870
8	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	PAG	50.0	Trimethyl Amine	$(CH_3)_3N$	59.11	0.0021	0.141	50.0	355
9	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	PAG	50.0	None/Control						
10	R-290	C_3H_8	A3	44.10	2.10	PAG	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.54	150.0	279
11	R-290	C_3H_8	A3	44.10	2.10	PAG	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	1.32	150.0	114
12	R-290	C_3H_8	A3	44.10	2.10	PAG	50.0	Trimethyl Amine	$(CH_3)_3N$	59.11	0.0021	1.07	50.0	47
13	R-290	C_3H_8	A3	44.10	2.10	PAG	50.0	Ethyl Mercaptan**	C_2H_6S	62.14	0.001	0.54	60.0	112
14	R-290	C_3H_8	A3	44.10	2.10	PAG	50.0	None/Control						
15	R-32	CH_2F_2	A2L	52.00	14.00	POE	50.0	Hydrogen Sulfide	H_2S	34.08	0.00047	0.0176	50.0	2841
16	R-32	CH_2F_2	A2L	52.00	14.00	POE	50.0	Carbonyl Sulfide	COS	60.07	0.055	3.63	50.0	13.8
17	R-32	CH_2F_2	A2L	52.00	14.00	POE	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.068	150.0	2196
18	R-32	CH_2F_2	A2L	52.00	14.00	POE	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	0.17	150.0	882
19	R-32	CH_2F_2	A2L	52.00	14.00	POE	50.0	None/Control						
20	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	POE	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.070	150.0	2133
21	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	POE	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	0.17	150.0	870
22	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	POE	50.0	Trimethyl Amine	$(CH_3)_3N$	59.11	0.0021	0.141	50.0	355
23	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	POE	50.0	None/Control						
24	R-290	C_3H_8	A3	44.10	2.10	POE	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.54	150.0	279
25	R-290	C_3H_8	A3	44.10	2.10	POE	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	1.32	150.0	114
26	R-290	C_3H_8	A3	44.10	2.10	POE	50.0	Trimethyl Amine	$(CH_3)_3N$	59.11	0.0021	1.07	50.0	47
27	R-290	C_3H_8	A3	44.10	2.10	POE	50.0	None/Control						
28	R-32	CH_2F_2	A2L	52.00	14.00	PVE	50.0	Hydrogen Sulfide	H_2S	34.08	0.00047	0.0176	50.0	2841
29	R-32	CH_2F_2	A2L	52.00	14.00	PVE	50.0	Carbonyl Sulfide	COS	60.07	0.055	3.63	50.0	13.8
30	R-32	CH_2F_2	A2L	52.00	14.00	PVE	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.068	150.0	2196
31	R-32	CH_2F_2	A2L	52.00	14.00	PVE	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	0.17	150.0	882
32	R-32	CH_2F_2	A2L	52.00	14.00	PVE	50.0	None/Control						
33	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	PVE	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.070	150.0	2133
34	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	PVE	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	0.17	150.0	870
35	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	PVE	50.0	Trimethyl Amine	$(CH_3)_3N$	59.11	0.0021	0.141	50.0	355
36	R-1234yf	$CF_3CF{=}CH_2$	A2L	114.00	6.20	PVE	50.0	None/Control						
37	R-290	C_3H_8	A3	44.10	2.10	PVE	50.0	Dimethyl Sulfide	$(CH_3)_2S$	62.14	0.001	0.54	150.0	279
38	R-290	C_3H_8	A3	44.10	2.10	PVE	50.0	Methyl Ethyl Sulfide	$CH_3SC_2H_5$	76.16	0.002	1.32	150.0	114
39	R-290	C_3H_8	A3	44.10	2.10	PVE	50.0	Trimethyl Amine	$(CH_3)_3N$	59.11	0.0021	1.07	50.0	47
40	R-290	C_3H_8	A3	44.10	2.10	PVE	50.0	None/Control						

MW – Molecular Weight, LFL – Lower Flammable Limit concentration in air, *Min use odorant concentration based on twice the detection threshold when the refrigerant is at 25% of the lower flammable limit

Test Performance

These tests were performed by Spauschus Associates at their facility in Bethlehem, GA.

Sample tubes were prepared in accordance with ASHRAE 97-2007. The tubes were cleaned, rinsed with distilled water, and dried prior to use.

First, the metal coupons (aluminum, steel, copper) were cleaned, dried, and cut to a nominal size of 3 x 50 mm (1/8 x 2 in) by 0.15 mm (0.006 in) thick. The coupons were placed in the tubes with the aluminum coupon between the steel and copper coupons. Then the lubricant was then added to the tube. The odorant was added to the tube either pre-mixed with the lubricant or pre-mixed with Argon. The refrigerant was added to the tubes through a calibrated manifold. The tubes were then sealed.

Control tubes were prepared similarly without the addition of the odorant.

Four tubes were prepared for each of the mixtures in the test matrix. Two tubes with 1 g of refrigerant, 1 g of lubricant and odorant at the desired concentration. The other two tubes with 2 g of refrigerant, 2 g of lubricant and odorant at the desired concentration. The increased amount of the second set of tubes was used to facilitate the inductively coupled plasma (ICP) analysis of the lubricant at the conclusion of the tests.

The hydrogen sulfide, carbonyl sulfide and trimethylamine odorants were initially diluted with argon to a concentration of 1000 ppm (wt). They were then mixed with the refrigerant to obtain the 50 ppm (wt) of the odorant in the refrigerant. This results with the added argon representing 4.995% (wt) in the mixture. The mixtures were then added to the sample tubes. This corresponds to an odorant amount of 50 µg and 100 µg in the smaller and larger tubes, respectively.

The dimethyl sulfide and methyl ethyl sulfide odorants were added as a liquid to the lubricant prior to the addition to the sample tubes. These odorants were added by weight to achieve the 150 ppm (wt) desired odorant concentration. This corresponds to an odorant amount of 150 µg and 300 µg in the smaller and larger tubes, respectively.

The ethyl mercaptan odorant was added to the lubricant similarly to the dimethyl sulfide and methyl ethyl sulfide, except that the desired odorant concentration was 60 ppm (wt). This corresponds to an odorant amount of 60 µg and 120 µg in the smaller and larger tubes, respectively.

After preparation, the sample tubes were placed in an aluminum block with holes prepared to accept the tubes. The sealed tubes were then heated to and kept at a temperature of 175 ^{o}C (347 ^{o}F) for 14 days, which represented accelerated aging.

At the conclusion of the exposure period, the refrigerant, lubricant, and metal coupons were tested and examined for adverse effects of the exposure.

First the tubes were visually inspected for any color changes of the lubricant, or surface appearance of the tube walls and metal coupons, any appearance of cloudiness or of a precipitate was also noted, and any other visible changes.

Then the tubes were opened, and the exposed lubricant was collected for further analysis. An Ion Chromatograph (IC) was used to analyze for fluoride ions which indicate refrigerant decomposition and for organic acid anions (TOA) which indicate lubricant decomposition. An Inductively Coupled Plasma (ICP) analyzer was also used to analyze the lubricant for trace metals such as Iron, Copper, Aluminum and Sulfur. The trace metal presence in the lubricant would be an indication of erosion of the metal coupons, while the presence of sulfur would indicate a breakdown or reaction of the sulfur containing odorants. In addition, the lubricant was be analyzed for total acid number (TAN) utilizing a modified ASTM D644 method.

The results from the tubes with odorants were compared to the results from the control tubes.

Results

The results of the material compatibility tests are summarized in Tables 7 through 9. Bold and highlighted fields mark notable differences in comparison to the control tubes which did not have the odorant present. More detailed results are presented in Appendix C. The hydrogen sulfide and the ethyl mercaptan odorants evidenced the largest effects on the exposed metal coupons and in the changes in the cloudiness of the liquid or formation of a particulate as observed at the conclusion of the aging period. With these exceptions, the evidenced reactions and changes observed were mild, correlating to the low odorant concentrations utilized during these tests. However, none of the odorants completed the test matrix without showing some response during these tests. Trimethylamine was the closest with only an elevated TAN evidenced in the R-290, PVE lubricant combination.

Table 7 – Odorant, refrigerant and lubricant material compatibility results summary for R-32 (difluoromethane) – LFL: 14% - ASHRAE Class A2L

Refrigerant			Lubricant		Odorant		Results														
		LFL		Composition		Test Comp.		Liquid			Metals						Total Visual Score	Total Acid Number (TAN)	Fluoride Ion	Total Organic Acids (TOA)
Name	Class	[%]	Name	[%]	Name	[ppm(wt)]	Test		Color	Cloudiness or Deposit	Steel	Score	Copper	Score	Aluminum	Score		[mg KOH/g]	[ppm]	[ppm]
R-32	A2L	14.00	PAG	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.03		24
							aged	Clear	2.25	0	Unchanged	0	Unchanged	0	Unchanged	0	2.3	0.08	0	111
R-32	A2L	14.00	PAG	50.0	Carbonyl Sulfide	50.0	aged	**light Cloudiness**	2.5	**2**	Slight Darkening	0.5	Unchanged	0	Unchanged	0	**5.0**	0.05	0	121
R-32	A2L	14.00	PAG	50.0	Hydrogen Sulfide	50.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	**Mottled (Bluish Purple)**	**3**	Unchanged	0	**6.8**	0.06	3	164
R-32	A2L	14.00	PAG	50.0	Dimethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.05	2	103
R-32	A2L	14.00	PAG	50.0	Methyl Ethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.05	1	166
R-32	A2L	14.00	POE	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.04		24
							aged	Very Faint Cloudiness	2.5	0.5	Slight Darkening	0.5	Unchanged	0	Unchanged	0	3.5	0.25	0	186
R-32	A2L	14.00	POE	50.0	Carbonyl Sulfide	50.0	aged	Faint Cloudiness	2.5	1	light Darkening	1	Unchanged	0	Unchanged	0	4.5	0.22	0	158
R-32	A2L	14.00	POE	50.0	Hydrogen Sulfide	50.0	aged	Very Faint Cloudiness	2.25	0.5	**light-Med Brown**	**1.5**	**Mottled (Faint Blue)**	**3**	Unchanged	0	**7.3**	**0.53**	0	242
R-32	A2L	14.00	POE	50.0	Dimethyl Sulfide	150.0	aged	Faint Cloudiness	2.25	1	Unchanged	0	Unchanged	0	Unchanged	0	3.3	0.28	0	208
R-32	A2L	14.00	POE	50.0	Methyl Ethyl Sulfide	150.0	aged	Faint Cloudiness	2.25	1	Slight Darkening	1	Unchanged	0	Unchanged	0	4.3	0.17	0	222
R-32	A2L	14.00	PVE	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.01		33
							aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.04	0	85
R-32	A2L	14.00	PVE	50.0	Carbonyl Sulfide	50.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	0.5	Unchanged	0	Unchanged	0	3.3	0.03	0	63
R-32	A2L	14.00	PVE	50.0	Hydrogen Sulfide	50.0	aged	Very Faint Cloudiness	2.25	0.5	**light-Med Brown**	**1.5**	**Mottled (Faint Blue)**	**3**	Unchanged	0	**7.3**	**0.09**	1	115
R-32	A2L	14.00	PVE	50.0	Dimethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.03	1	84
R-32	A2L	14.00	PVE	50.0	Methyl Ethyl Sulfide	150.0	aged	Very Faint Cloudiness	2	0.5	Slight Bluish Gray Tint	0.5	Unchanged	0	Unchanged	0	3.0	0.03	1	80

Table 8 - Odorant, refrigerant and lubricant material compatibility results summary for R-1234yf – LFL: 6.2% - ASHRAE Class A2L

Refrigerant			Lubricant		Odorant		Results													
		LFL		Composition		Test Comp.		Liquid			Metals						Total Visual Score	Total Acid Number (TAN)	Fluoride Ion	Total Organic Acids (TOA)
Name	Class	[%]	Name	[%]	Name	[ppm(wt)]	Test		Color	Cloudiness or Deposit	Steel	Score	Copper	Score	Aluminum	Score		[mg KOH/g]	[ppm]	[ppm]
R-1234yf	A2L	6.20	PAG	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.03		24
							aged	Clear	2.5	0	Unchanged	0	Unchanged	0	Unchanged	0	2.5	0.25	65	56
R-1234yf	A2L	6.20	PAG	50.0	Trimethylamine	50.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.15	32	61
R-1234yf	A2L	6.20	PAG	50.0	Dimethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.08	10	61
R-1234yf	A2L	6.20	PAG	50.0	Methyl Ethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.07	7	55
R-1234yf	A2L	6.20	POE	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.04		24
							aged	Clear	2.5	0	Unchanged	0	Unchanged	0	Unchanged	0	2.5	0.09	0	101
R-1234yf	A2L	6.20	POE	50.0	Trimethylamine	50.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.07	0	78
R-1234yf	A2L	6.20	POE	50.0	Dimethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	Unchanged	0	Unchanged	0	3.8	0.08	1	126
R-1234yf	A2L	6.20	POE	50.0	Methyl Ethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.5	0.5	Slight Darkening	1	Slight Darkening	1	Unchanged	0	**5.0**	**0.21**	1	154
R-1234yf	A2L	6.20	PVE	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.01		33
							aged	Clear	2.5	0	Unchanged	0	Unchanged	0	Unchanged	0	2.5	0.14	0	83
R-1234yf	A2L	6.20	PVE	50.0	Trimethylamine	50.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.07	35	69
R-1234yf	A2L	6.20	PVE	50.0	Dimethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	Unchanged	0	Unchanged	0	3.8	0.06	19	**347**
R-1234yf	A2L	6.20	PVE	50.0	Methyl Ethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.5	0.5	Slight Darkening	1	Faint Darkening	0.5	Unchanged	0	4.5	0.05	25	**394**

Table 9 - Odorant, refrigerant and lubricant material compatibility results summary for R-290 (propane) – LFL: 2.1% - ASHRAE Class A3

Refrigerant			Lubricant		Odorant		Results													
		LFL		Composition		Test Comp.		Liquid			Metals						Total Visual Score	Total Acid Number (TAN)	Fluoride Ion	Total Organic Acids (TOA)
Name	Class	[%]	Name	[%]	Name	[ppm(wt)]	Test		Color	Cloudiness or Deposit	Steel	Score	Copper	Score	Aluminum	Score		[mg KOH/g]	[ppm]	[ppm]
R-290	A3	2.10	PAG	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.03		24
							aged	Clear	2.25	0	Faint Darkening	0.5	Unchanged	0	Unchanged	0	2.8	0.03	0	77
R-290	A3	2.10	PAG	50.0	Trimethylamine	50.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.05	9	45
R-290	A3	2.10	PAG	50.0	Ethyl Mercaptan	60.0	aged	**Faint Cloudiness - Faint White Deposit**	2.25	**2.5**	Slight Darkening	1	**Bluish-Purple**	**2**	Unchanged	0	**7.8**	**0.06**	1	66
R-290	A3	2.10	PAG	50.0	Dimethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	Unchanged	0	Unchanged	0	3.8	0.03	2	72
R-290	A3	2.10	PAG	50.0	Methyl Ethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	0	Unchanged	0	Unchanged	0	2.8	0.04	2	77
R-290	A3	2.10	POE	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.04		24
							aged	Clear	2.5	0	Faint Darkening	0.5	Unchanged	0	Unchanged	0	3.0	0.1	0	147
R-290	A3	2.10	POE	50.0	Trimethylamine	50.0	aged	Very Faint Cloudiness	2.25	0.5	Unchanged	0	Unchanged	0	Unchanged	0	2.8	0.1	0	71
R-290	A3	2.10	POE	50.0	Dimethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	**Medium Darkening**	**1.5**	Unchanged	0	**5.3**	0.07	1	98
R-290	A3	2.10	POE	50.0	Methyl Ethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	Unchanged	0	Unchanged	0	3.8	0.09	1	130
R-290	A3	2.10	PVE	50.0	None/Control		unaged	Very Faint Cloudiness	2									0.01		33
							aged	Clear	2.5	0	Faint Darkening	0.5	Unchanged	0	Unchanged	0	3.0	0.01	1	49
R-290	A3	2.10	PVE	50.0	Trimethylamine	50.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	Unchanged	0	Unchanged	0	3.8	**0.04**	7	68
R-290	A3	2.10	PVE	50.0	Dimethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	Faint Darkening	0.5	Unchanged	0	4.3	0.02	1	46
R-290	A3	2.10	PVE	50.0	Methyl Ethyl Sulfide	150.0	aged	Very Faint Cloudiness	2.25	0.5	Slight Darkening	1	Slight Darkening	1	Unchanged	0	4.8	0.01	2	**404**

Visual Observations and Scoring

After completion of the aging period, the sample tubes were observed for changes in color, cloudiness, formation of a precipitate or film deposition, and changes in color or deposition of the metal coupons. The liquid in the sample tubes were observed to have a very faint or faint cloudiness in all of the combinations tested with the exceptions of the ethyl mercaptan test which evidenced the development of a precipitate in the sample tubes, and the carbonyl sulfide tests which had an increased cloudiness in comparison to the controls, especially for the R-32 refrigerant, PAG lubricant combination.

The steel coupons generally had a slight or faint darkening in comparison to the control samples, with the exception of the tests with the hydrogen sulfide odorant where it was light to medium brown after exposure with both the R-32 refrigerant, POE and PVE lubricant combinations. With the R-32 refrigerant PAG lubricant, and hydrogen sulfide odorant combination, the steel was darkened in comparison to the controls, but not to the extent with the other lubricants.

The copper coupons were turned a mottled bluish purple during the exposures with the hydrogen sulfide odorant and the ethyl mercaptan odorant. The copper coupons were faintly darkened when exposed to the combination of dimethyl sulfide (DMS), R-290 and PVE Lubricant and the combination of methyl ethyl sulfide (MES), R-1234yf and PVE Lubricant. They were slightly darkened when exposed to the combination of MES, R-1234yf and PVE Lubricant and the combination of MES, R-290 and PVE lubricant. Only the DMS odorant, R-290 refrigerant and POE lubricant combination exceeded the medium darkening threshold.

The aluminum coupons were unchanged during these exposures.

In order to facilitate a comparison between the test results, a scoring system was developed for the results which is outlined in Table 10. The scoring of the visual results are given in Tables 7 through 9 and compared in Figures 13 through 15. The hydrogen sulfide and ethyl mercaptan tests exhibited the highest adverse scores. The red bars in the Figures signify that the values for the odorant, lubricant, refrigerant combination are greater by a factor of two (2) or more relative to what was scored for the corresponding control test.

Table 10 – Visual observation scoring metrics

Score Keys for Visual Inspection Results								
Visual Score	Liquid color	Cloudiness	Particulate /deposit	Film/deposit on tube walls or in bottom of tube	Aluminum Corrosion	Copper Corrosion	Steel Corrosion	Copper plating
0	Water clear	Clear	No particulate/ no deposit	No film	Shiny	Shiny	Shiny	No copper plating
1	Water clear	Faint; very light cloudiness	Faint; very small amount	Faint; very light film or deposit on walls and in bottom of tube	Dull; dark gray or dull with coating	Slightly dull; slightly darker color	Dull; slightly darker	Light plating or plating on edges of coupon
2	Water clear	Light cloudiness	Small amount	Light film or deposit on walls and in bottom of tube	Darker color; spot or stain on surface	Dull; darker color	Dull; dark gray	Plating on surface
3	Pale yellow	Cloudy; medium cloudiness	Medium amount	Medium Film or deposit on walls and in bottom of tube	Black (with spots)	Dull with stains, film or coating	Spots or coating on surface	Heavy copper plating
4	Yellow	Very cloudy; Heavy cloudiness	Large, heavy amount	Heavy film or deposit on walls and in bottom of tube; ring at liquid/gas interface	Black; corroded	Black	Black	---
5	Light orange	Extremely heavy cloudiness	Extremely heavy amount	Extremely heavy deposit and extremely heavy ring	---	---	---	---
6	Orange-brown	---	---	---	---	---	---	---

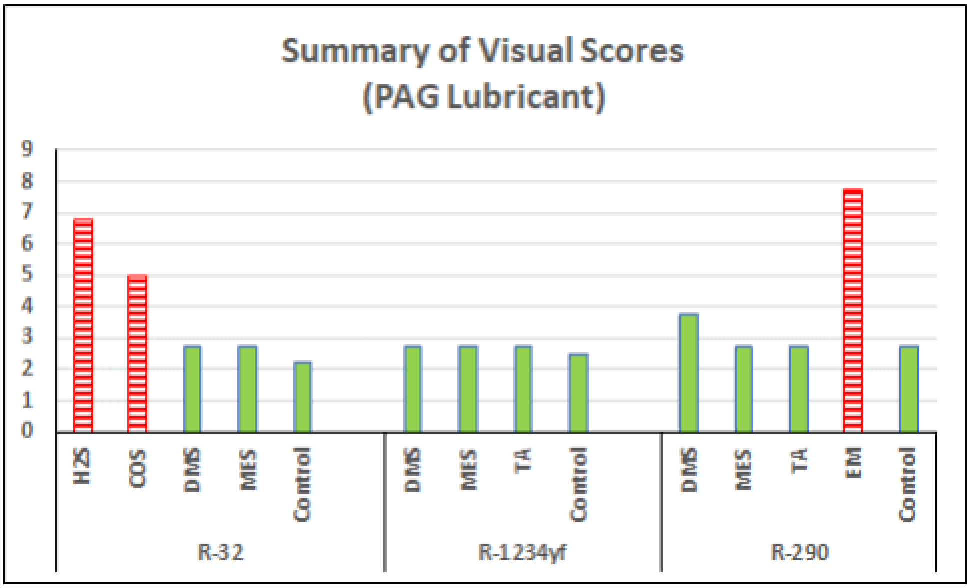


Figure 13 – Visual observation scoring comparison for combinations involving the PAG lubricant

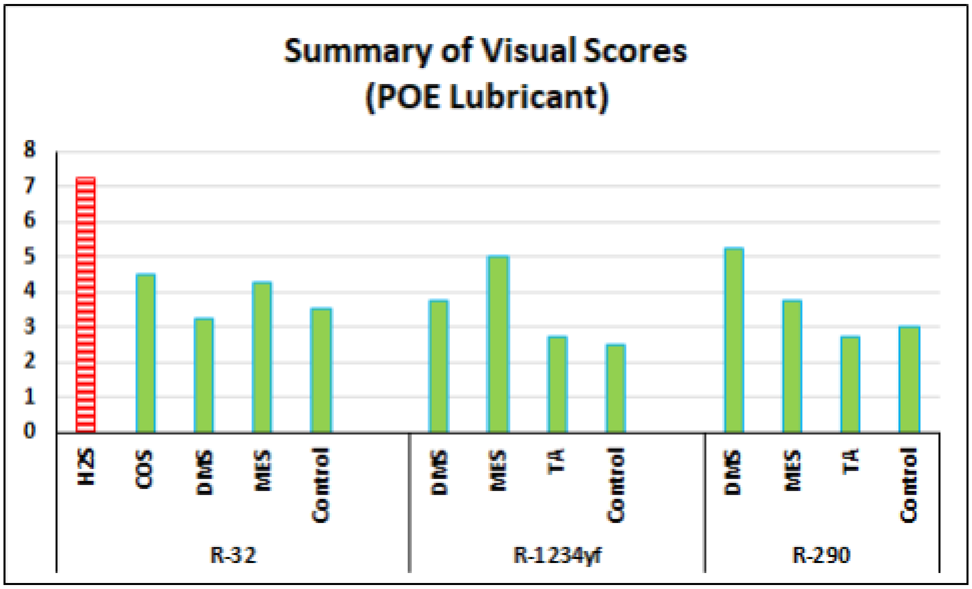


Figure 14 - Visual observation scoring comparison for combinations involving the POE lubricant

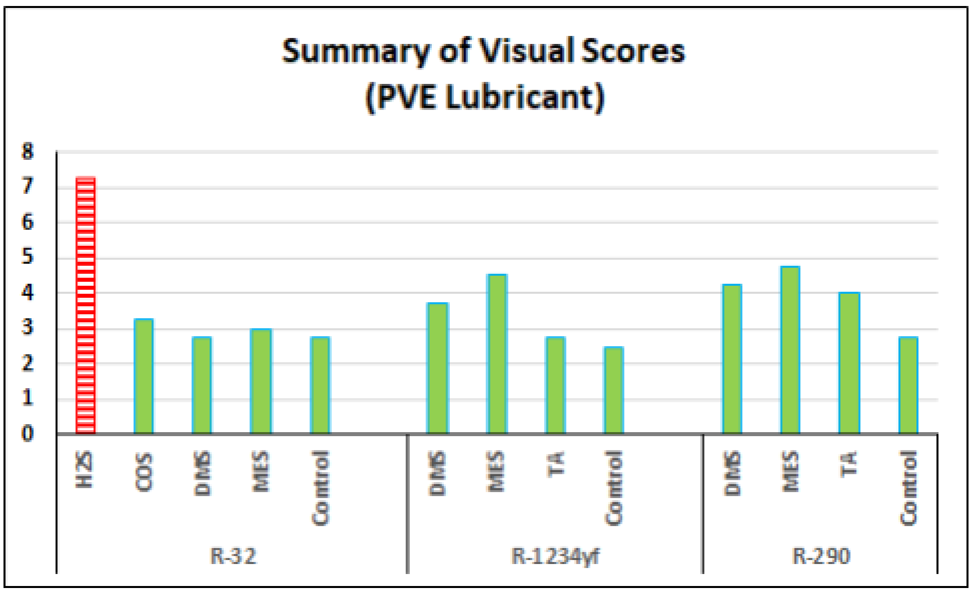


Figure 15- Visual observation scoring comparison for combinations involving the PVE lubricant

Total Acid Number

The determined Total Acid Number (TAN) for each of the refrigerant lubricant odorant combinations was given in Tables 7 through 9 and compared to the control tests in Figures 16 through 18. In general, the TAN values were small with the values ≤0.25 mg KOH/g for the combinations involving the PAG lubricant, ≤0.53 mg KOH/g for combinations involving the POE lubricant and ≤0.09 mg KOH/g for combinations involving the PVE lubricant. The combinations with the highest TAN values were nominally the same as those that had the highest visual observation scores, i.e., those involving the hydrogen sulfide and the methyl mercaptan odorants. The TAN values for the combinations involving the trimethylamine odorant and the R-290 refrigerant exceeded or equaled that of the controls for all three lubricants. While still a low value of 0.04 mg KOH/g in combination of R-290 and PVE, the trimethylamine value was four times that of the control test, 0.01 mg KOH/g. The TAN value for the R-1234yf refrigerant, MES odorant and POE lubricant combination was more than twice that of the control at a value of 0.21 mg KOH/g (0.09 mg KOH/g for the control set).

For the combinations involving the R-1234yf refrigerant and either the PAG or PVE lubricant, the TAN values were higher than when the odorant was present. This maybe an indication that the odorant inhibited the breakdown of the refrigerant to an extent. Note that the lubricants utilized for these tests were without some of the additives that would normally have been present.

The red bars in the Figures signify that the values for the odorant, lubricant, refrigerant combination are greater by a factor of two (2) or more relative to what was scored for the corresponding control test.

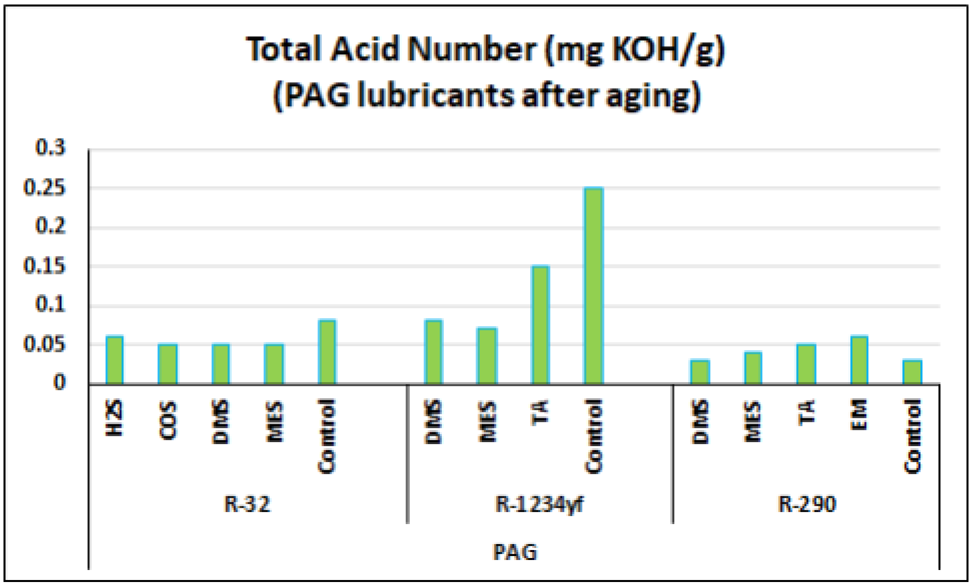


Figure 16 – Total acid number comparison for the combinations involving the PAG lubricant

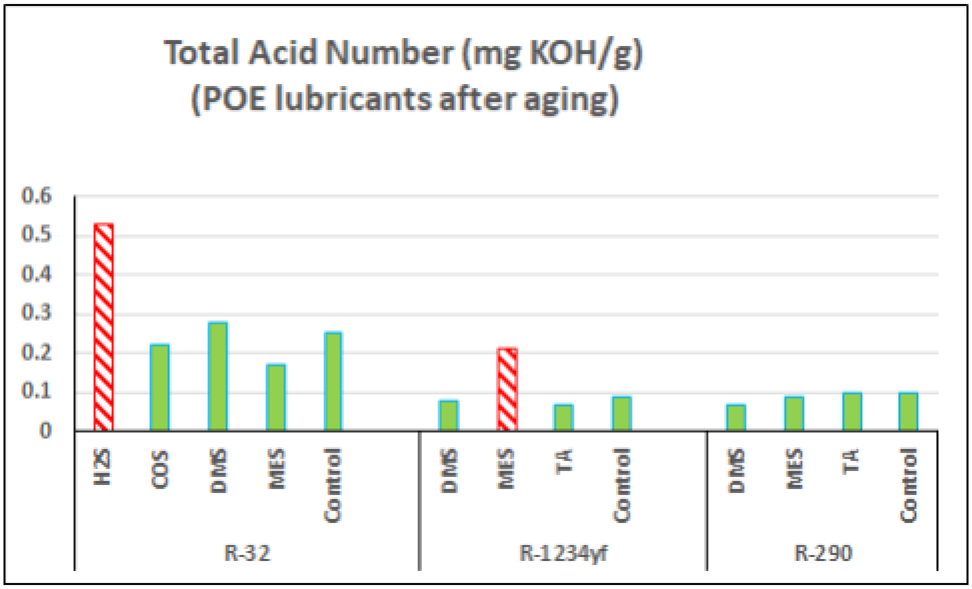


Figure 17 – Total acid number comparison for the combinations involving the POE lubricant

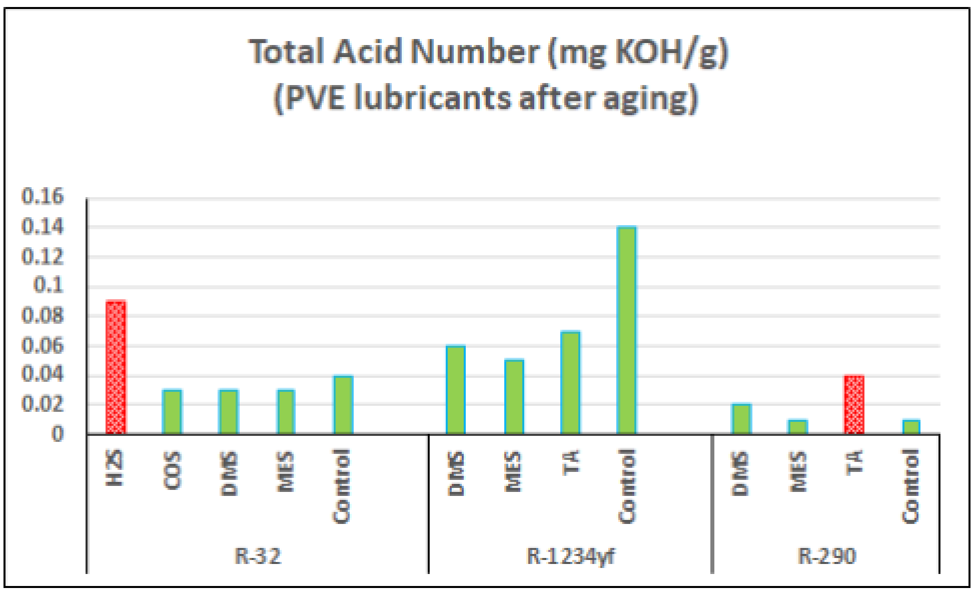


Figure 18 – Total acid number comparison for the combinations involving the PVE lubricant

Total Organic Acid Anions

The total organic acid anions (TOA) is determined with an ion chromatographic technique and is the sum of the values [ppm] for the propanoate, butyrate, pentanoate, hexanoate, 2-ethyl hexanoate and heptanoate concentrations. The determined values were small for the combinations with the PAG lubricant (≤164 ppm), with the POE lubricant (≤242 ppm) and with the PVE lubricant (≤115 ppm) with the exception of the R-1234yf Refrigerant, PVE lubricant, and DMS and MES odorant combinations and the R-290 refrigerant, PVE lubricant and MES odorant combination. These three combinations had TOA values in excess of 340 ppm, more than five time that of the control tests. The determined TOA values are given in Tables 7 through 9 and Figures 19 through 21. The red bars in the Figures signify that the values for the odorant, lubricant, refrigerant combination are greater by a factor of two (2) or more relative to what was scored for the corresponding control test.

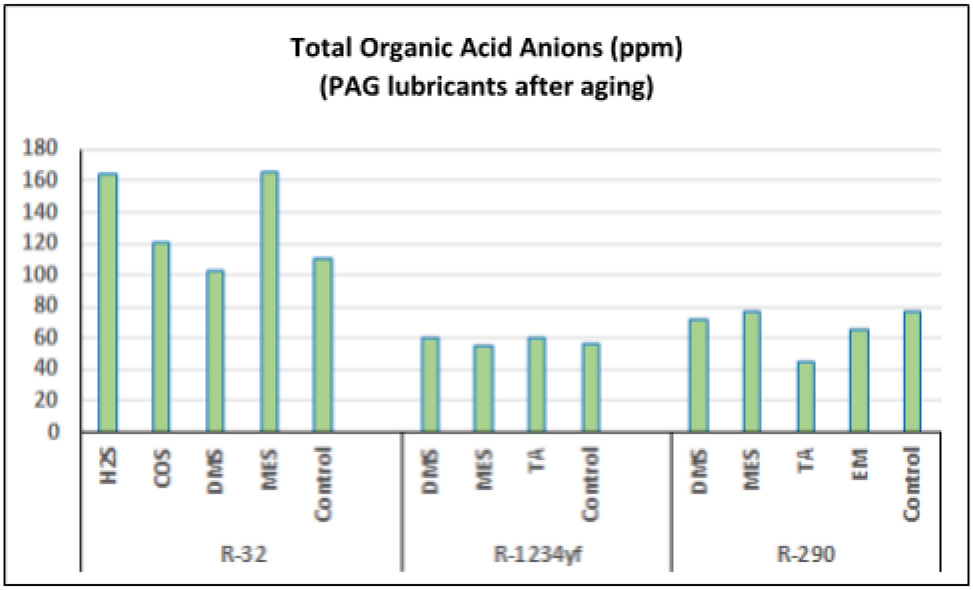


Figure 19 – Determined total organic acid anions (TOA) for combinations involving the PAG lubricant.

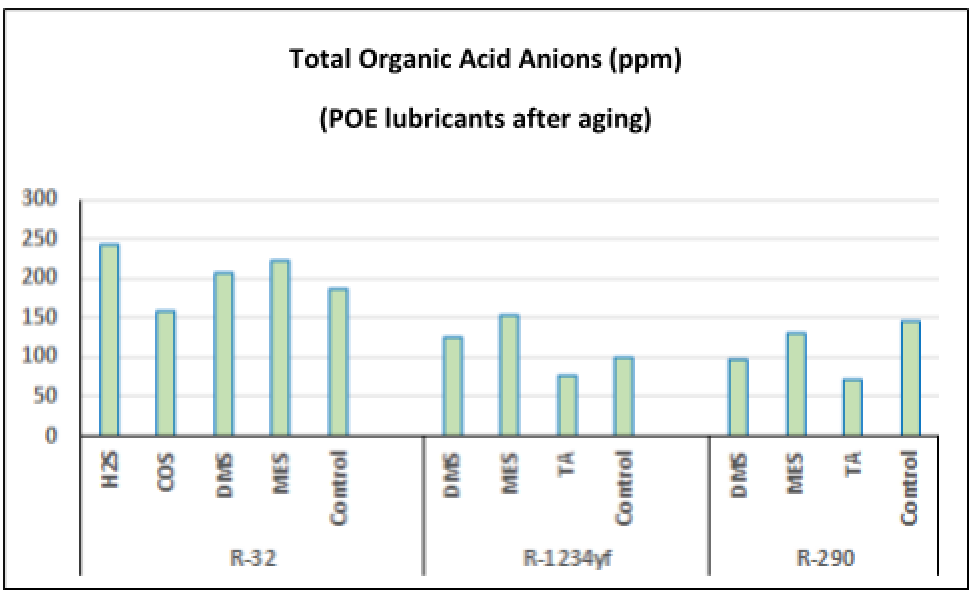


Figure 20 – Determined total organic acid anions (TOA) for combinations involving the POE lubricant

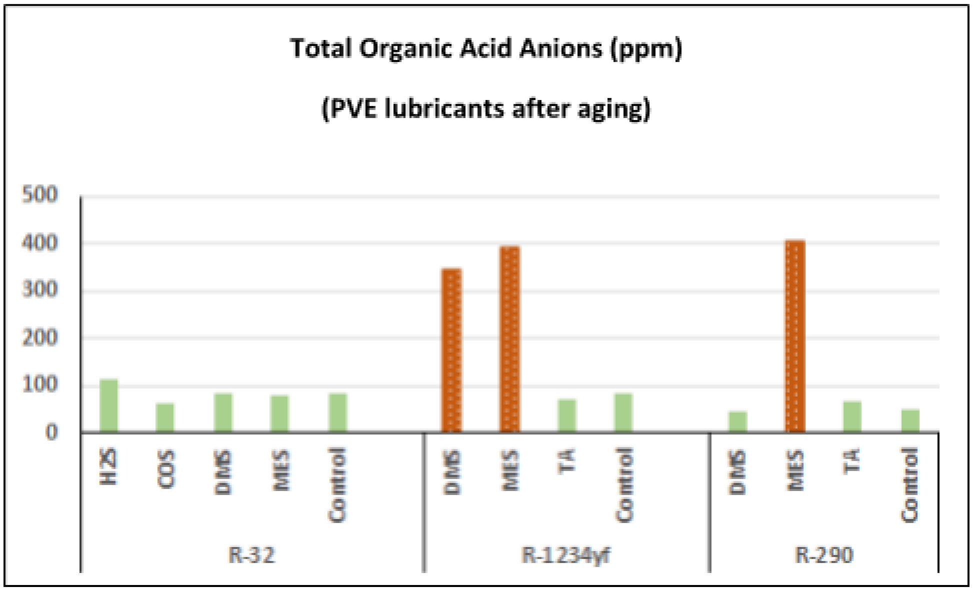


Figure 21 – Determined total organic acid anions (TOA) for combinations involving the PVE lubricant

Fluoride Ion Concentrations

The fluoride ion concentration in the liquid phase is also determined via an ion chromatographic technique. It can be an indication of the of the decomposition of a hydrofluorocarbon-based refrigerant like R-32 and R-1234yf. The fluoride ion concentration was in general low with all of concentrations less than 70 ppm. The only values that were greater than 9 ppm were for combinations that involved the R-1234yf refrigerant and either the PAG or PVE lubricant. The highest concentration was determined for the R-1234yf refrigerant and PAG Lubricant control without any odorant with a fluoride ion concentration of 65 ppm.

Summary

Six candidate odorants were evaluated with regards to their compatibility with the materials of construction commonly used in the HVAC&R industry: steel, copper and aluminum. The odorants were combined with three low global warming potential (GWP) refrigerants: R-32, R-1234yf and R290; and three type of lubricants: PAG, POE and PVE. This evaluation utilized the method outlined in the ASHRAE 97-2007 Standard and were performed to address concerns regarding the material compatibility (or reactivity) of the four candidate odorants identified in the previous ASHRAE white paper study [1]. The six candidate odorants evaluated were hydrogen sulfide (H_2S), carbonyl sulfide (COS), trimethylamine ($(CH_3)_3N$), dimethyl sulfide ($(CH_3)_2S$), methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and ethyl mercaptan (C_2H_5SH). Methyl mercaptan that was identified as a candidate odorant in the ASHRAE white paper study was not included in this evaluation due to difficulties in acquiring and safe handling of this material. It is believed that the compatibility of the ethyl mercaptan would be similar to that of the methyl mercaptan. Dimethyl sulfide (DMS) and methyl ethyl sulfide (MES) were included as they are commonly used as odorants in the flammable gas industry in Europe.

The results of this evaluation are summarized in Table 11. The labels in the boxes of this table states the primary reason(s) for concern where the result for the combination with the odorant present was notably different than that for the control test without the odorant present. Visual would include changes in color of the liquid in the sample tube, the cloudiness of the liquid or development of a precipitate, as well as the darkening or changes in appearance of the metal coupons. Note that the color coding of the boxes in the table is not in and of itself a pass fail criterion and is primarily used to signify a noticeable difference for the odorant, lubricant, refrigerant combination relative to the control test without the odorant present.

Table 11 – Summary of material compatibility test results

		Odorants					
		Hydrogen Sulfide	Carbonyl Sulfide	Dimethyl Sulfide	Methyl Ethyl Sulfide	Trimethylamine	Ethyl Mercaptan
Refrigerants	Lubricants	H2S	COS	DMS	MES	TA	EM
R-32	PAG	**Visual**	**Visual**			Not Tested	Not Tested
	POE	**Visual-TAN**				Not Tested	Not Tested
	PVE	**Visual-TAN**				Not Tested	Not Tested
R-1234yf	PAG	Not Tested	Not Tested				Not Tested
	POE	Not Tested	Not Tested		**TAN**		Not Tested
	PVE	Not Tested	Not Tested	**TOA**	**TOA**		Not Tested
R-290	PAG	Not Tested	Not Tested				**Visual-TAN**
	POE	Not Tested	Not Tested	**Visual**			Not Tested
	PVE	Not Tested	Not Tested		**TOA**	**TAN**	Not Tested

The hydrogen sulfide (H_2S) candidate odorant had the lowest boiling point of the candidate odorants and was evaluated in combination with R-32 which had the lowest boiling point of the three refrigerants. During the evaluation, the exposed steel and copper coupons were discolored which is an indication of a reaction between the odorant and these metals. The total organic acid anions (TOA) and total acid number (TAN) were elevated during these tests. These results likely preclude H_2S from further consideration as an odorant in this application. H_2S is difficult to handle and transport safely in its pure state prior to mixing with the refrigerant for use in this application.

The carbonyl sulfide (COS) candidate odorant was only tested in combination with the R-32 refrigerant. A light cloudiness in appearance of the liquid developed over the exposure, especially in combination with the PAG lubricant, and as a slight darkening of the exposed steel coupons was observed.

The ethyl mercaptan candidate odorant was tested with the R-290 refrigerant and PAG lubricant. This combination resulted in the formation of a precipitate during the exposure as well as the discoloration of copper coupon. The steel coupon was also discolored, but not to the extent that the copper coupon was. This test also had an elevated TAN value relative to the control tests without an added odorant. This was the only combination evaluated with the ethyl mercaptan. The methyl mercaptan originally identified as a candidate odorant would be expected to have performed similarly during these tests.

The two added candidates, DMS and MES, were the only candidates evaluated with all three refrigerants and lubricants. The evaluations with the POE and PVE lubricants in combination with the R-1234yf and R-290 refrigerants resulted in slight discoloration of the steel and copper coupons. The discoloration of the copper coupon was more pronounced for the DMS odorant, R-290 refrigerant and POE lubricant combination. The combinations with these two odorants and the PVE lubricant and R-1234yf refrigerant resulted in elevated TOA values. The combination of MES odorant, R-290 Refrigerant and PVE lubricant had an elevated TOA value as well.

Trimethylamine was evaluated with R-1234yf and R-290. The exposed metal coupons were unchanged with the exception of the R-290 refrigerant, PVE lubricant combination where the steel coupon was slightly darkened. The TAN values for the trimethylamine odorant, R-290 refrigerant, and PAG or PVE lubricant combinations were elevated.

Unfortunately, the concentration of the odorant after the exposure and aging could not be measured during this evaluation. While the test results, in general, indicate mild responses to the exposure and imply that only limited reactions occurred during the exposure, the amount of the odorant at the end of the exposure was not determined.

It should be noted that the lubricants were utilized without some of the additives that would normally be added to assist with the long-term stability of the lubricant refrigerant combination. These additives, if they were present, may have had an impact on the results obtained.

In conclusion, Trimethylamine, MES and DMS would be recommended for further development. MES and DMS would be excluded from applications involving the POE or PVE lubricants unless a suitable additive could be found to mitigate the interactions evidenced during these tests. Carbonyl sulfide performed well during these tests. However, it was tested with a relatively low safety factor over its minimum use concentration and has a limited margin below its adverse toxic effect threshold concentrations. Hydrogen sulfide and ethyl mercaptan did not perform well during these tests and would not be recommended for further development.

Further Development of Candidate Odorants

This project represented one step in the development of an odorant for use with the low global warming, flammable refrigerants. Further development and analysis efforts are needed in order to fully evaluate the application of an odorant for use with these refrigerants. Additional evaluation needed would include the following efforts:

- Confirmation of the Odorant Amount Required. The odorant concentration in the mixtures tested were estimated to result in odorant concentrations that would be higher than twice the lower detection threshold for the odorant when the refrigerant was at 25% of its lower flammable limit. Research should be conducted to determine if the margins above the lower detection threshold is sufficiently noticeable to provide the intended warning.

- Chemical Stability Testing. The stability of the added odorant in the refrigerant lubricant mixture should be evaluated. If the odorant is reacting with the refrigerant, lubricant or the materials of construction to form compounds that are not as easily detected (higher odor detection threshold), then the ability of the odorant to provide the desired warning would fade over time.

- Impact of odorant addition on refrigerant loop performance: This effort would include measuring the loop efficiency and design compensations (larger coils, higher/lower pressure) due to addition of odorant in the refrigeration loop.

- Additional Material Compatibility tests: This effort would include performing the material compatibility tests for standard materials such as brass, copper, rubber, nylon etc. These tests would address issues related to solvation, crazing, and any reactions due to addition of odorant in the refrigerant.

- Refrigerant and odorant dispersion modeling and testing: This effort would include performing both testing and computer modeling to assess performance of odorant for different leak scenarios. These scenarios can include vapor/liquid leaks with conditions corresponding to different refrigeration components such as compressor, evaporator etc.

- Toxicity evaluation: This effort would include evaluation of toxicity levels due to exposure of odorant to appliance manufacturers, technicians, and owners.

- Odorant distribution measurement: This effort would include measurement of odorant in different locations within the refrigeration systems such as compressor, condenser, evaporator etc. As the odorants concentration may be non-uniform throughout the loop, the task would help to evaluate the quantity of odorant to be added to a particular refrigerant.

- Odorant effectiveness with time: This effort would include measurement of odorant effectiveness once it has been used in refrigeration loop for an elongated period of time. The pipe wall adsorption of odorants can have adverse impact on its effectiveness and the suggested test would help in understanding this issue.

Some of the standard tests which will address the issues stated above are:

- ASTM E679-91, Standard Practice for Determination of Odor and Taste Threshold by a Forced-Choice Ascending Concentration Series Method of Limits, American Society for Testing and Materials, Philadelphia, PA: 1991.

- ASTM E544-99, Standard Practice for Suprathreshold Odor Intensity Measurement, American Society for Testing and Materials, Philadelphia, PA: 1999.

- ASHRAE 97 – Sealed Glass Tube Method to Test the Chemical Stability of Material for Use within Refrigeration Systems

- AHRI 340/360: Performance Rating of Commercial and Industrial Unitary Air-Conditioning and Heat Pump Equipment

Disclaimer: The evaluation of the identified odorants presented in this report is preliminary in nature. Further, in depth evaluation is required to assess the suitability of these candidates in this application.

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2. ANSI/ASHRAE, "Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use within Refrigerant Systems", ANSI/ASHRAE Standard 97-2007 (RA 2017), American Society of Heating, Refrigeration, and Air Conditioning Engineers, Atlanta, GA, 2017.

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Appendix A

Odorant Certificates of Conformity

The certificates of conformity/analysis for the acquired odorants utilized during this project are presented in Figures A-1 through A-5. The certificate for the acquired carbonyl sulfide could not be obtained.

SIGMA-ALDRICH®

sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA
Website: www.sigmaaldrich.com
Email USA: techserv@sial.com
Outside USA: eurtechserv@sial.com

Certificate of Analysis

Product Name:
Hydrogen sulfide – ≥99.5%

Product Number:	**295442**
Batch Number:	**MKBQ6512V**
Brand:	ALDRICH
CAS Number:	7783-06-4
Formula:	H2S
Formula Weight:	34.08 g/mol
Quality Release Date:	03 JAN 2014

H_2S

Test	**Specification**	**Result**
Purity Guaranteed Purity Of 99.5% (Minimum) By Supplier	Conforms	Conforms

Jamie Gleason

Jamie Gleason, Manager
Quality Control
Milwaukee, Wisconsin US

Sigma-Aldrich warrants, that at the time of the quality release or subsequent retest date this product conformed to the information contained in this publication. The current Specification sheet may be available at Sigma-Aldrich.com. For further inquiries, please contact Technical Service. Purchaser must determine the suitability of the product for its particular use. See reverse side of invoice or packing slip for additional terms and conditions of sale.

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Figure A 1 – Certificate of analysis for the acquired hydrogen sulfide

SYNQUEST LABORATORIES

PO BOX 309 - ALACHUA, FLORIDA 32616 - PHONE (386) 462-0788 - FAX (386) 462-7097

SynQuest Laboratories, Inc.
Certificate of Analysis / QC Results

Customer PO # :

Packaged Product: 3132-1-05
_Trimethylamine [75-50-3] UN1083

Test	Target/UOM	Range	Result
PURITY (GC/FID), %		99 - 100	99
IDENTITY			CONFORMS
BSE/TSE - SYNTHETIC MATERIAL			YES

Lot # 00003036

This document is electronically signed and is valid without a handwritten signature. SynQuest Laboratories warrants that at the time of quality release this product conformed to the information contained in this publication. Purchaser must determine the suitability of the product for its particular use. For further inquiries, please contact Customer Service.

Page: 1

Figure A 2 – Certificate of Analysis for the acquired trimethylamine

SIGMA-ALDRICH®

3050 Spruce Street, Saint Louis, MO 63103 USA
Email USA: techserv@sial.com Outside USA: eurtechserv@sial.com

Certificate of Analysis

Product Name:	Dimethyl sulfide >= 99 %
Product Number:	471577
Batch Number:	STBJ8594
Brand:	Sigma-Aldrich
CAS Number:	75-18-3
Formula:	$(CH_3)_2S$
Formula Weight:	62.13
Quality Release Date:	22 JUL 2020

TEST	SPECIFICATION	RESULT
APPEARANCE (COLOR)	COLORLESS TO LIGHT YELLOW	COLORLESS
APPEARANCE (FORM)	LIQUID	LIQUID
PURITY (GC AREA %)	≥ 99.0 %	99.6 %
INFRARED SPECTRUM	CONFORMS TO STRUCTURE	CONFORMS

Claudia Mayer

Claudia Mayer
Manager Quality Control
Steinheim, Germany

Sigma-Aldrich warrants that at the time of the quality release or subsequent retest date this product conformed to the information contained in this publication. The current specification sheet may be available at Sigma-Aldrich.com. For further inquiries, please contact Technical Service. Purchaser must determine the suitability of the product for its particular use. See reverse side of invoice or packing slip for additional terms and conditions of sale.

Sigma-Aldrich Certificate of Analysis - Product 471577 Lot STBJ8594 Page 1 of 1

Figure A 3 – Certificate of Analysis for the acquired dimethyl sulfide

SIGMA-ALDRICH®

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3050 Spruce Street, Saint Louis, MO 63103, USA
Website: www.sigmaaldrich.com
Email USA: techserv@sial.com
Outside USA: eurtechserv@sial.com

Certificate of Analysis

Product Name:
Ethyl methyl sulfide - 96%

$CH_3CH_2SCH_3$

Product Number:	**238317**
Batch Number:	**MKCL6369**
Brand:	ALDRICH
CAS Number:	624-89-5
MDL Number:	MFCD00009268
Formula:	C3H8S
Formula Weight:	76.16 g/mol
Quality Release Date:	31 DEC 2019

Test	Specification	Result
Appearance (Color)	Colorless	Colorless
Appearance (Form)	Liquid	Liquid
Proton NMR Spectrum	Conforms to Structure	Conforms
Purity (GC)	$\geq$ 95.5 %	99.4 %

Michael Grady, Manager
Quality Control
Milwaukee, WI US

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Figure A 4 – Certificate of Analysis for the acquired methyl ethyl sulfide

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3050 Spruce Street, Saint Louis, MO 63103, USA
Website: www.sigmaaldrich.com
Email USA: techserv@sial.com
Outside USA: eurtechserv@sial.com

Certificate of Analysis

Product Name:
Ethanethiol (ethyl mercaptan) - analytical standard

CH_3CH_2SH

Product Number:	**506818**
Batch Number:	**MKCJ9048**
Brand:	SUPELCO
CAS Number:	75-08-1
Formula:	C2H6S
Formula Weight:	62.13 g/mol
Storage Temperature:	Store at 2 - 8 °C
Quality Release Date:	17 MAY 2019
Expiration Date:	MAY 2022

Test	**Specification**	**Result**
Infrared Spectrum	Conforms to Structure	Conforms
Purity (GC)	$\geq$ 96.0 %	99.6 %
GC - Mass Spec	Matches: NIST	Matches: NIST
Expiration Date Period 3 Years	-------------------------	---------------------------

Michael Grady, Manager
Quality Control
Milwaukee, WI US

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Figure A 5 – Certificate of Analysis for the acquired ethyl mercaptan

Appendix B

Odorant Refrigerant Lubricant Phase Composition Estimates

For a multicomponent mixture, the composition of the vapor phase and the liquid phase changes as the mixture is vaporized. Initially, the vapor phase is richer in the lower boiling point (higher vapor pressure) component of the mixture. As the vaporization continues, the concentration of the lower boiling point component in the vapor phase is reduced, trending toward the feed/liquid composition prior to the start of the vaporization. For the liquid phase, the concentration of the higher boiling point components increases as the more volatile components are vaporized. An increase in temperature or reduction in pressure generally accompanies the progression toward complete vaporization. The temperature or pressure change would represent a loss of efficiency in the refrigerant loop due to either the increase in compressor work or the lower heat transfer coefficient and reduced temperature differential across the heat exchanger (condenser or evaporator).

For condensation, these processes reversed, with the liquid phase initially richer in the higher boiling point components with the liquid composition trending toward the feed/vapor composition as condensation progresses.

Incomplete vaporization of the odorant in the evaporator, would lead to a build-up of the odorant in the lubricant trap at the entrance to the compressor. Incomplete condensation of the odorant in the condenser would cause a build-up of vapor in the condenser, reducing the heat transfer area available to the refrigerant and could interfere with the flow through the capillary tubes.

In order to investigate the effect of the volatility of the odorant added on its distribution in a refrigeration loop, a series of calculation on the equilibrium composition of the refrigerant-odorant phase composition and refrigerant-odorant-lubricant composition during the vaporization or condensation process were done. An equation of state, Peng Robinson, will be used in these calculations utilizing geometric mixing rules without binary interaction parameters.

Peng-Robinson Equation of State [B1, B2]

The Peng Robinson equation of state (PR) is a cubic equation of state that was refined from the Soave modification (SRK) of the Redlich Kwong equation of state (RK). The Peng Robinson equation of state has the following form:

$$Z^3 - (1 - B)Z^2 + Z(A - 2B - 3B^2) - AB + B^2 + B^3 = 0.0$$

$$A = 0.45724\, a_z \left({P_r}/{T_r}^2 \right)$$

$$a_z = \left(1 + z_m\left(1 - {T_r}^{0.5}\right)\right)^2$$

$$z_m = 0.37464 + 1.54226w - 0.26992w^2$$

$$B = 0.0778\left({P_r}/{T_r} \right)$$

$$Z = {Pv}/{RT}$$

Where Z is the compressibility, P is the pressure, v is the molar volume, R is the ideal gas constant, T is the temperature, P_r is the reduced pressure (P/P_c), T_r is the reduced temperature (T/T_c), P_c is the pressure at the critical point, T_c is the temperature at the critical point and w is the Pitzer acentric factor. The cubic nature of the PR equation of state yields up to three zeros with the maximum and minimum zeros corresponding to the vapor and liquid phases respectively and a single zero when only one phase is present. With the PR equation of state, it is possible to determine the pressure temperature and volume relationships and other thermodynamic properties of a fluid with only knowledge of the Pitzer acentric factor and the critical point of the fluid.

To utilize the Peng Robinson equation of state for a mixture, mixing rules are applied to determine the constants A_m and B_m for use in the equation based on the constants for the individual components A_i and B_i. For the commonly used geometric mixing rules, the mixture constants are composition weighted averages of the pure component constants as follows:

$$A_m = \sum_i \sum_j y_i y_j \left(A_i A_j\right)^{0.5}$$

$$B_m = \sum_i y_i B_i$$

Where y_i is the mole fraction of component i in the mixture.

The vapor-liquid phase equilibrium composition was determined through the distribution coefficients, K_i, based upon the mixture fugacity coefficients, $\phi_{i,l}$, for each phase as follows:

$$K_i = \frac{y_i}{x_i} = \frac{\emptyset_{i,l}}{\emptyset_{i,v}}$$

$$\emptyset_i = exp\left[(Z-1)\left(\frac{B_i}{B_m}\right) - LOG(Z-B_m) - \left(\frac{A_m}{8^{0.5}B_m}\right)\left(\frac{2{A_i}^{0.5}}{{A_m}^{0.5}} - \frac{B_i}{B_m}\right)LOG\left(\frac{Z+(1+2^{0.5})B_m}{Z+(1-2^{0.5})B_m}\right)\right]$$

The Rachford-Rice procedure was then employed to the actual composition of each phase [B2]. In this procedure, the fraction of the total mass in the vapor phase, φ, is guessed and then iterated on until the component masses balance. In this particular case, the fraction of the total mass vaporized was given and the system temperature was iterated on to satisfy the component mass balance.

$$0.0 = \sum_i z_i \left(\frac{(1-K_i)}{1+\varphi(K_i-1)}\right)$$

$$x_i = \frac{z_i}{1+\varphi(K_i-1)}$$

$$y_i = K_i x_i$$

Where z_i is the mole fraction of component i in the total mixture or feed. As the mixture fugacity coefficients in each phase and the compressibility of each phase are functions of the phase composition. The composition of each phase is solved for in an iterative manner.

Phase Composition Estimates for refrigerant, odorant and Lubricant mixtures

The calculated phase compositions for the refrigerant, odorant and lubricant mixtures are given in Figures B-1 through B-55. In performing these calculations, diphenyl ether, $C_{12}H_{10}O$, was used as a surrogate for lubricant. It was selected due to its similarity in boiling point which is 258 °C (496 °F) in comparison to the approximate 280 °C (536 °F) for PAG oil. The other two lubricants are assumed to not impact the phase composition significantly and only one set of calculations are included. The over-all/feed composition of the mixtures was set with the odorant at 50 ppm (wt) relative to the refrigerant for hydrogen sulfide, carbonyl sulfide or trimethylamine. The feed concentration for dimethyl sulfide and methyl ethyl sulfide odorants was set at 150 ppm (wt) relative to the refrigerant. The feed concentration for ethyl mercaptan was 60 ppm (wt) relative to the refrigerant. The lubricant feed composition was set at 2% by wt relative to the refrigerant. The pressure was set at the vapor pressure of the refrigerants at 32°C (90°F). The temperature was iterated on to achieve the targeted fraction vaporized. The temperature increases with the fraction vaporized, particularly on the high end of the target range as more of the higher boiling point lubricant and odorant is needed to be vaporized to meet the target vaporization fraction.

The graphs are similar with other initial temperatures, with higher temperatures increasing the amount of the higher boiling point odorants and lubricant in the vapor phase. Only the 32°C (90°F) initial temperature graphs are presented.

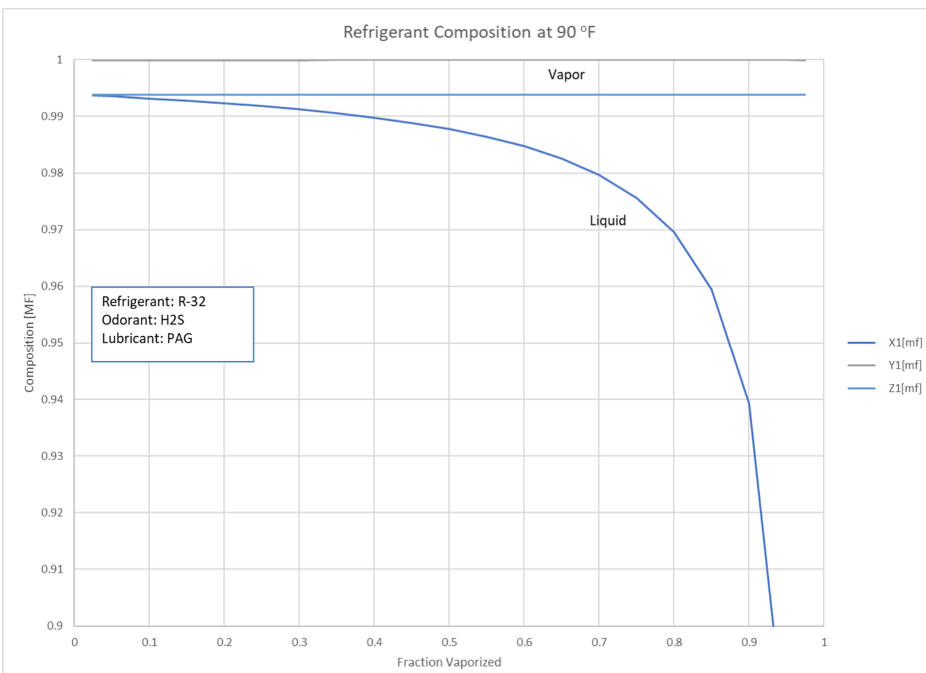

Figure B 1 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, hydrogen sulfide (H_2S) and PAG lubricant

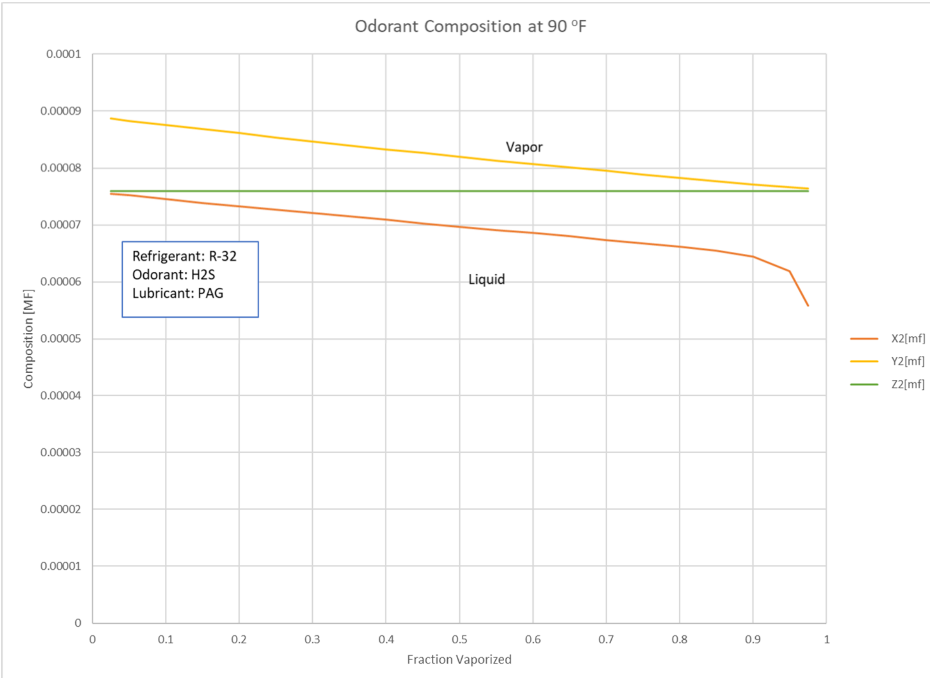

Figure B 2 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, hydrogen sulfide (H_2S) and PAG lubricant

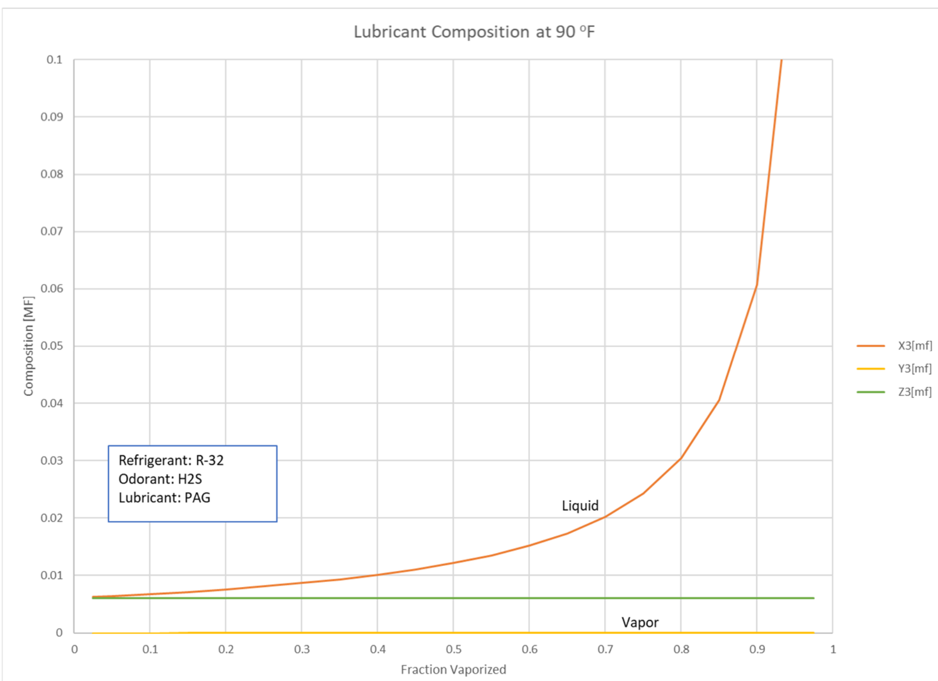

Figure B 3 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, hydrogen sulfide (H_2S) and PAG lubricant

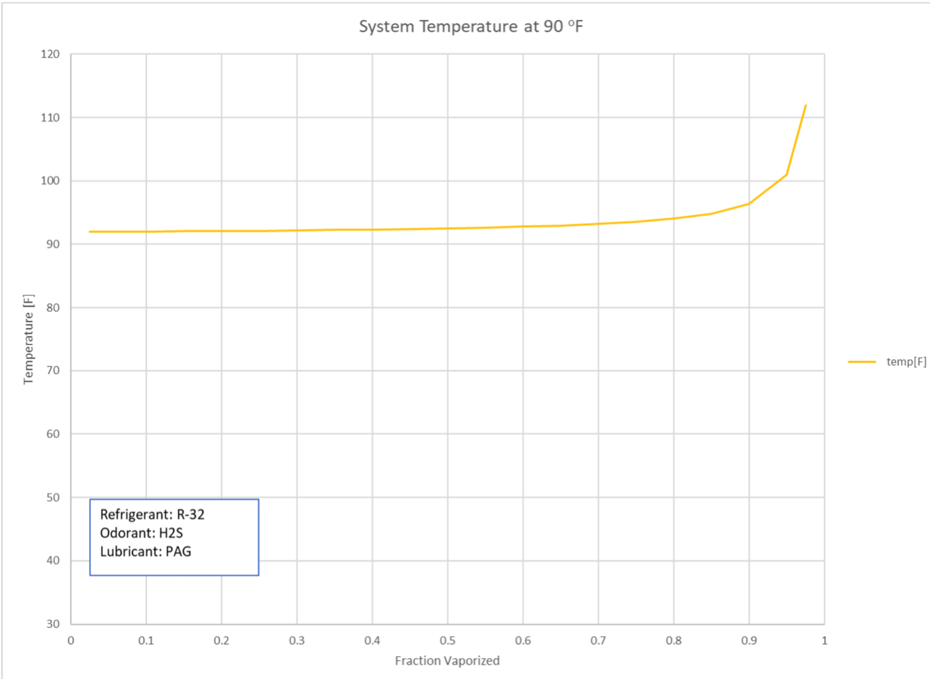

Figure B 4 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, hydrogen sulfide (H_2S) and PAG lubricant

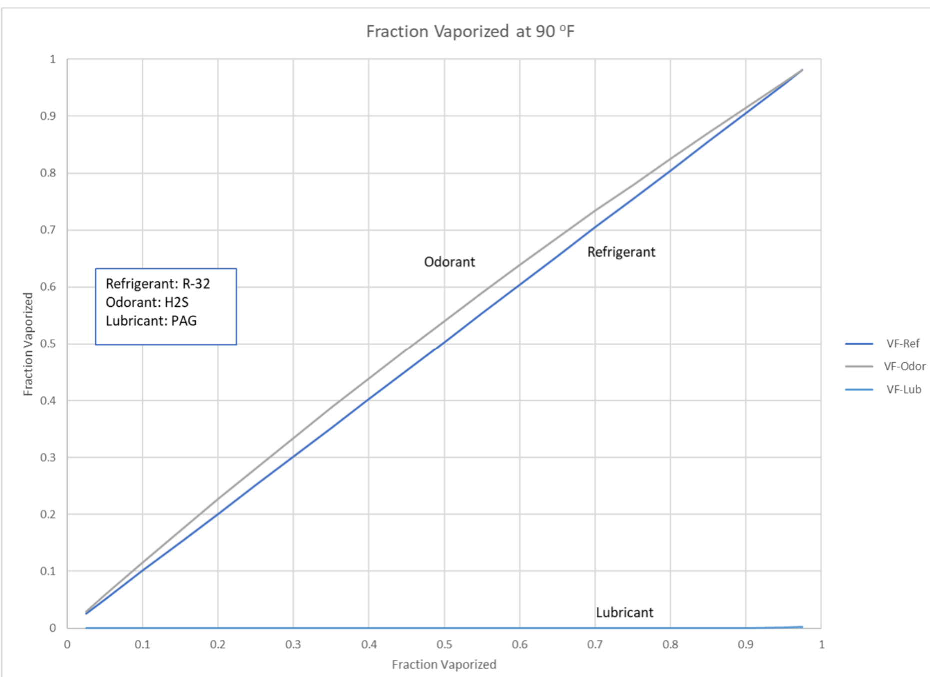

Figure B 5 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, hydrogen sulfide (H_2S) and PAG lubricant

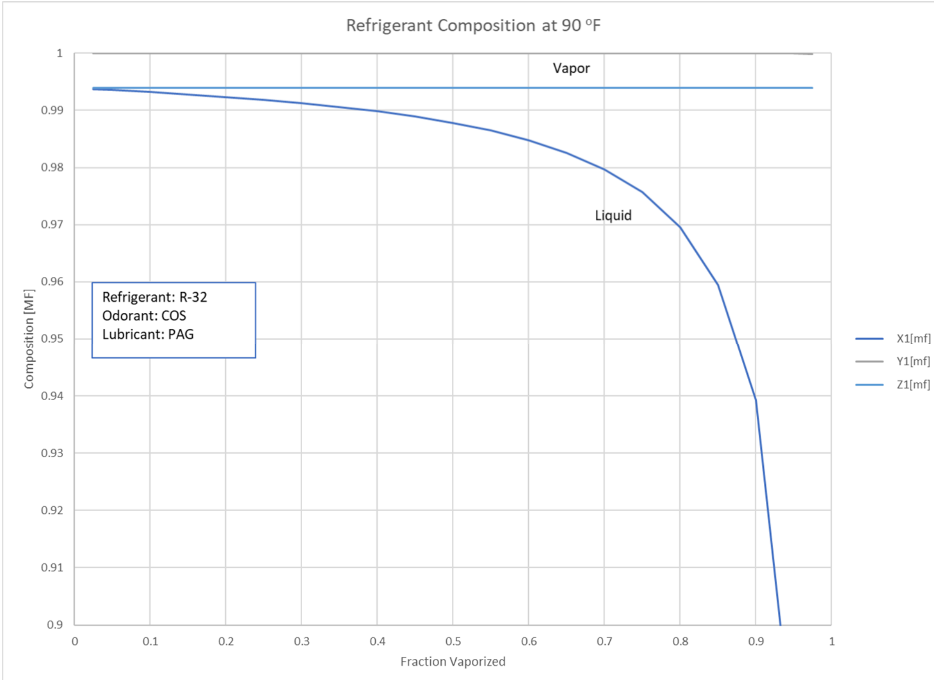

Figure B 6 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, carbonyl sulfide (COS) and PAG lubricant

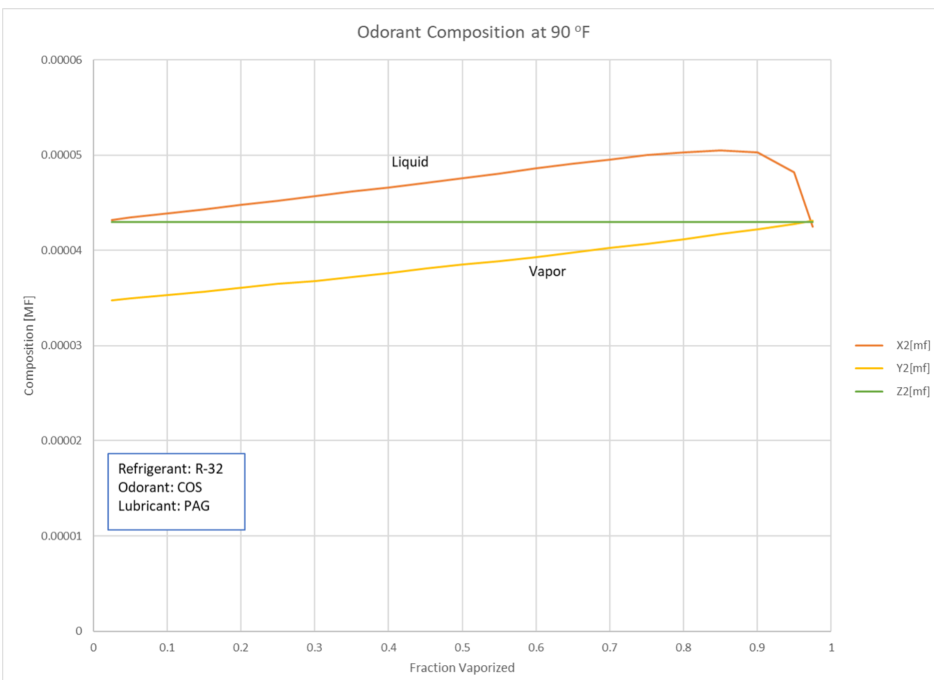

Figure B 7 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, carbonyl sulfide (COS) and PAG lubricant

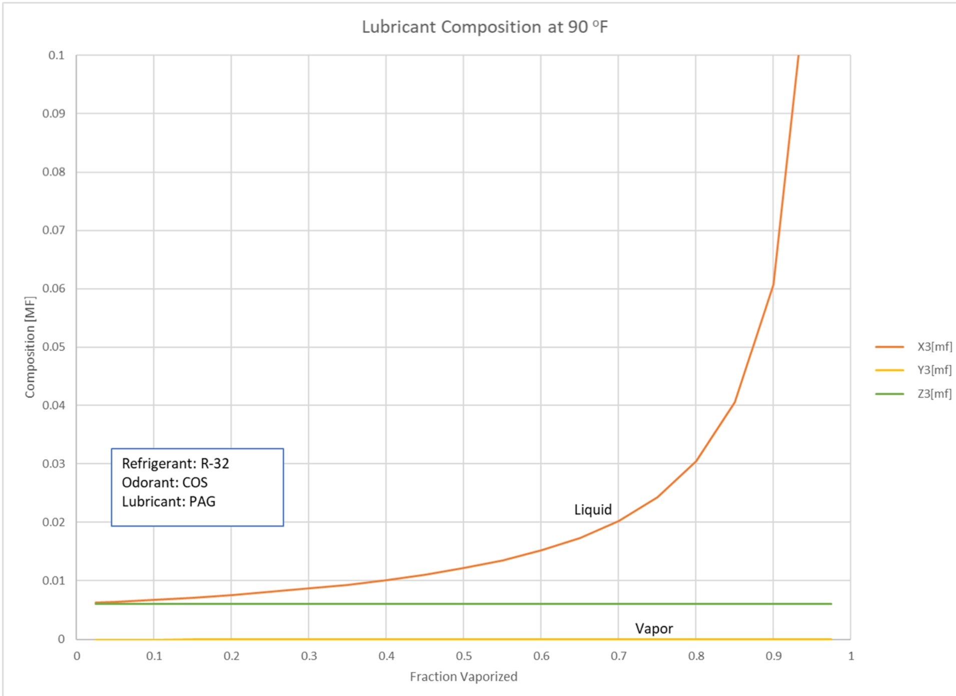

Figure B 8 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, carbonyl sulfide (COS) and PAG lubricant

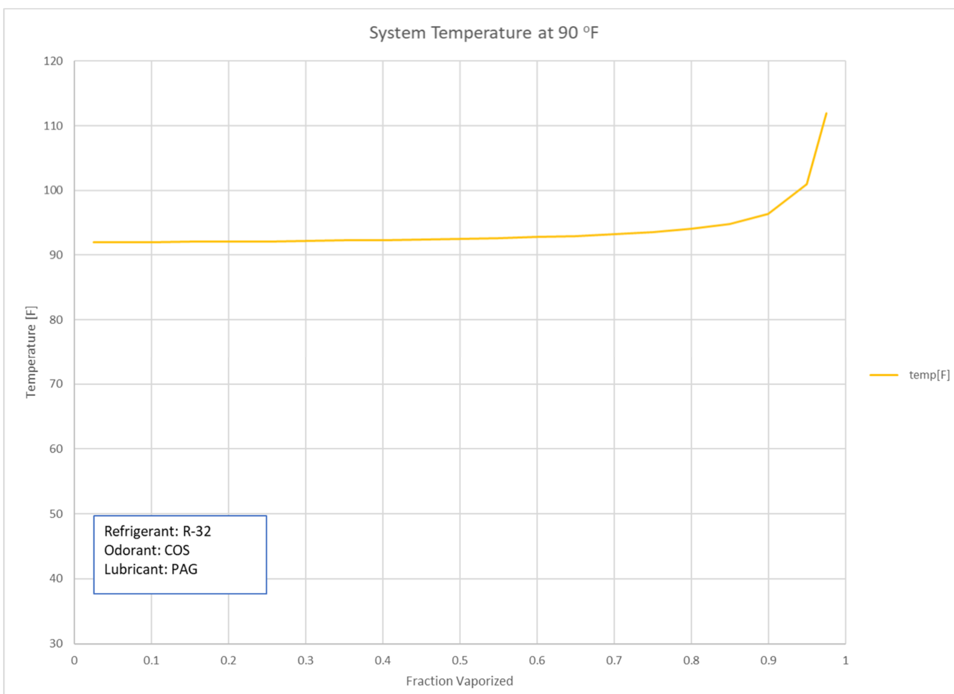

Figure B 9 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, carbonyl sulfide (COS) and PAG lubricant

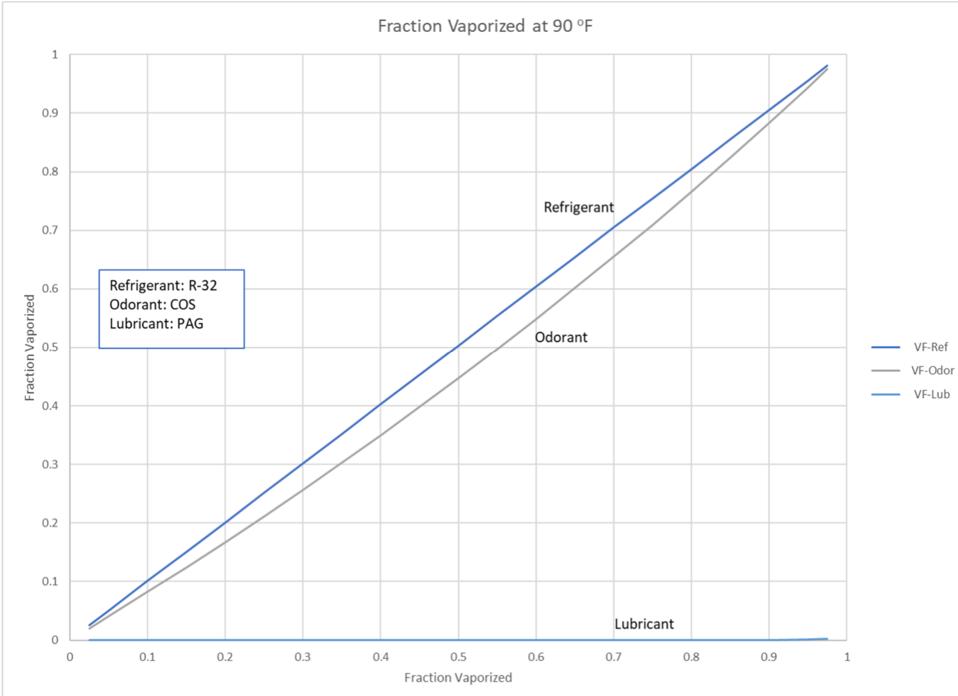

Figure B 10 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, carbonyl sulfide (COS) and PAG lubricant

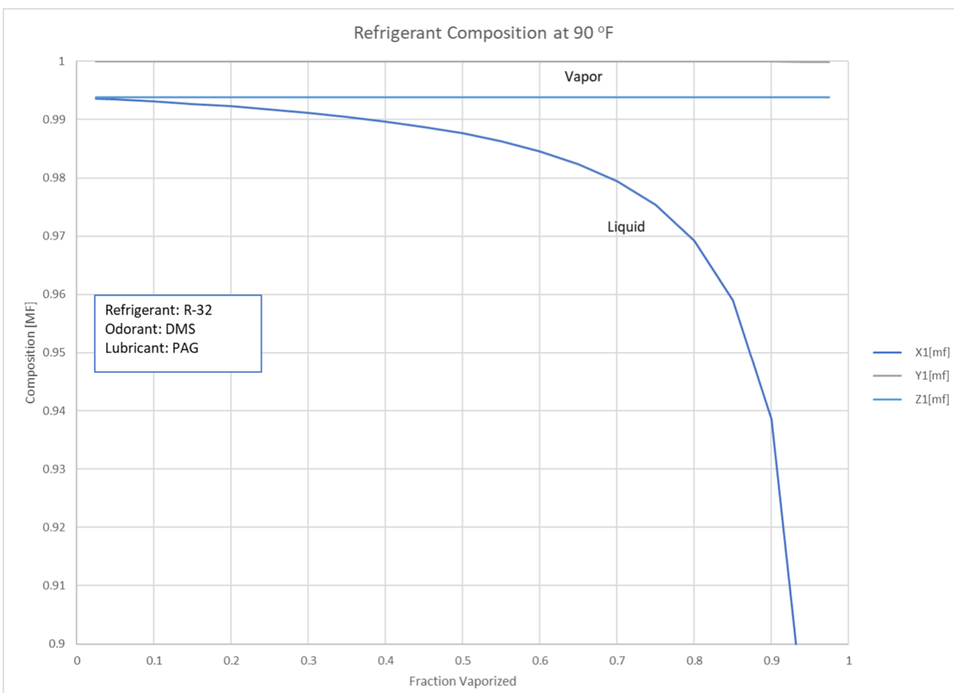

Figure B 11 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

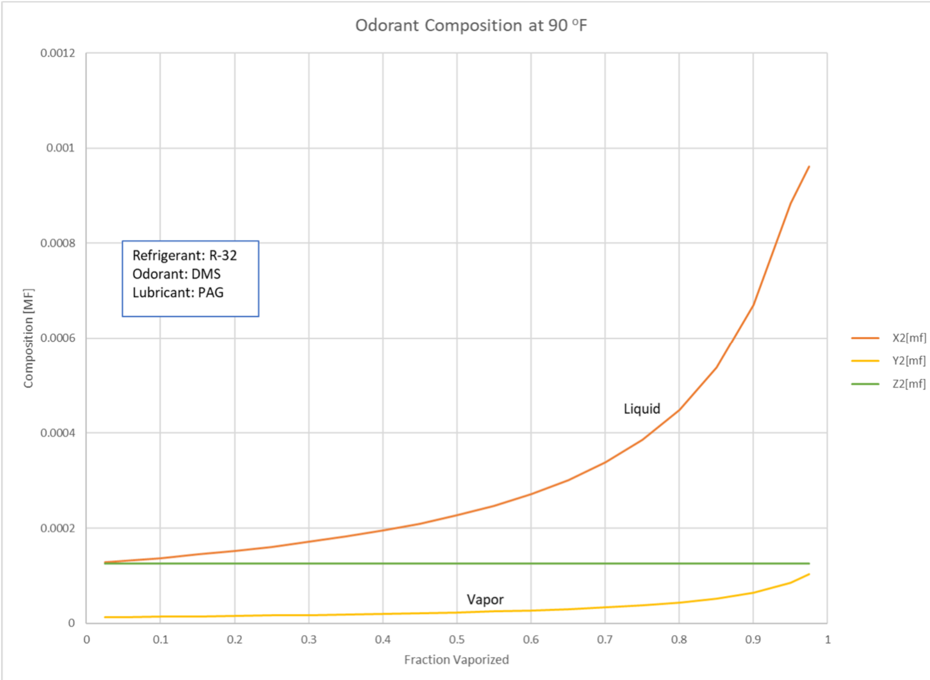

Figure B 12 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, dimethyl sulfide (($(CH_3)_2S$) and PAG lubricant

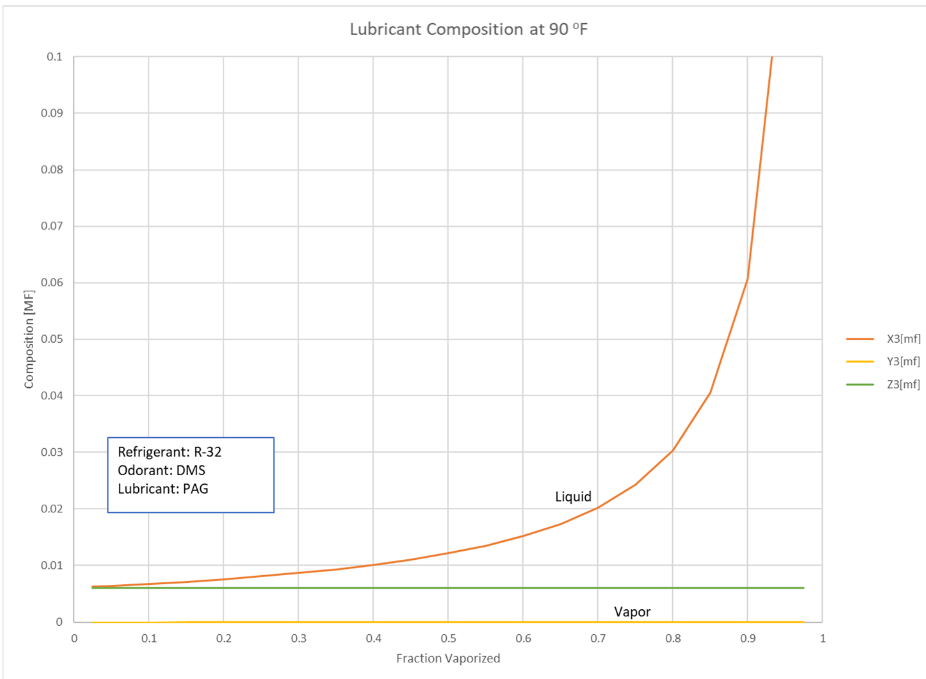

Figure B 13 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, dimethyl sulfide (($(CH_3)_2S$) and PAG lubricant

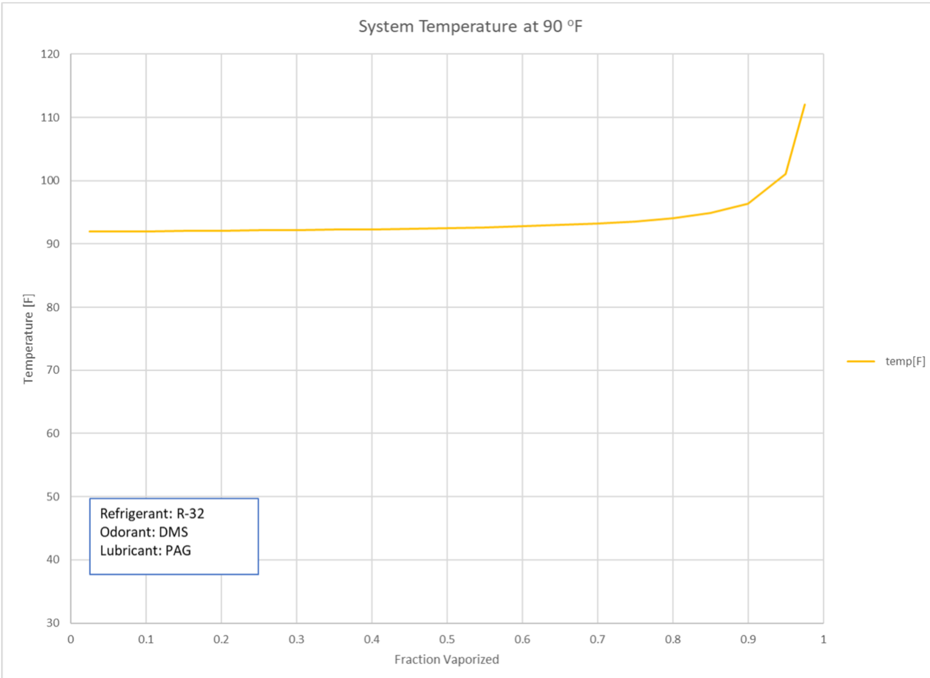

Figure B 14 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

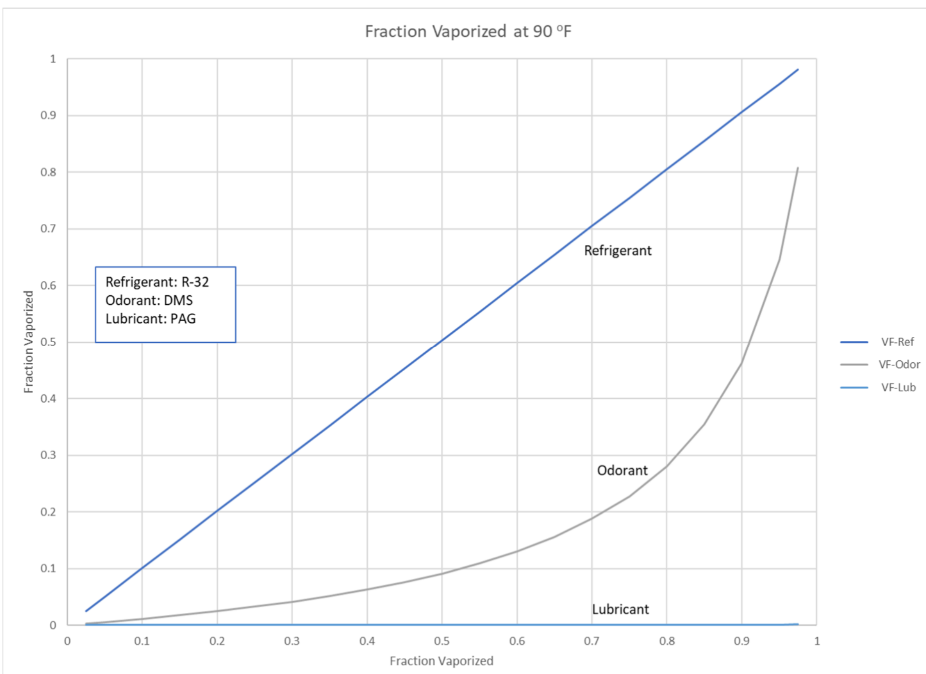

Figure B 15 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

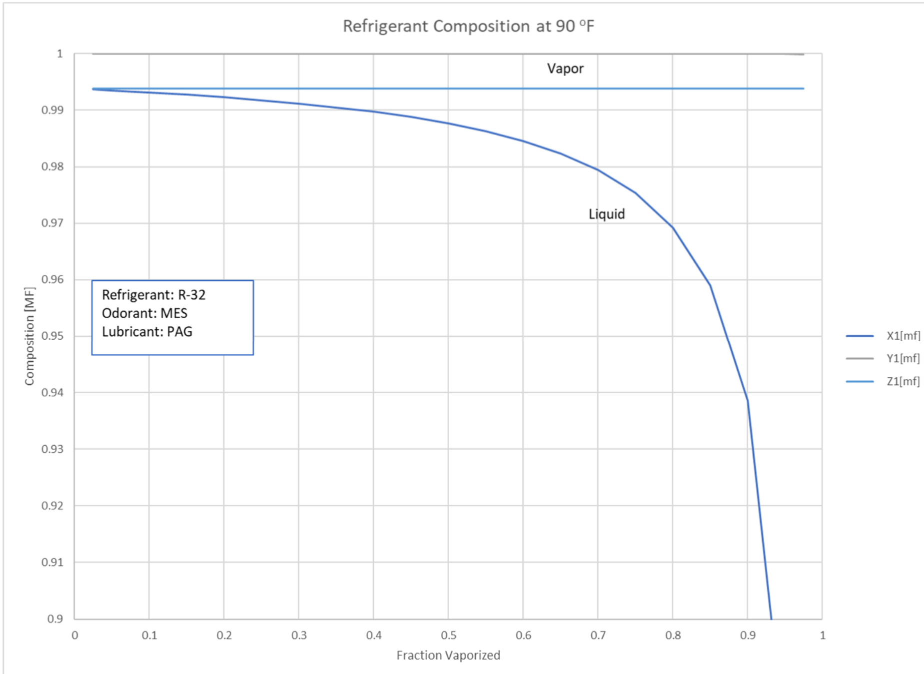

Figure B 16 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, methyl ethyl sulfide ((CH$_3$)S(C$_2$H$_5$)) and PAG lubricant

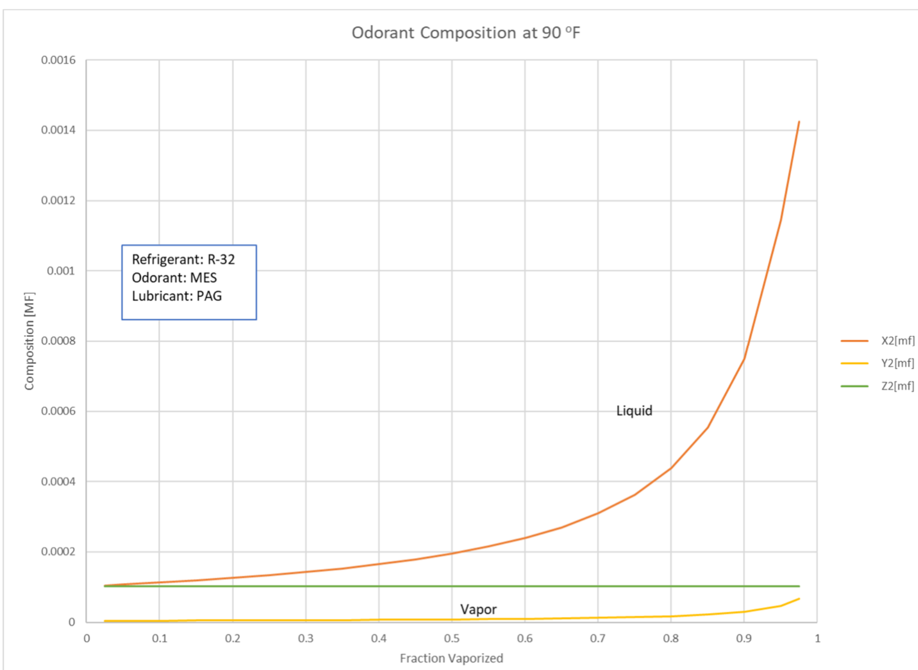

Figure B 17 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, methyl ethyl sulfide ((CH$_3$)S(C$_2$H$_5$)) and PAG lubricant

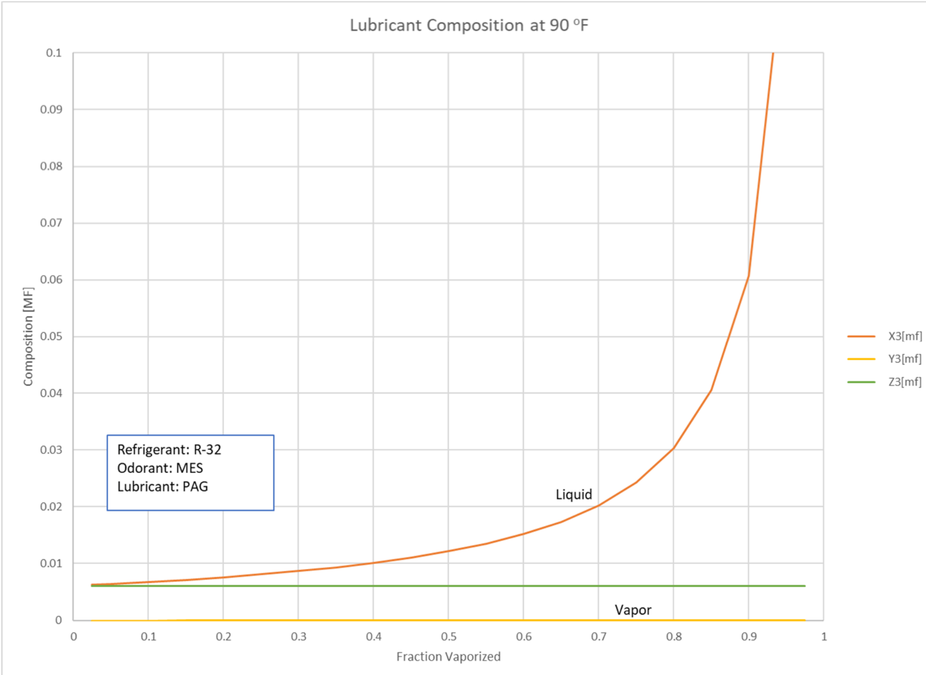

Figure B 18 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

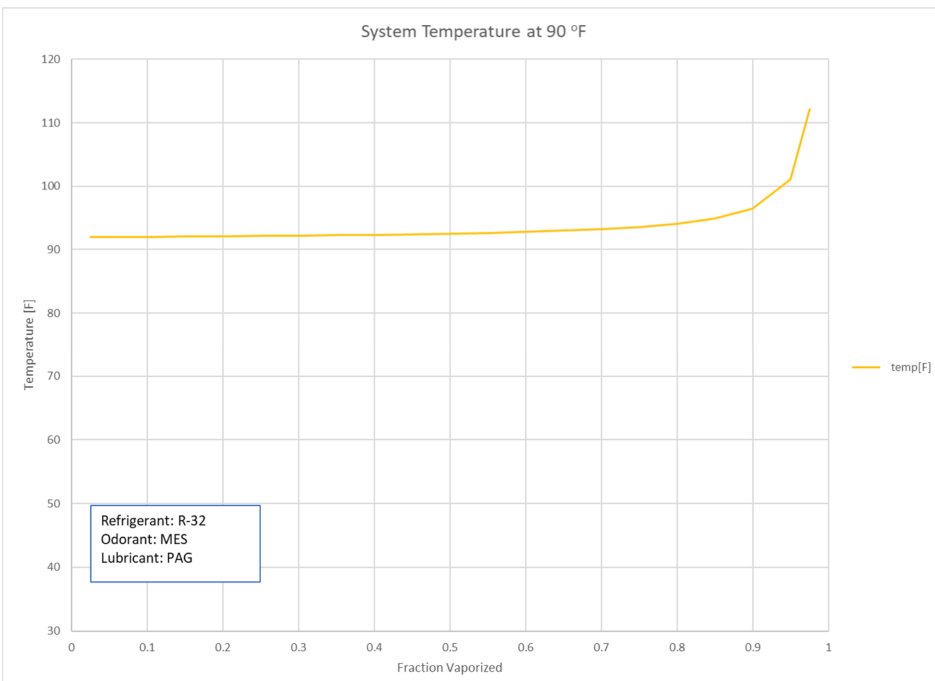

Figure B 19 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

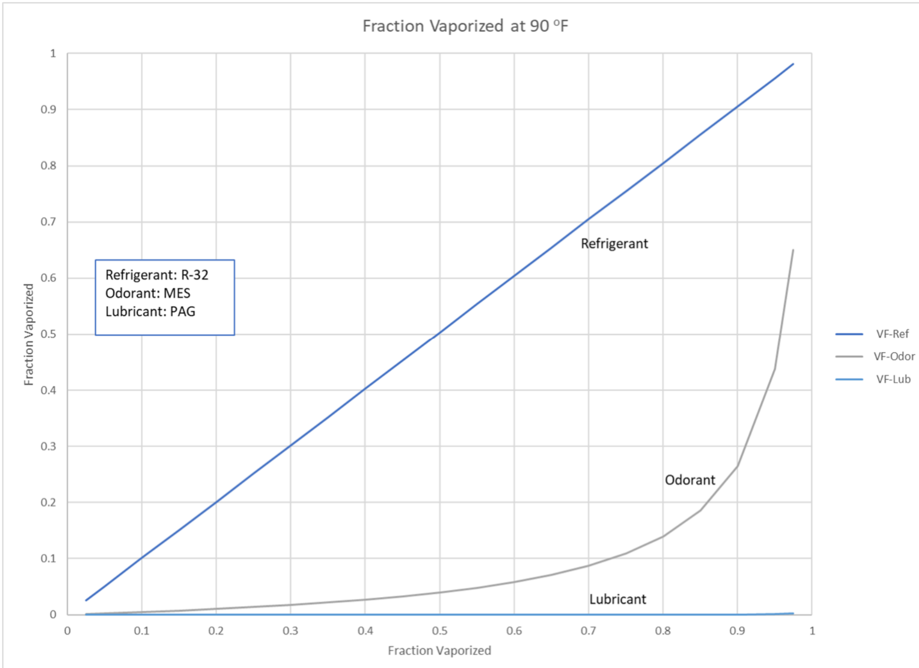

Figure B 20 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 20.1 Bar (291 psig) for R-32, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

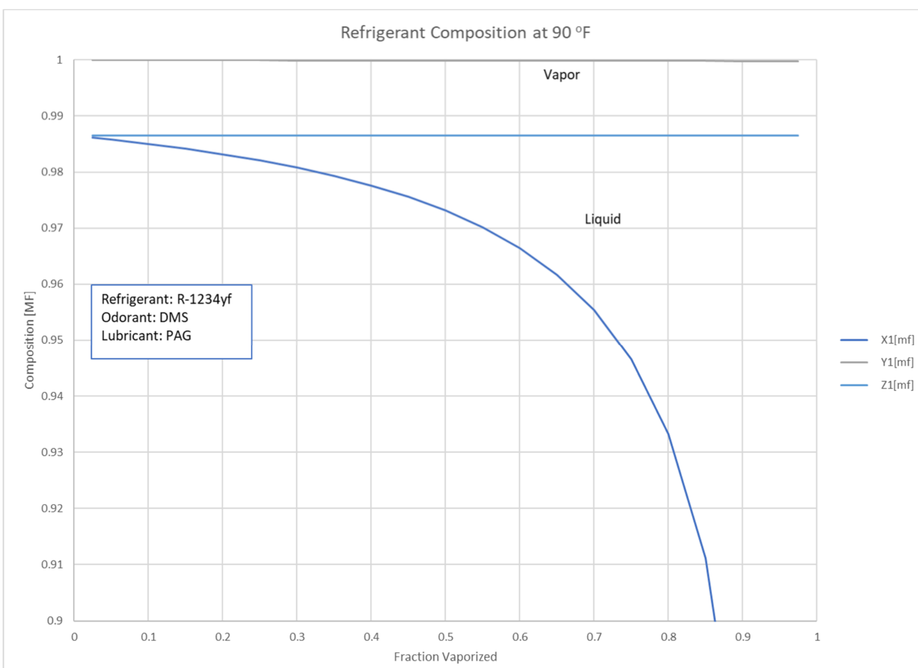

Figure B 21 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

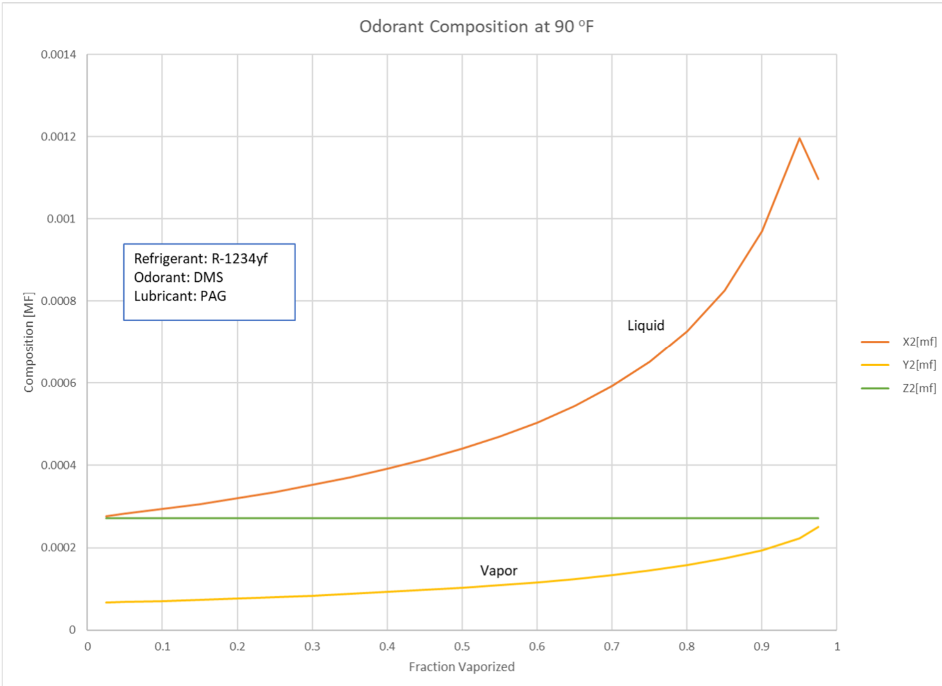

Figure B 22 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

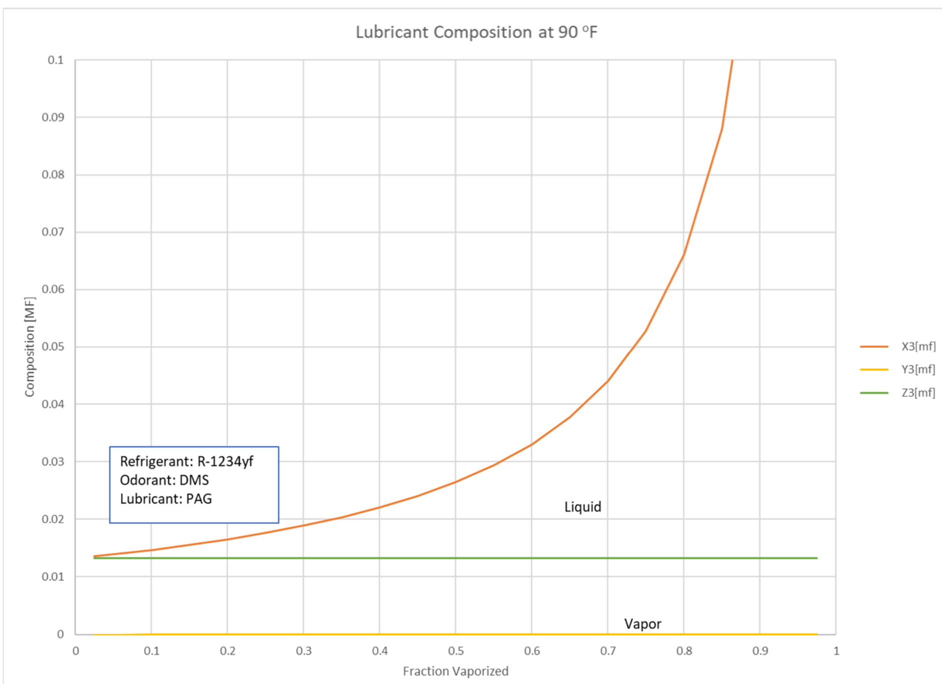

Figure B 23 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

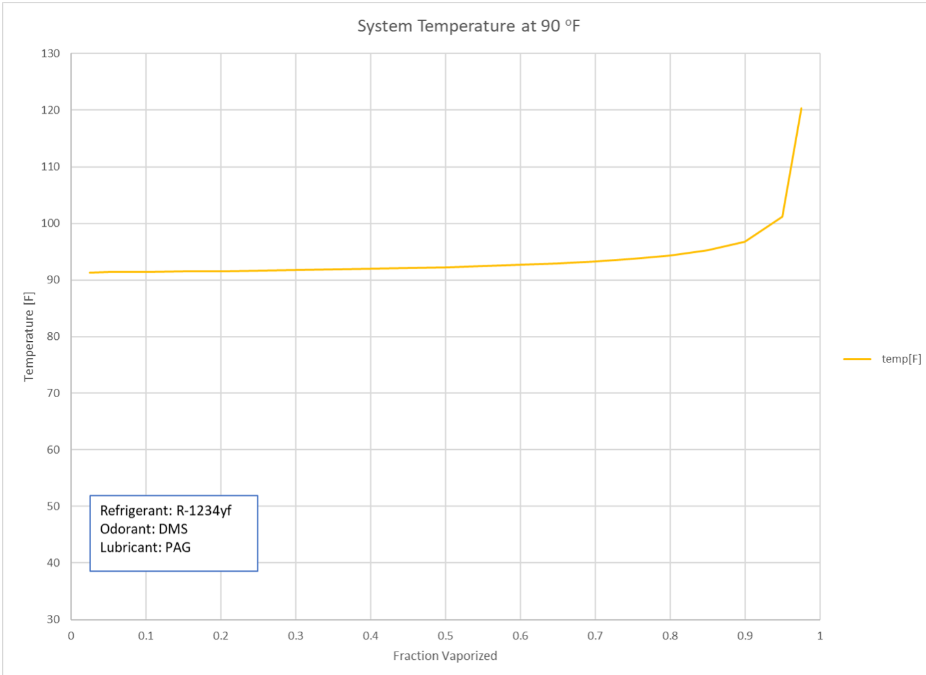

Figure B 24 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

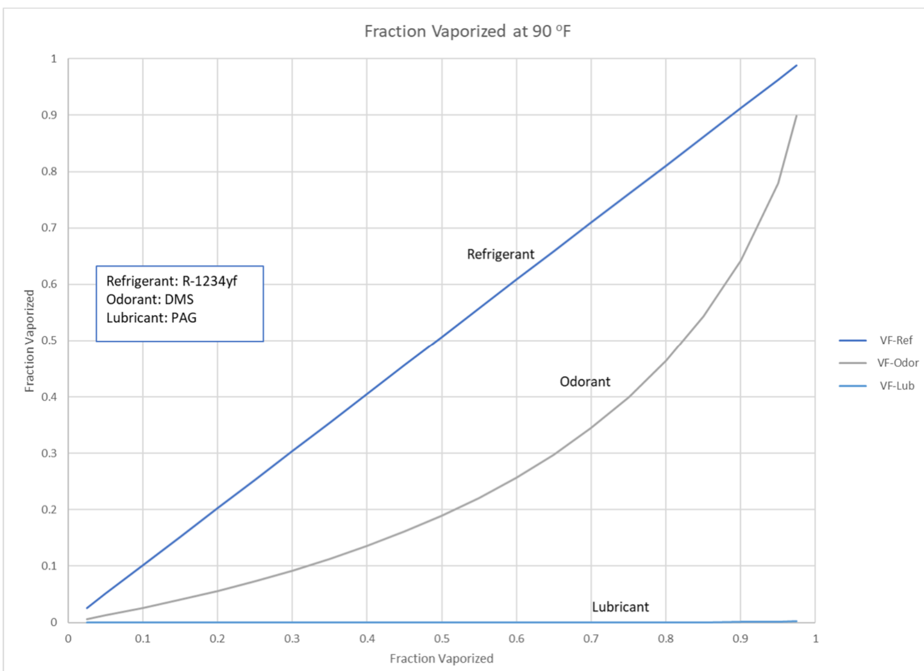

Figure B 25 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

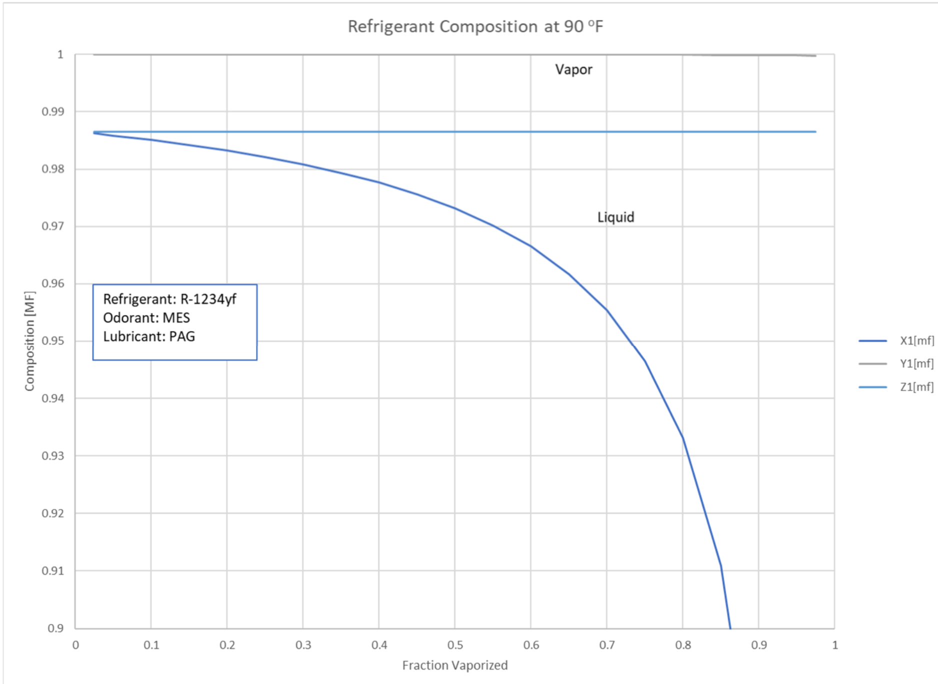

Figure B 26 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

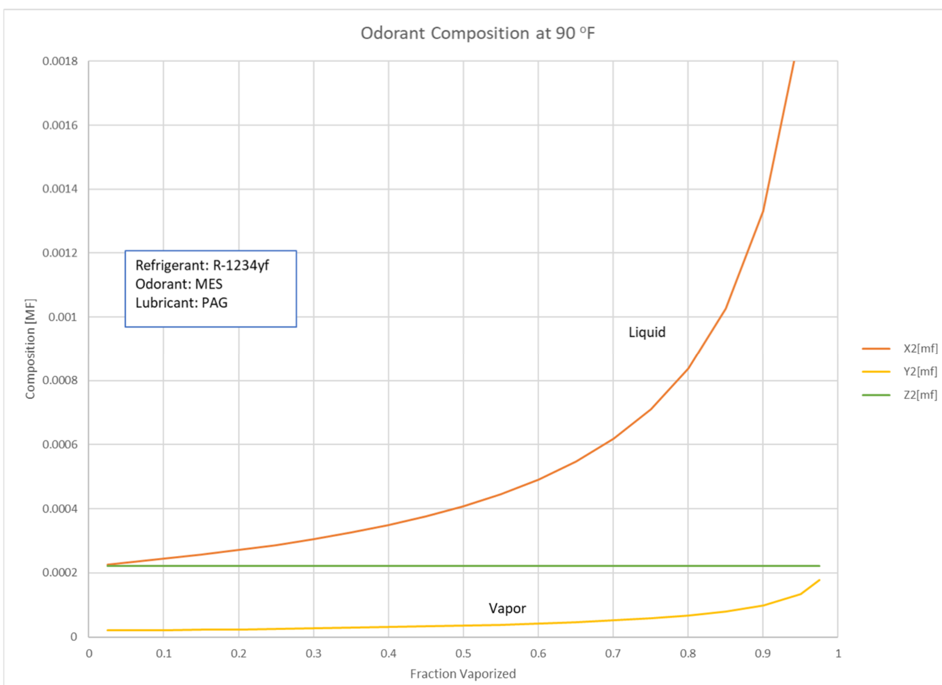

Figure B 27 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

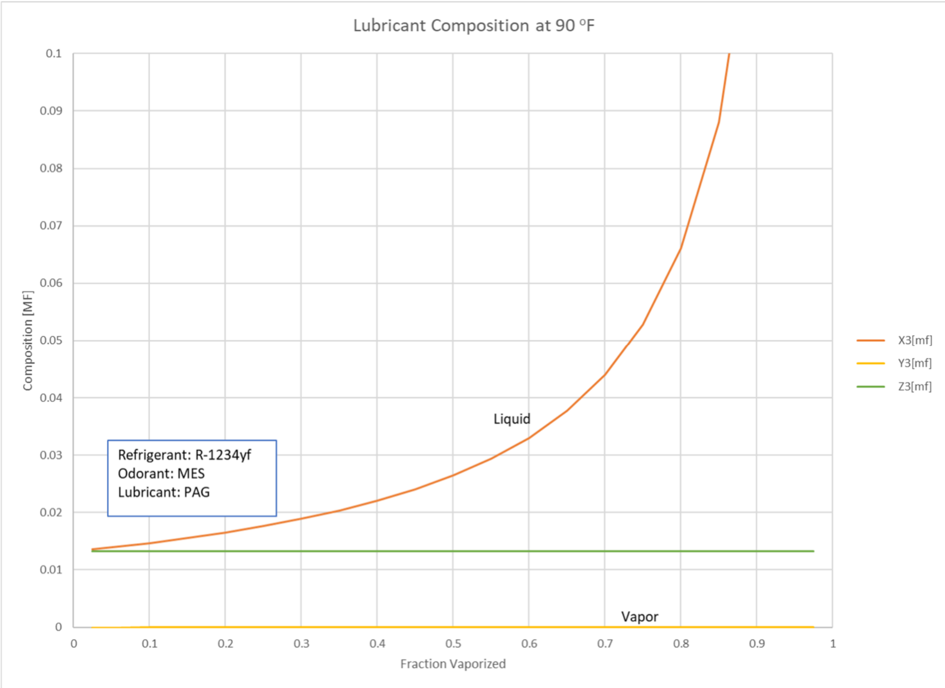

Figure B 28 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

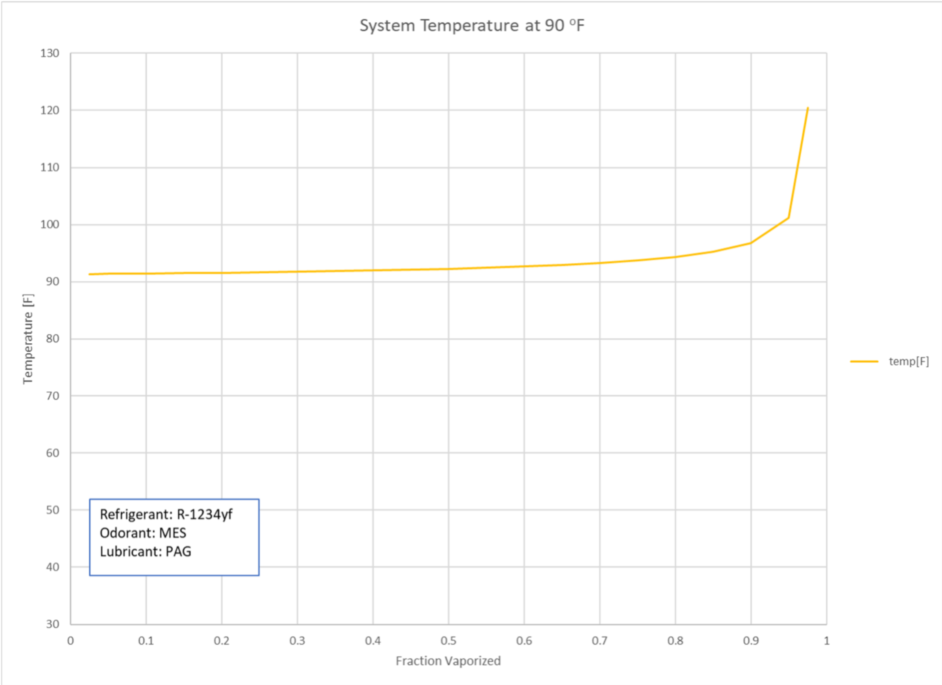

Figure B 29 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

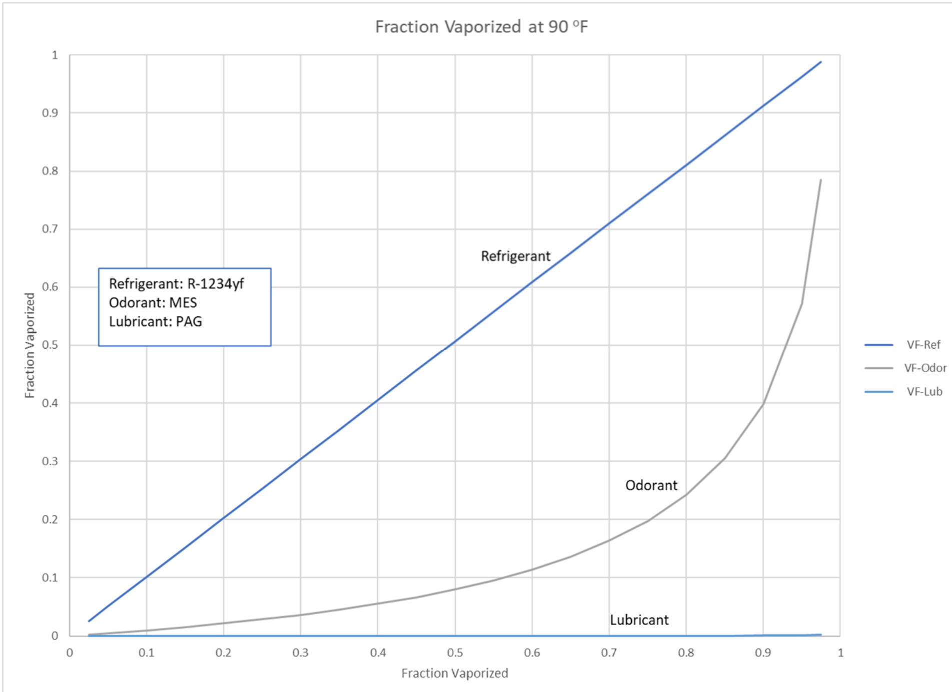

Figure B 30 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

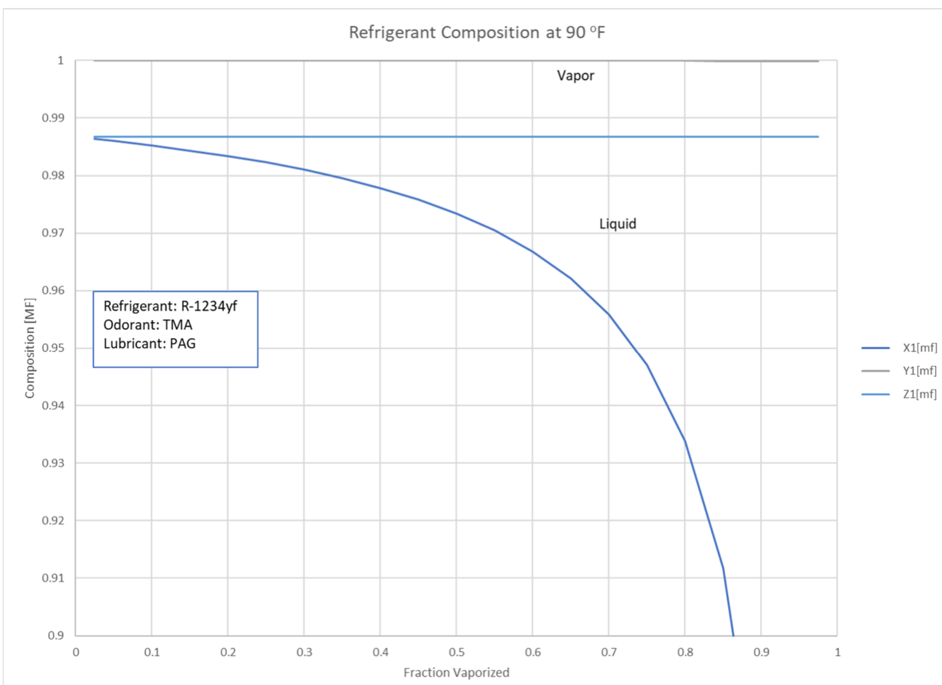

Figure B 31 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, trimethylamine ($(CH_3)_3N$) and PAG lubricant

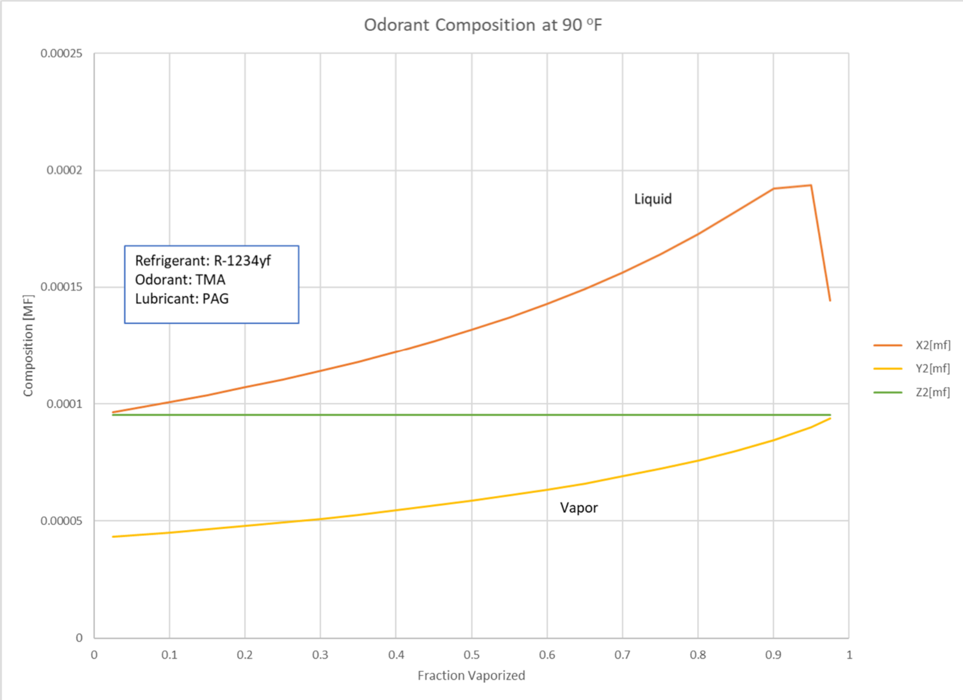

Figure B 32 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, trimethylamine ($(CH_3)_3N$) and PAG lubricant

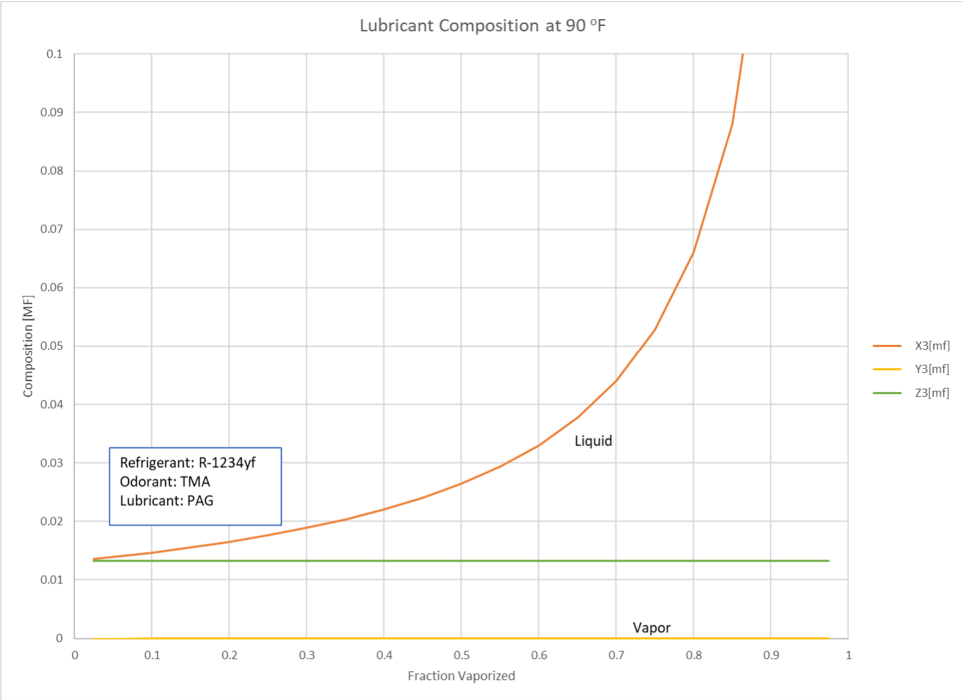

Figure B 33 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, trimethylamine ($(CH_3)_3N$) and PAG lubricant

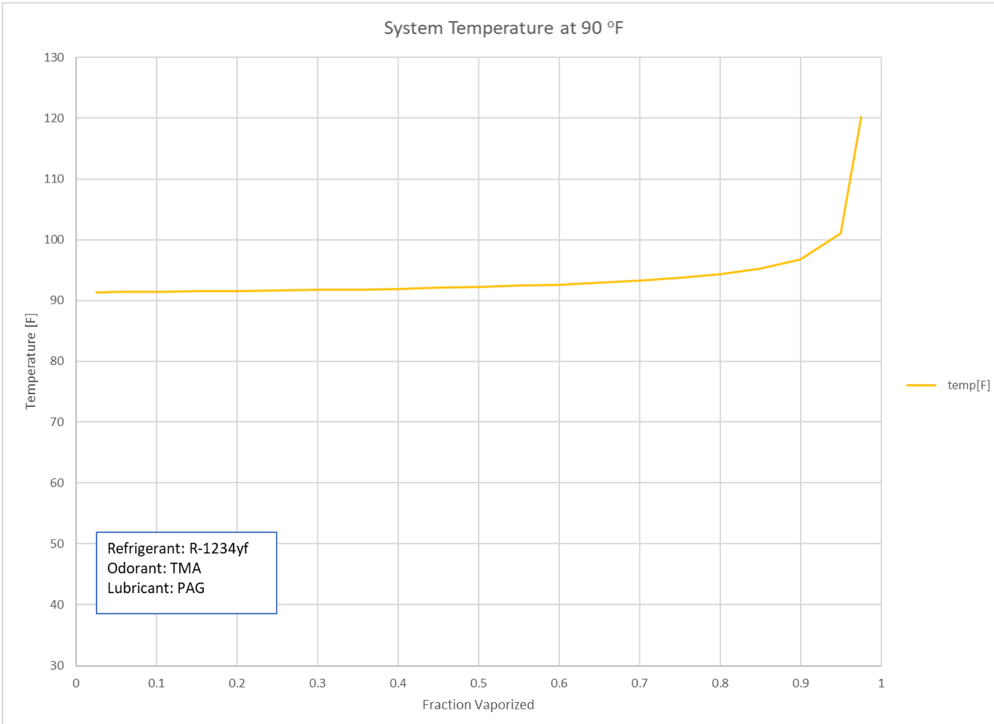

Figure B 34 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, trimethylamine ($(CH_3)_3N$) and PAG lubricant

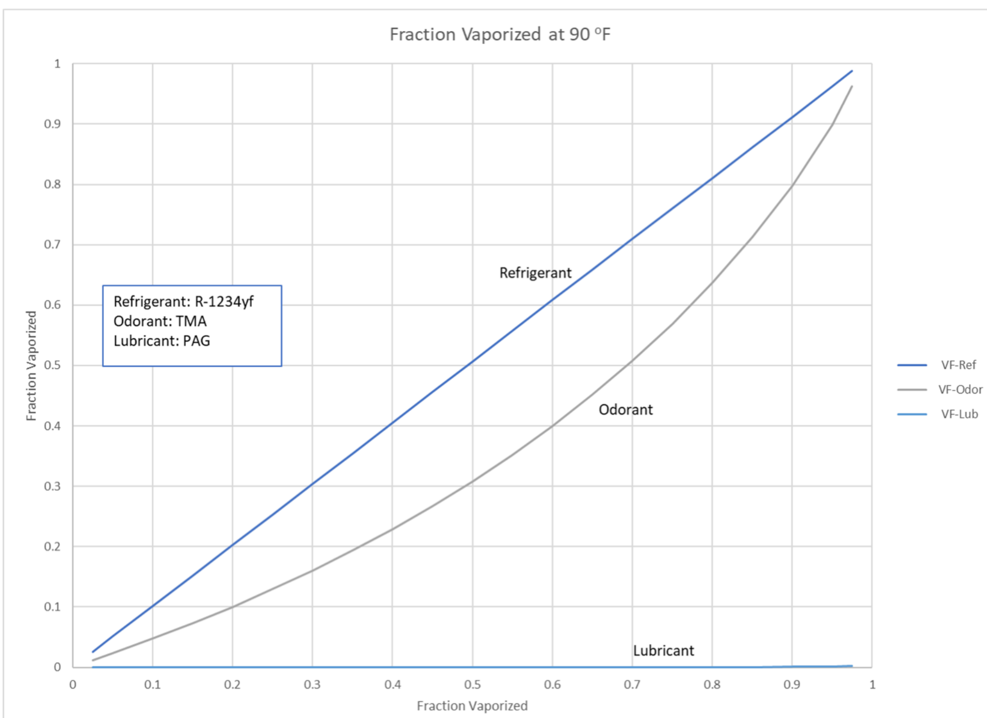

Figure B 35 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 7.3 Bar (106 psig) for R-1234yf, trimethylamine ($(CH_3)_3N$) and PAG lubricant

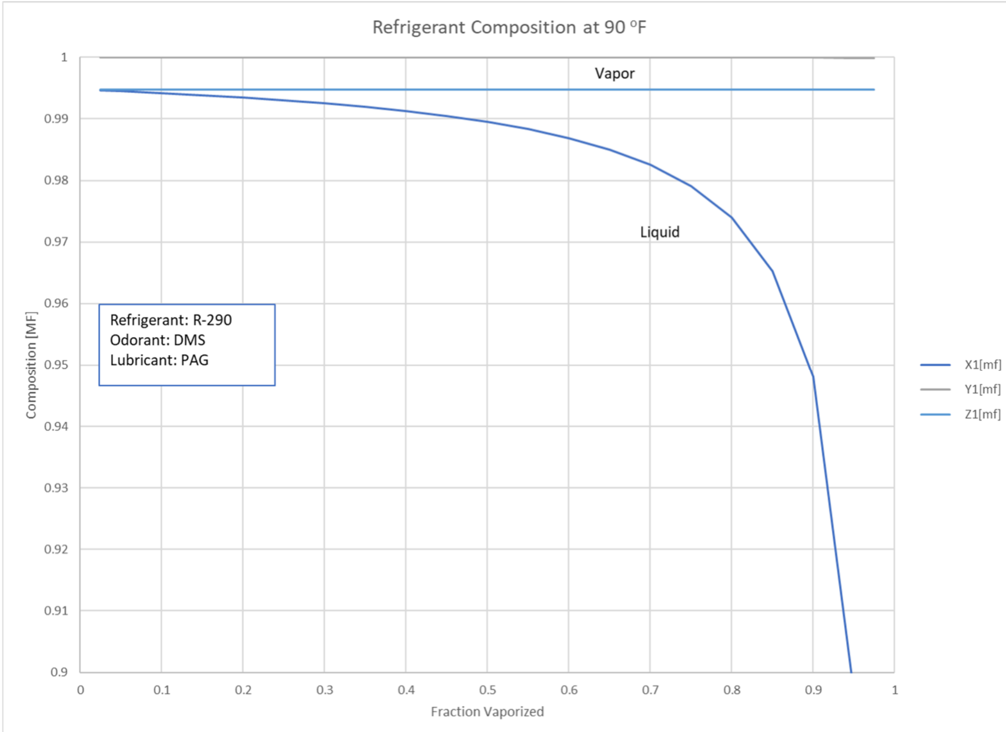

Figure B 36 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

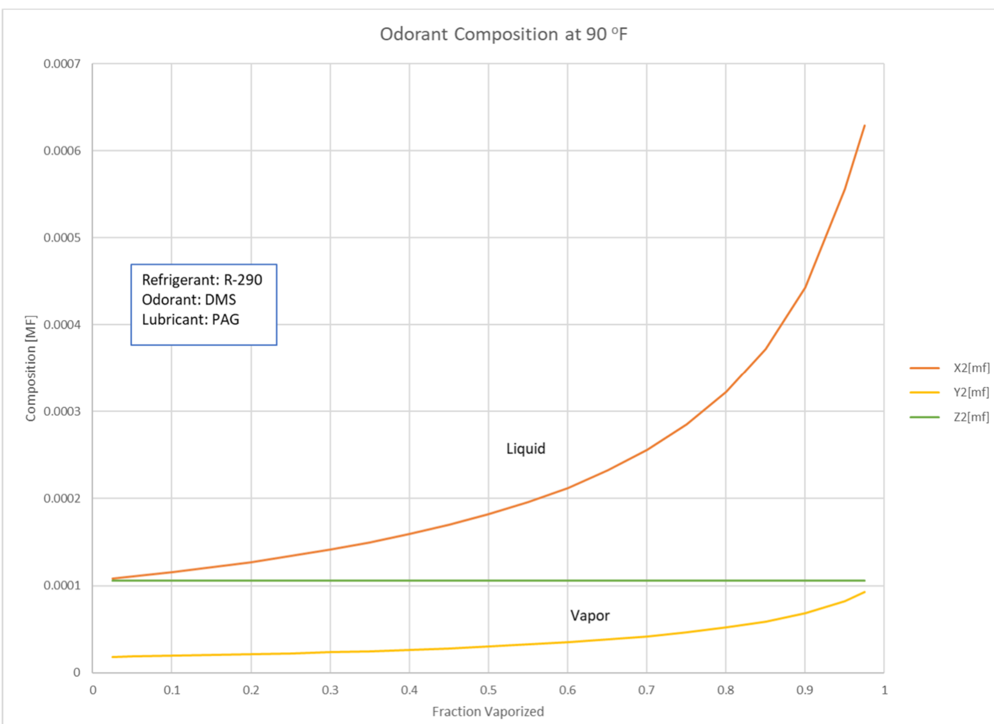

Figure B 37 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

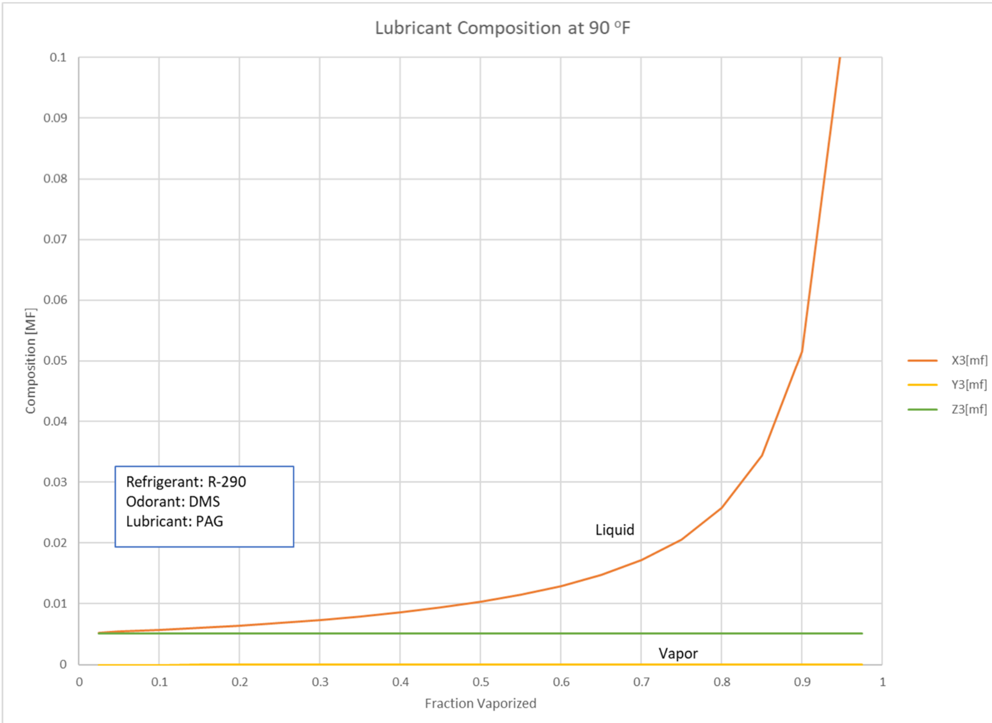

Figure B 38 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

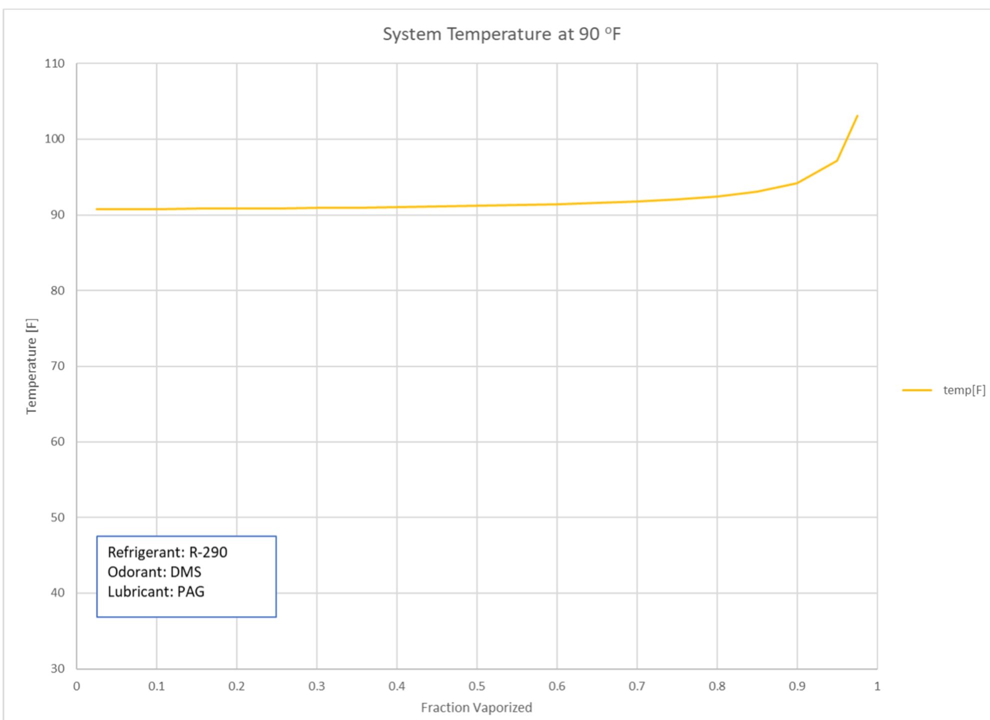

Figure B 39 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

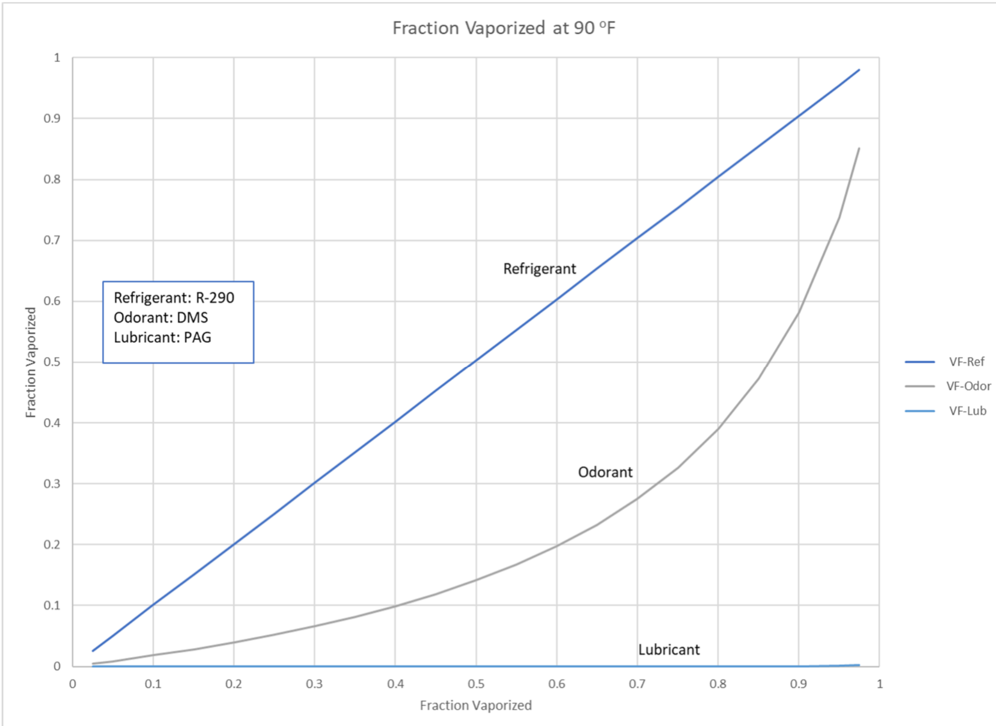

Figure B 40 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, dimethyl sulfide ($(CH_3)_2S$) and PAG lubricant

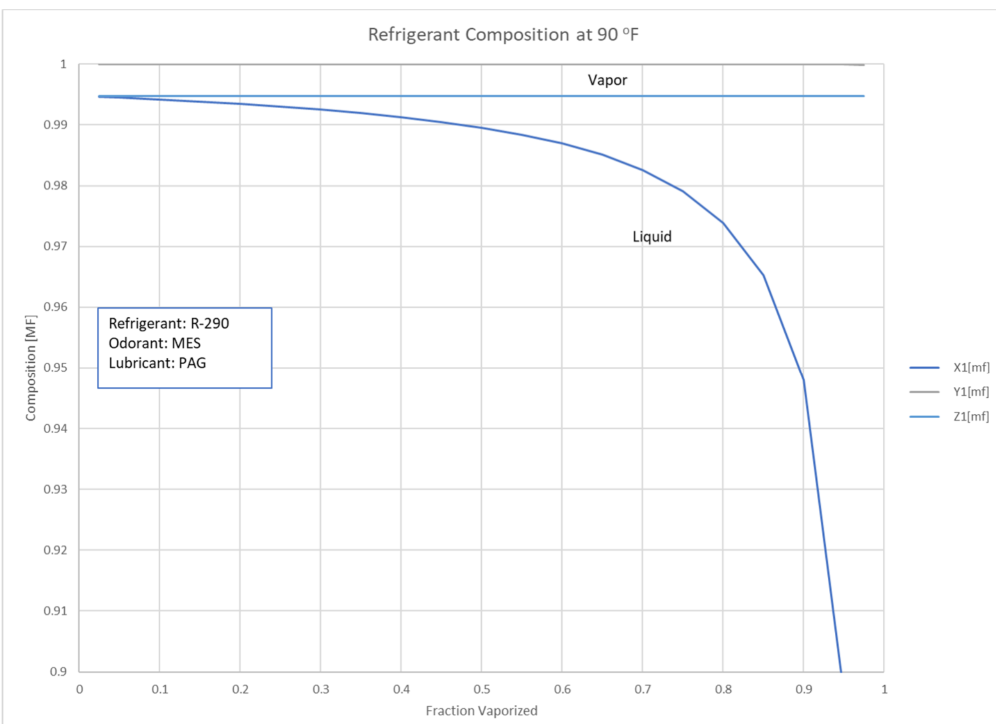

Figure B 41 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

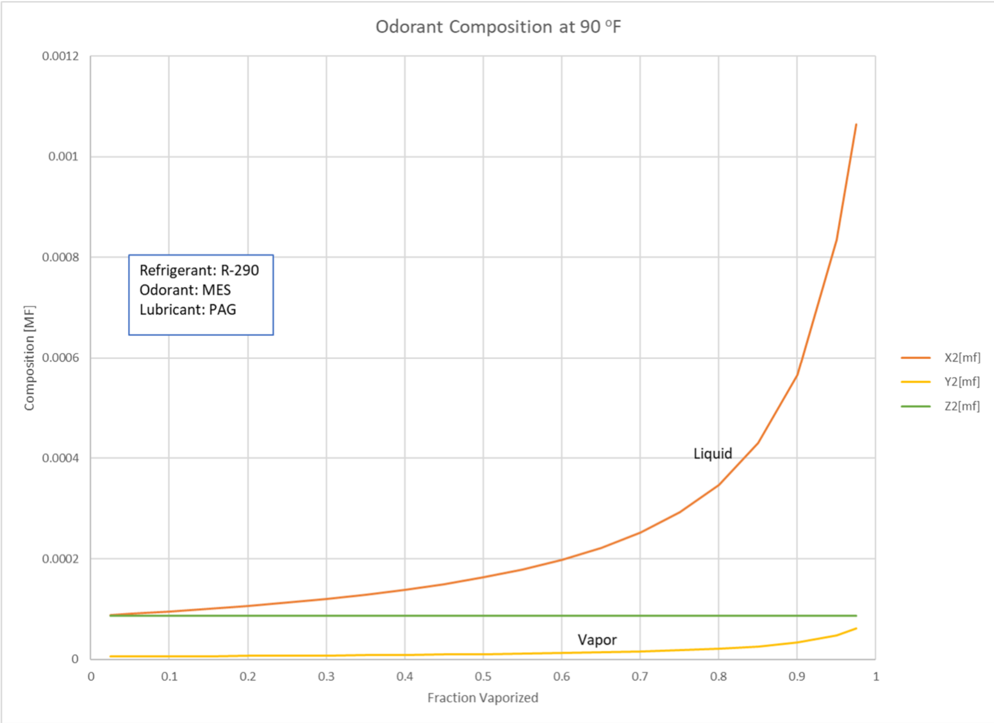

Figure B 42 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

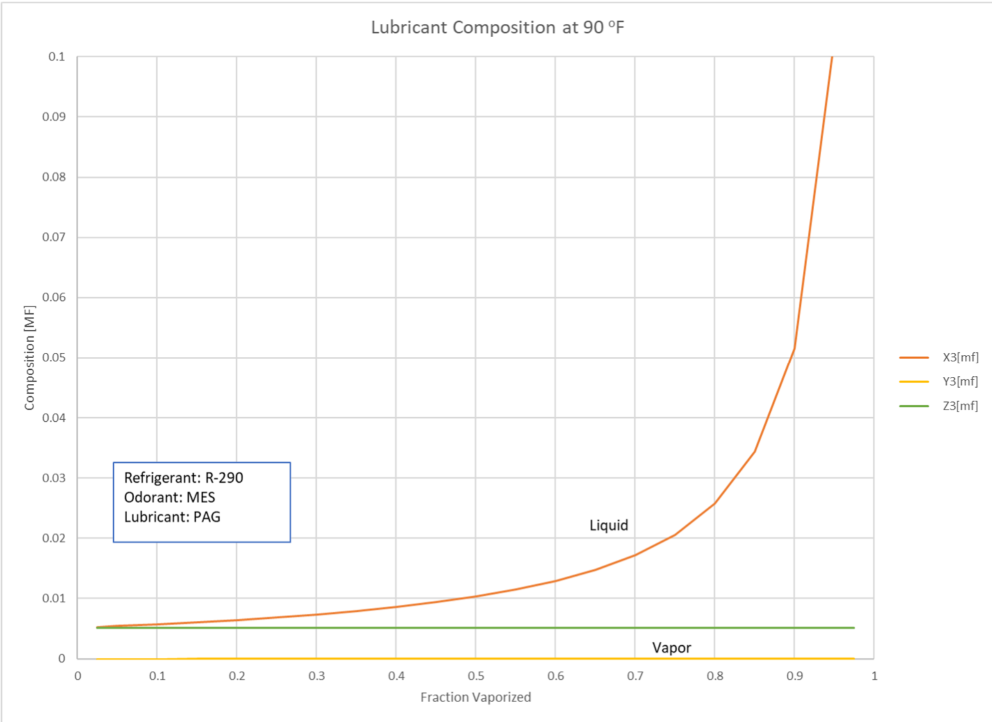

Figure B 43 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

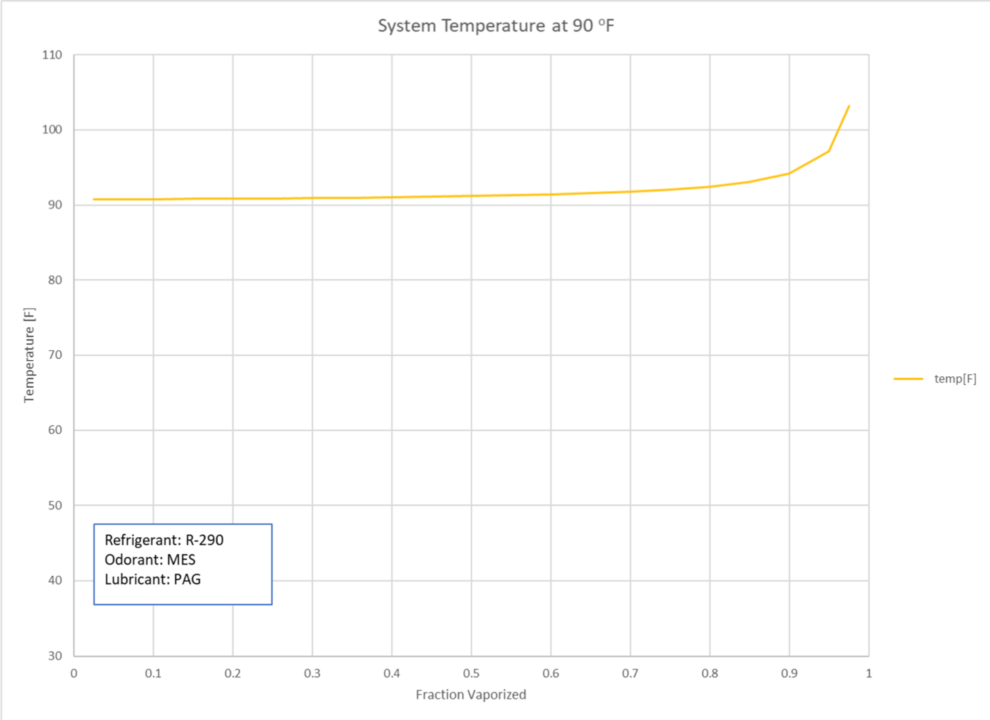

Figure B 44 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

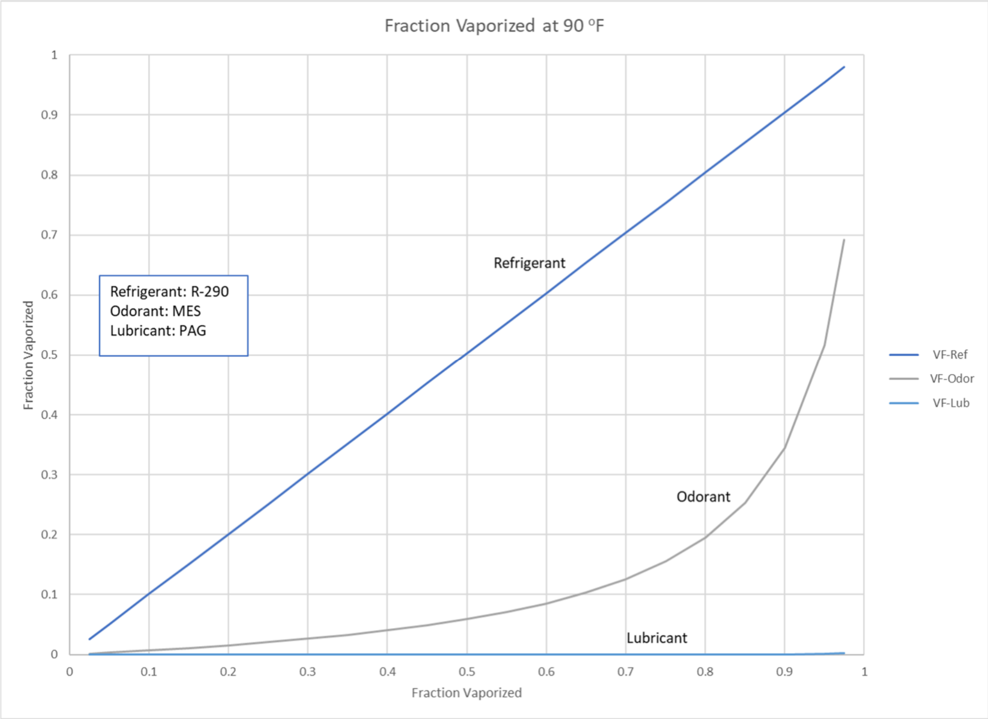

Figure B 45 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, methyl ethyl sulfide ($(CH_3)S(C_2H_5)$) and PAG lubricant

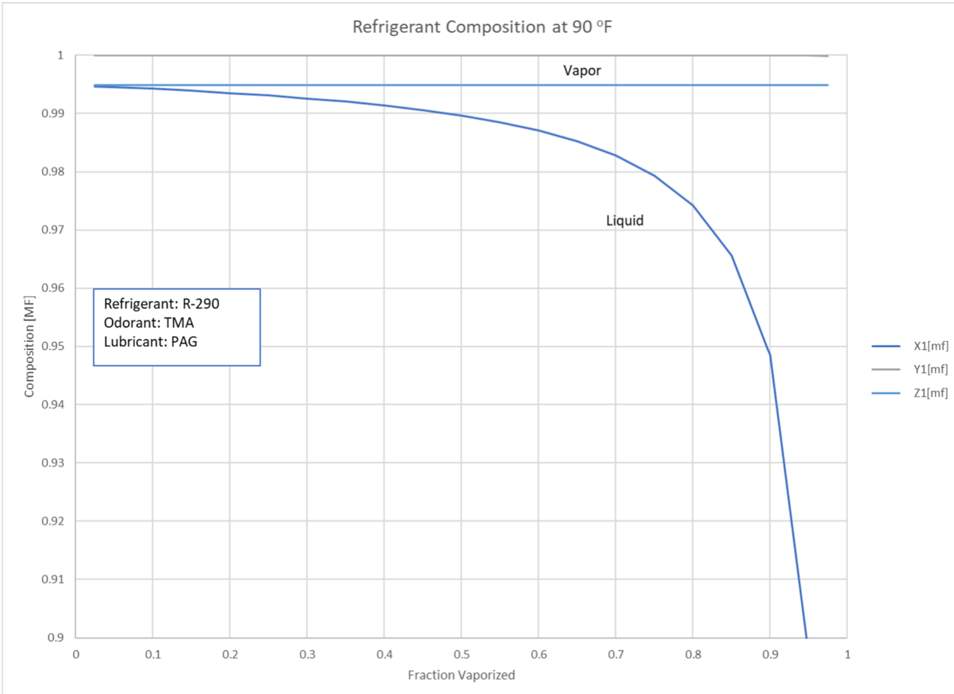

Figure B 46 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, trimethylamine ($(CH_3)_3N$) and PAG lubricant

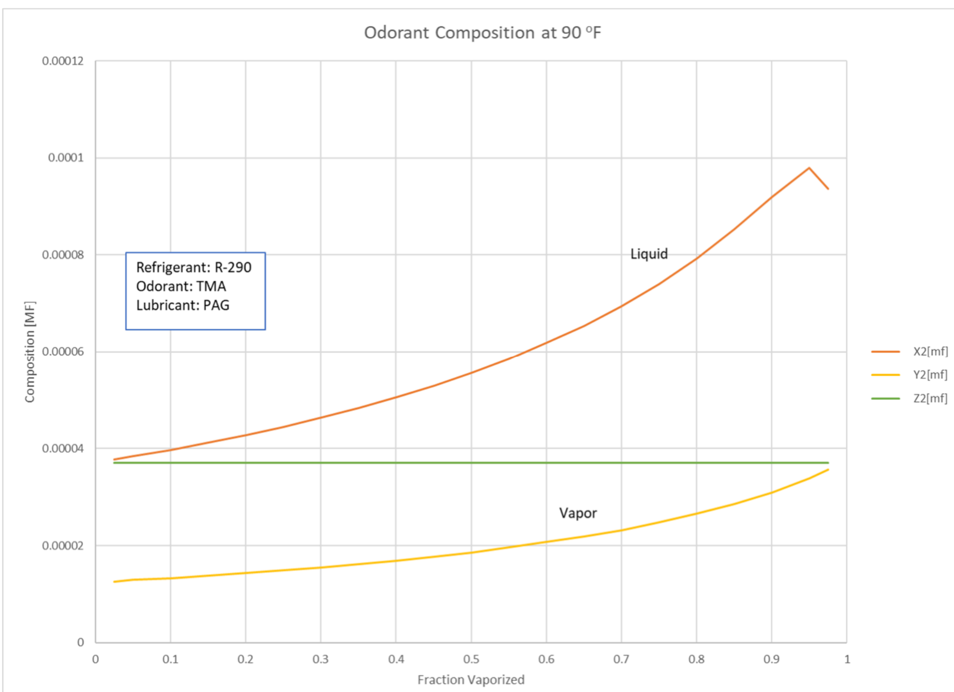

Figure B 47 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, trimethylamine ($(CH_3)_3N$) and PAG lubricant

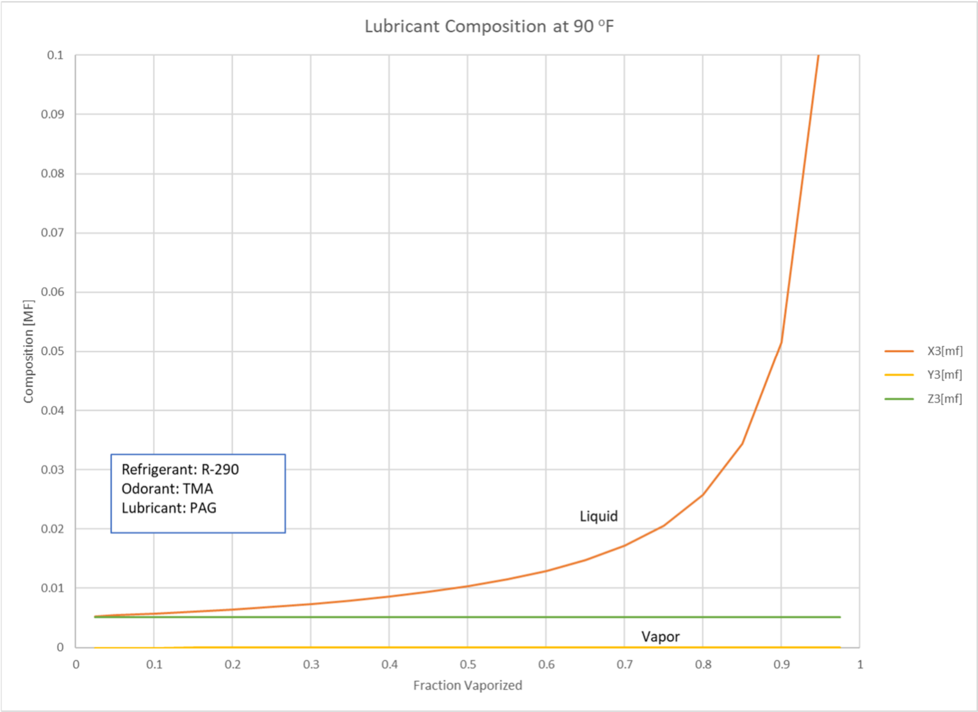

Figure B 48 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, trimethylamine ($(CH_3)_3N$) and PAG lubricant

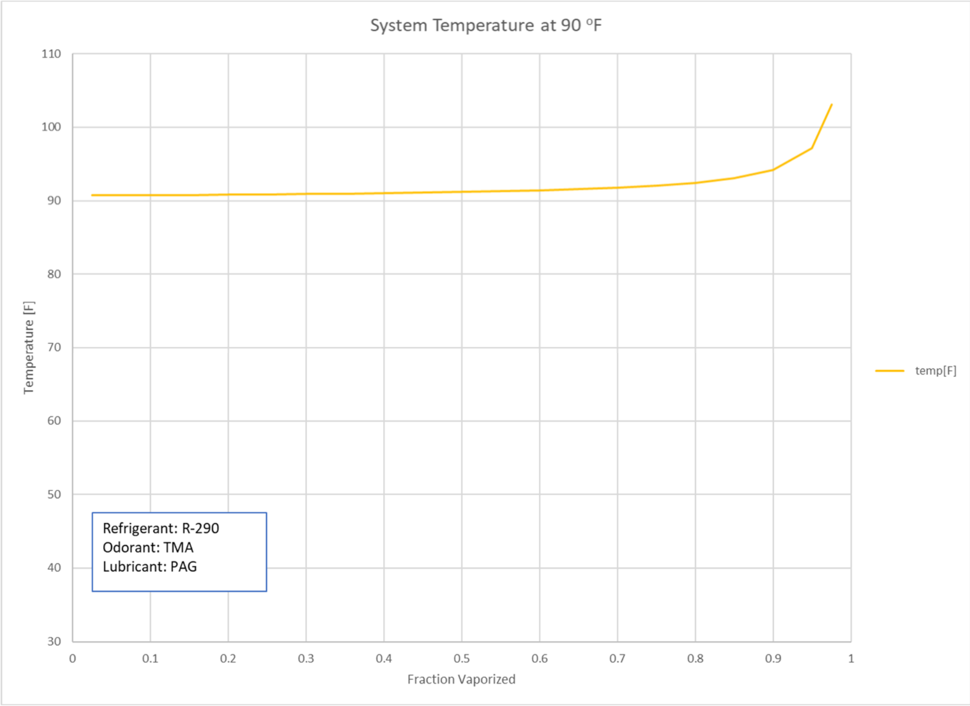

Figure B 49 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, trimethylamine ($(CH_3)_3N$) and PAG lubricant

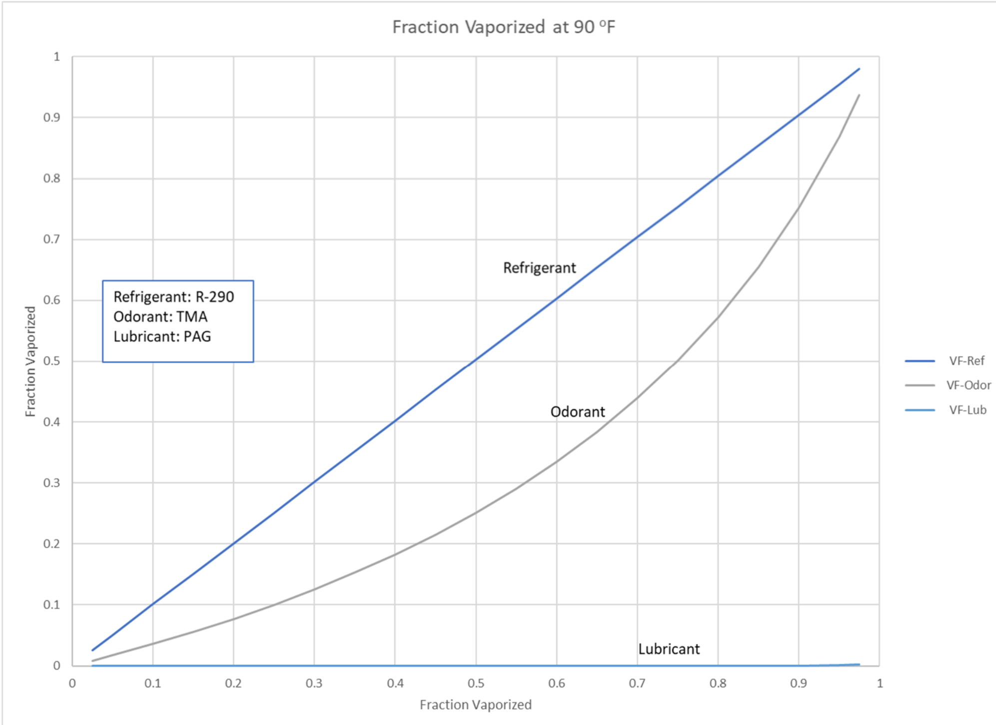

Figure B 50 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, trimethylamine ($(CH_3)_3N$) and PAG lubricant

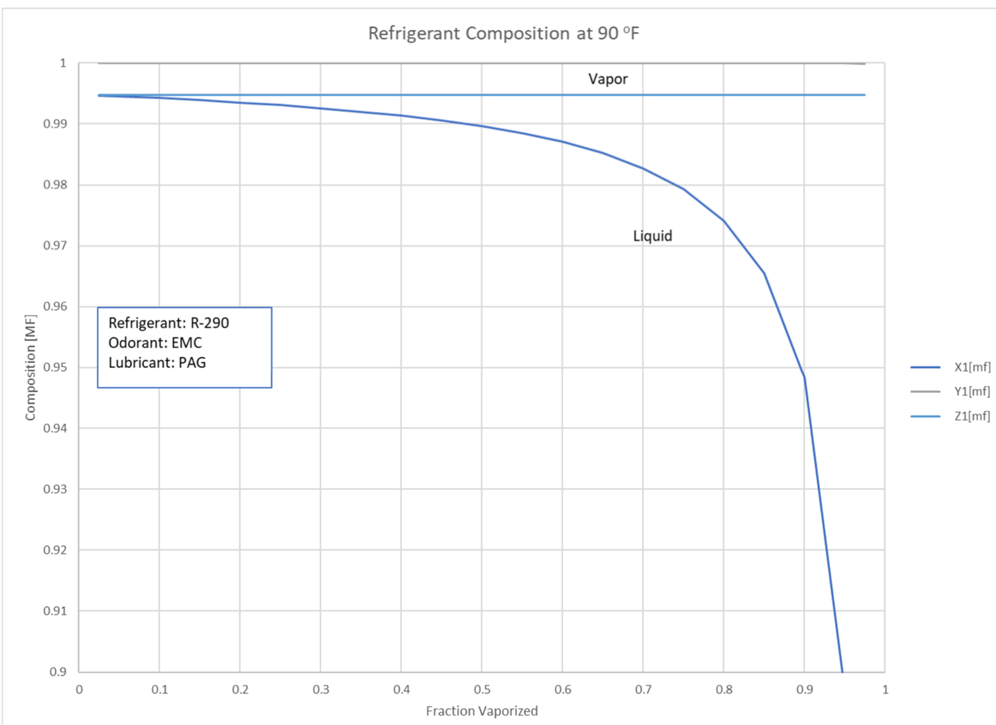

Figure B 51 – Refrigerant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, ethyl mercaptan (C_2H_5SH) and PAG lubricant

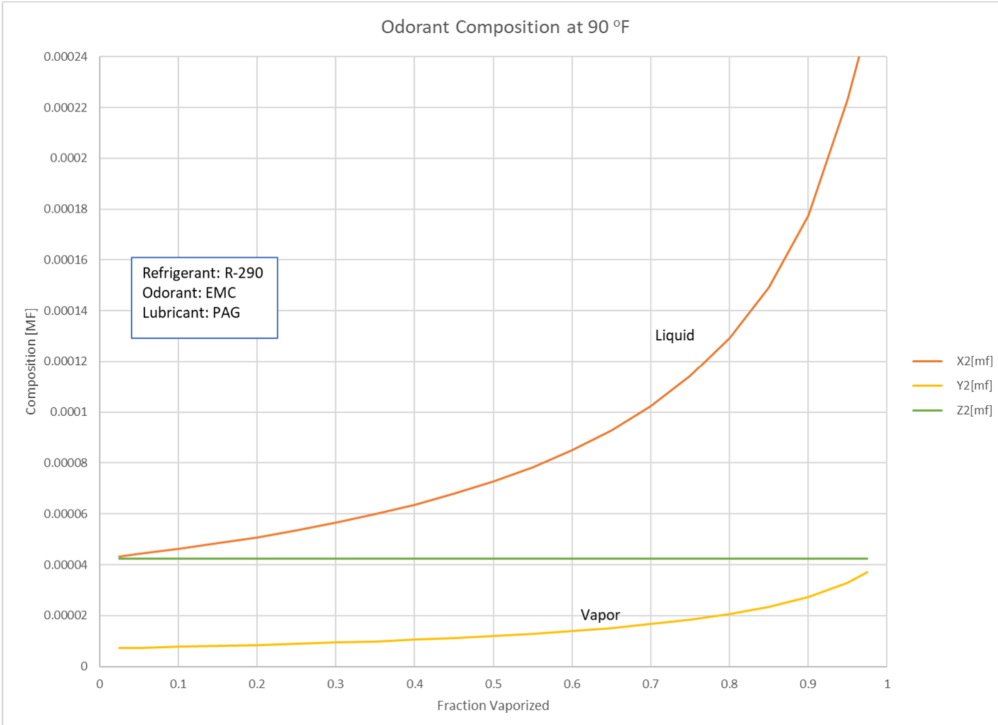

Figure B 52 – Odorant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, ethyl mercaptan (C_2H_5SH) and PAG lubricant

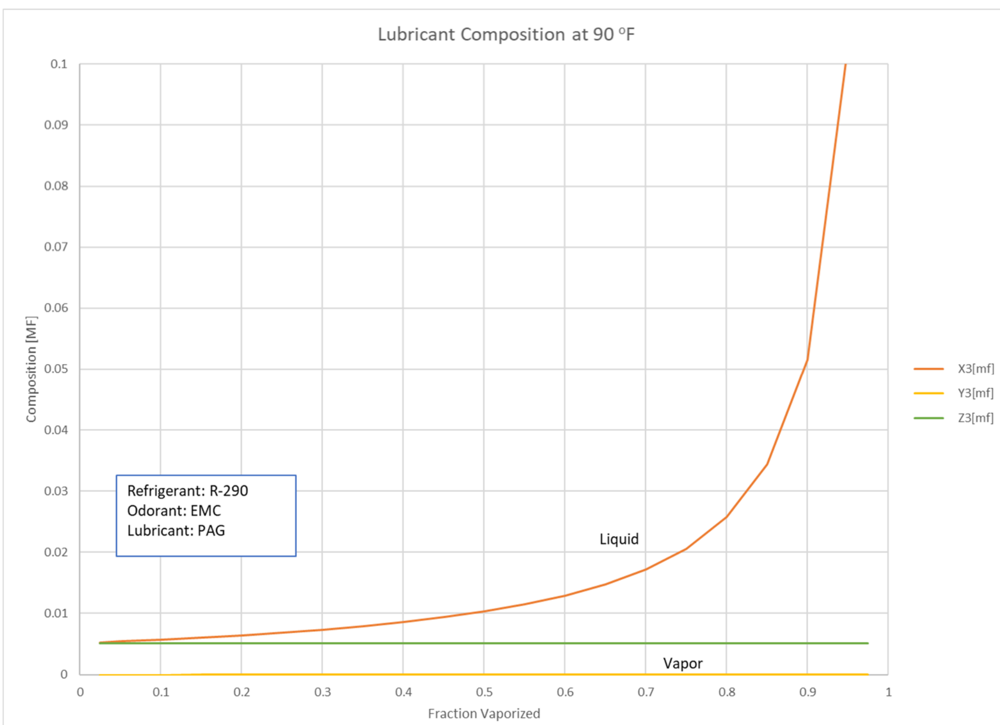

Figure B 53 – Lubricant composition in the liquid and vapor phases at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, ethyl mercaptan (C_2H_5SH) and PAG lubricant

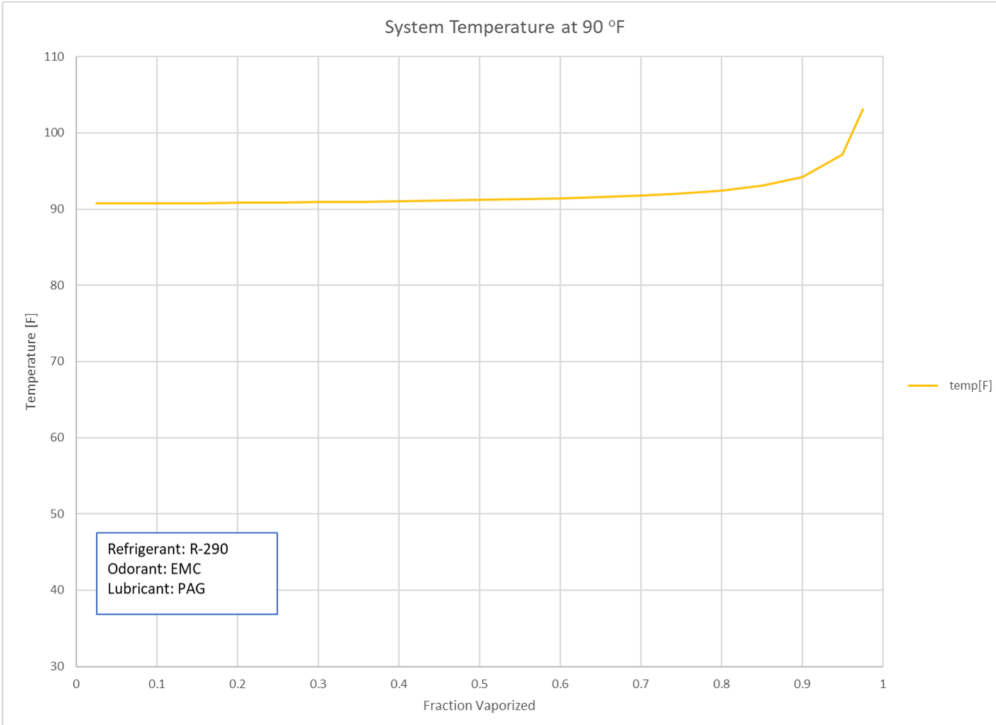

Figure B 54 – Temperature variation with increasing vaporization fraction at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, ethyl mercaptan (C_2H_5SH) and PAG lubricant

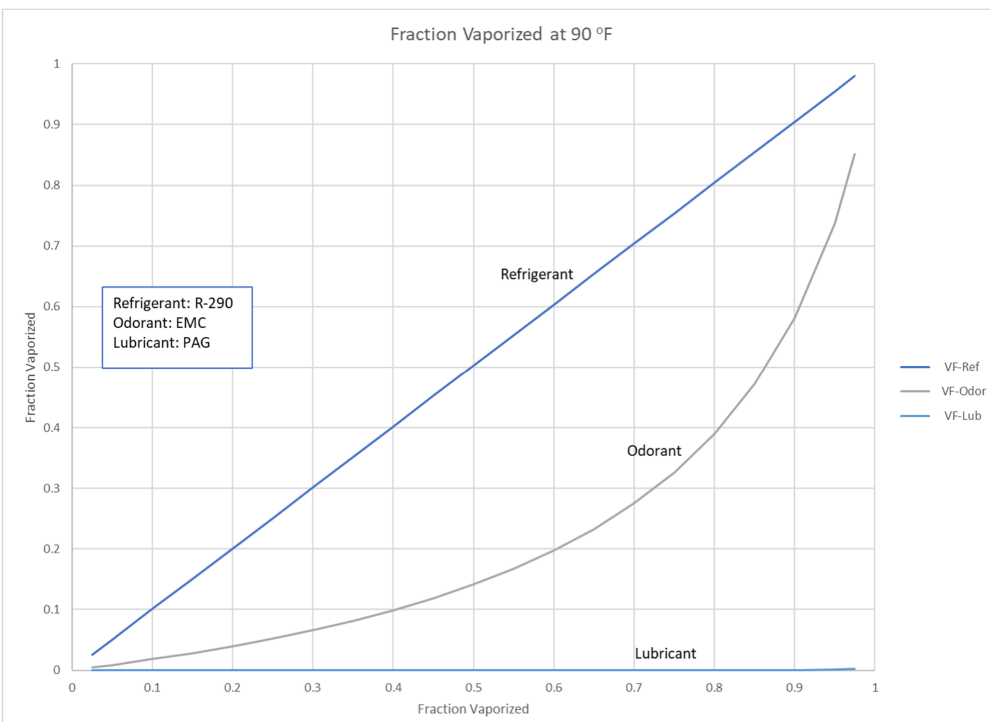

Figure B 55 – Species fraction vaporized with increasing overall fraction vaporized at an initial temperature of 32 °C (90 °F) and 10.5 Bar (152 psig) for R-290, ethyl mercaptan (C_2H_5SH) and PAG lubricant

Appendix B References

B1. Reid, Robert C., Prausnitz, John M., and Poling, Bruce E., "The Properties of Gases and Liquids", Fourth Edition, McGraw-Hill, Inc. New York, NY, 1987.

B2. Henley, Ernest J. and Seader, J.D., "Equilibrium-Stage Separation Operations in Chemical Engineering", John Wiley & Sons, New York, NY, 1981.

Appendix C

Spauschus Associates Compatibility Test Report

SPAUSCHUS ASSOCIATES, INC.

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COMPATIBILITY OF ODORANTS WITH REFRIGERANT/LUBRICANT MIXTURES

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Spauschus Associates, Inc.

September 2, 2021

COMPATIBILITY OF ODORANTS WITH REFRIGERANT/LUBRICANT MIXTURES

EXECUTIVE SUMMARY

As the HVAC&R industry transitions to the use of low GWP flammable refrigerants (such as R-290 and R-32) in household appliances, the addition of odorants to the refrigerants in refrigeration and air-conditioning systems was proposed to provide safety, life and property protection in case of accidental leakage. The addition of an odorant has been used for this purpose in other industries and could potentially be used in the HVAC&R industry if suitable odorants could be identified. In addition, the compatibility of the selected odorants with the refrigerant/lubricant systems needs to be determined to ensure the long-term reliability of air-conditioning and refrigeration equipment.

In this research project, as part of a program undertaken by the Consumer Product Safety Commission (CPSC), different odorants (including Hydrogen Sulfide, Carbonyl Sulfide, Trimethyl Amine, Dimethyl Sulfide, Mehyl Ethyl Sulfide, and Ethyl Mercaptan, were tested for compatibility with refrigerant/lubricant mixtures, including three refrigerants (R-32, R-1234yf and R-290) each with three different lubricants (PAG, POE and PVE). The compatibility tests were conducted in sealed tubes according to ASHRAE standard 97, at 175ºC (347ºF) for 14 days. After aging the tube contents were visually examined for change in lubricant color, cloudiness in the lubricant, floc or particulate formation, corrosion of metal coupons, and copper plating on the steel surfaces. The exposed lubricants were analyzed for Total Acid Number (TAN), by Ion Chromatography (IC) and by Inductively Coupled Plasma (ICP).

The compatibility test results identified twenty-one refrigerant/lubricant/odorant systems with no significant compatibility concern, based on visual observations of the sealed tubes after aging, as well as TAN, TOA, fluoride ion concentrations and elemental metal concentrations. Ten refrigerant/lubricant/odorant ystems were highlighted that may cause some compatibility problems.

However, to fully evaluate candidate odorants for applications in refrigeration and air-conditioning (AC&R), additional analyses are needed, such as odorant toxicity evaluation, odorant threshold detection verification, refrigerant and odorant dispersion modeling and verification, evaluation of the impact of odorant addition on the AC&R equipment, odorant distribution evaluation within the equipment, and odorant effectiveness with time.

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1. INTRODUCTION

As the HVAC&R industry transitions to the use of low GWP flammable refrigerants (such as R-290 and R-32) in household appliances, the addition of odorants to the refrigerants in refrigeration and air-conditioning systems was proposed to provide safety, life, and property protection in case of accidental leakage. Forssell (2020) conducted a literature survey to identify more than 200 candidate odorants, which are used in the natural gas industry or in the cosmetic and consumer product industries. The boiling points of these refrigerants ranged from -53.2ºC (-63.8ºF) to -0.4ºC (31.2ºF). Eleven candidate odorants were identified, which have boiling points similar to the boiling points of the refrigerants of interest (such as R-32, R-452B, R-1234yf, R-1234ze(E), R-290, R-600 and R-600a). An initial toxicity screen requiring odorant thresholds to be less than the published safe exposure limits eliminated four of the eleven candidates. Analysis of the available compatibility data of the odorants with system materials reduced the number of potential odorants to four: Hydrogen Sulfide (H_2S), Carbonyl Sulfide (COS), Trimethylamine ($(CH_3)_3N$) and Methyl Mercaptan (CH_4S). The addition of an odorant has been used for this purpose in other industries and could potentially be used in the HVAC&R industry if suitable odorants could be identified. In addition, the compatibility of the selected odorants with the refrigerant/lubricant systems needs to be determined to ensure the long-term reliability of air-conditioning and refrigeration equipment.

In this research project, as part of a program undertaken by the Consumer Product Safety Commission (CPSC), three additional odorants that are used with natural gas (including Dimethyl Sulfide ($(CH_3)_2S$), Methyl Ethyl Sulfide ($(C_2H_5)S(CH_3)$), and Ethyl Mercaptan (C_2H_6S)), along with three of the four candidates previously identified, were tested for compatibility with refrigerant/lubricant mixtures.

2. SCOPE

The compatibility tests of odorants with refrigerant/lubricant systems were conducted in sealed tubes according to ASHRAE standard 97. The refrigerant tested included R-32, R-1234yf and R-290. They were tested in combination with PAG, POE and PVE lubricants as shown in Table 1. The tests were conducted at 175ºC (347ºF) for 14 days. After aging the tube contents were visually examined for change in lubricant color, cloudiness in the lubricant, floc or particulate formation, corrosion of metal coupons, and copper plating on the steel surfaces. The exposed lubricants were analyzed for Total Acid Number (TAN), by Ion Chromatography (IC) and by Inductively Coupled Plasma (ICP).

Table 1: Test Matrix

Table 1: Test Matrix				
Test Number	Refrigerant	Lubricant	Odorant	Concentration, ppm based on refrigerant weight
1	R-32	PAG	Hydrogen Sulfide H_2S	50
2			Carbonyl Sulfide COS	50
3			(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
4			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
5			Control	---
6	R-1234yf	PAG	(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
7			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
8			(TA) Trimethyl Amine $(CH_3)_3N$	50
9			Control	---
10	R-290	PAG	(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
11			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
12			(TA) Trimethyl Amine $(CH_3)_3N$	50
13			(EM) Ethyl Mercaptan C_2H_6S	60
14			Control	---
15	R-32	POE	Hydrogen Sulfide H_2S	50
16			Carbonyl Sulfide COS	50
17			(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
18			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
19			Control	---
20	R-1234yf	POE	(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
21			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
22			(TA) Trimethyl Amine $(CH_3)_3N$	50
23			CONTROL	---
24	R-290	POE	(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
25			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
26			(TA) Trimethyl Amine $(CH_3)_3N$	50
27			Control	---
28	R-32	PVE	Hydrogen Sulfide H_2S	50
29			Carbonyl Sulfide COS	50
30			(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
31			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
32			Control	---
33	R-1234yf	PVE	(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
34			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
35			(TA) Trimethyl Amine $(CH_3)_3N$	50
36			Control	---
37	R-290	PVE	(DMS) Dimethyl Sulfide $(CH_3)_2S$	150
38			(MES) Methyl Ethyl Sulfide $(CH_3SC_2H_5)$	150
39			(TA) Trimethyl Amine $(CH_3)_3N$	50
40			Control	---

3. EXPERIMENTAL METHODS

3.1 Sealed Tube Preparation

The odorants, refrigerants and the lubricants were supplied to Spauschus Associates, Inc. The Polyalkylene glycol (PAG) lubricant was unadditized double capped 46 cS and was labeled as PAG SHR1452. Its moisture level as measured by Karl Fischer was 469 ppm. The polyolester (POE) lubricant was mixed acid 32 cS with 0.1% BHT additive and was labeled POE LM6228A. Its moisture level was 306 ppm. The polyvinylether (PVE) lubricant was unadditized PVE 68 cS and was labeled PVE LM6228B. Its moisture level was 69 ppm. The copper, aluminum, steel catalyst coupons (copper was CDA 110 or C11000, steel 1010 and aluminum 1100) were prepared by punching 3.3x19.3 mm (0.13x 0.76 in) coupons from thin sheets. The coupons were held together by aluminum wire such that the steel and copper were separated by the aluminum. These prepared coupon sandwiches were thoroughly cleaned and kept dry prior to use. The test tubes were cleaned by rinsing first with deionized water, then by two rinses with methanol and one rinse with toluene. They were dried at 175^{o} C (347^{o}F) and kept dry in desiccators prior to use. The metal coupons were first placed in the tube, which was then necked down to a size through which a standard cannula could fit. Next the lubricant was added accurately with a syringe and cannula. The tube was evacuated to 30 microns followed by accurate charging of refrigerant through condensation from a calibrated gas handling system. Finally, the tube neck was sealed and annealed. The sealed tubes were placed in drilled holes in large aluminum blocks, which were heated in air circulating ovens.

The odorants Hydrogen Sulfide (H_2S), Carbonyl Sulfide (COS) and Trimethyl Amine (TA) were supplied pre-loaded in the ideal inert gas Argon at a concentration of 1000 ± 10 ppm. The gas pre-loaded with odorants was diluted with pure refrigerant to yield a calculated odorant concentration of 50 ppm through condensation from the calibrated gas handling system. The odorants Dimethyl Sulfide (DMS), Methyl Ethyl Sulfide (MES), and Ethyl Mercaptan (EM) were used as received. They were mixed with the lubricants (PAG, POE and PVE) at a concentration of 150 ppm for DMS and MES, and 60 ppm for EM before the lubricants were added to the test tubes, which were then kept in liquid nitrogen during evacuation of the gas handling system to 30 microns and subsequent charging of the refrigerant through condensation. Control tubes without odorant were also prepared and tested for comparison.

For each refrigerant/lubricant mixture, four sealed tubes were prepared. Each of the first two tubes contained 1 g of refrigerant, 1 g of lubricant (for a refrigerant/lubricant ratio of 50/50) and copper/aluminum/steel catalysts. These tubes were used for TAN and IC analyses. The other two tubes were larger to provide enough lubricant for post-aging analysis by ICP. Each tube contained 2 g of refrigerant, 2 g of lubricant and copper/aluminum/steel catalysts. The tests were conducted at 175^{o}C (347^{o}F), and the aging time was 14 days. After aging the tube contents were visually examined for change in lubricant color, cloudiness in the lubricant, floc or particulate formation, corrosion of metal coupons, and copper plating on the steel surfaces. Photographs of the tubes were taken before and after aging. The exposed lubricants were analyzed for TAN, by IC and by ICP.

3.2 Sample Analyses

3.2.1. Visual Inspections
Visual inspections were made on each tube after removal from the oven and cooling to reduce internal pressure. The lubricant in each tube was compared to standard liquid color references, which give a numerical value for the color from water white to jet-black. Similarly, changes in the presence of solid particulate, extent of metal corrosion, and formation of copper plating were noted and scaled numerically, as described in Table 2.
3.2.2. Total Acid Number (TAN)
The total acid number was determined for the lubricant according to a modified ASTM D664. The method was modified to accommodate the small one-milliliter sample size by reducing the alcoholic KOH titrant concentration from 0.1 Normal to 0.01 Normal. This yielded sufficient sensitivity to determine acid numbers down to 0.1 mg KOH/g with a standard deviation of ± 0.05.
3.2.3. Ion Chromatography (IC)
In the determination of anion concentrations by IC, about 1 g of the lubricant sample was added to a pre-weighed cup containing 30 mL of deionized water. The water/lubricant mixture was stirred continuously for 24 hours to allow for extraction of halide ions and acid anions from the lubricant. The water extract was then analyzed by ion chromatography. The concentrations of halide ions (such as Fluoride and Chloride), organic anions (such as Formate, Acetate, Butyrate, Pentanoate, Hexanoate, Heptanoate) were obtained by calibrating the ion chromatograph with standard solutions so that the peak areas are proportional to the anion concentrations.
3.2.4. Concentrations of Metals
Spectrochemical analysis by Inductively Coupled Plasma (ICP) was performed according to ASTM-D5185 to determine the elemental metal concentrations (in parts per million by weight) in the lubricant.

4. EXPERIMENTAL RESULTS

4.1. Visual Inspection

After aging, the tubes were observed for visual changes in the color of the lubricant, the presence of cloudiness, particulate or deposit, film formation on the tube walls, corrosion of the metal surfaces and copper plating on the steel coupons. The results are shown in Tables 3 to 8 and Figures 1 to 3. Photographs of the tubes before and after aging were also taken and shown in Appendix A. To allow for easy comparison between the different odorants tested and the controls, numerical values were assigned to the visual observations according to the score keys of Table 2. They are summarized in Tables 3 to 8 and shown graphically in Figures 1 to 3, where the areas of concern (with noticeable differences from the controls) are highlighted in red. In tables 6 to 8, the total visual score in the last column is the sum of the scores for lubricant color, cloudiness and/or deposit, and visuals of metal coupons (steel, copper, aluminum) after aging. When the total visual score of a test sample is higher than double the visual score of the control, the test sample is highlighted as possibly causing concern. It should be noted that this criterion is subjective and selected mainly to provide ways of comparing and ranking the different odorants tested. Different applications require different criteria and the one chosen here may either be too lenient or too stringent for a particular application.

Based on the visual inspection results, in most cases, it may be concluded that the presence of odorants at the concentration tested did not lead to significant visual changes compared to the controls, except for the following:

- H_2S at 50 ppm in R-32/PAG, R-32/POE and R-32/PVE, with the changes in color and appearance of the steel and copper coupons after aging.
- COS at 50 ppm in R-32/PAG with light cloudiness compared to very faint cloudiness for the control.
- Ethyl mercaptan at 60 ppm in R-290/PAG with faint white deposit on tube wall and change in color of the steel and copper coupons after aging.

4.2. Total Acid Number (TAN)

The TAN of the lubricants after aging are shown in Tables 1 to 3 and Figures 4 to 7. In general, the TAN values were small, ≤ 0.25 mg KOH/g for PAG lubricants, ≤ 0.53 mg KOH/g for POE, and ≤ 0.09 mg KOH/g for PVE. However, for consistency with the interpretation of the visual scores, when the TAN of a test sample is higher than double the TAN of the control, the test sample is highlighted as possibly causing concern. Based on the TAN results, it may be concluded that in most cases the presence of odorant did not lead to significant increases in TAN compared to the controls, except for the following:

- H_2S at 50 ppm in R-32/POE when the TAN of the aged lubricant was 0.53 mg KOH/g compared to the TAN of 0.25 mg KOH/g for the control, and R-32/PVE when the TAN of the aged lubricant was 0.09 mg KOH/g compared to the TAN of 0.04 mg KOH/g for the control.
- Methyl Ethyl Sulfide at 150 ppm in R-1234yf/POE when the TAN of the aged lubricant was 0.21 mg KOH/g compared to the TAN of 0.09 mg KOH/g for the control.
- Trimethyl Amine at 50 ppm in R-290/PVE when the TAN of the aged lubricant was 0.04 mg KOH/g compared to the TAN of 0.01 mg KOH/g for the control.

4.3. Ion Chromatography Results.

Ion Chromatography (IC) was conducted to measure the concentrations in ppm of halide ions (such as fluoride, chloride), and Total Organic Acid anions (TOA).

4.3.1. Total Organic Acid Anions

TOA along with TAN are indicative of lubricant decomposition and are shown in Tables 9 to 11 and Figures 7 to 11. The TOA, which is the sum of propanoate, butyrate, pentanoate, hexanoate, 2-ethyl hexanoate and heptanoate, were small for PAG (≤ 164 ppm) and POE lubricants (≤ 242 ppm). They were moderate for PVE lubricants (≤ 404 ppm). When the TOA of a test sample is higher than double the TOA of the control, the test sample is highlighted as possibly causing concern. Based on the TOA results, it may be concluded that in most cases, the presence of odorant did not lead to significant increases in TOA compared to the controls, except for the following:

- Dimethyl Sulfide at 150 ppm in R-1234yf/PVE when the TOA of the aged lubricant was 347 ppm compared to the TOA of 83 ppm for the control.
- Methyl Ethyl Sulfide at 150 ppm in R-1234yf/PVE when the TOA of the aged lubricant was 394 ppm compared to the TOA of 83 ppm for the control.
- Methyl Ethyl Sulfide at 150 ppm in R-290/PVE when the TOA of the aged lubricant was 404 ppm compared to the TOA of 49 ppm for the control.

4.3.2. Fluoride Ion Concentrations

The concentrations of fluoride ions as determined by IC after aging are indicative of refrigerant decomposition. They are shown in Tables 9 to 11. The fluoride ion concentrations of all the test samples were small (< 50 ppm), thus it may be concluded that the presence of the odorants did not lead to significant refrigerant decomposition.

4.4. CONCENTRATIONS OF METALS

The elemental metal concentrations (in parts per million by weight) in the lubricant were determined by Inductively Coupled Plasma (ICP). As shown in Tables 12 to 14, all the elemental metal concentrations after aging were small (< 60 ppm).

Table 2: Score Keys for Visual Inspection Results

Score Keys for Visual Inspection Results								
Visual Score	Liquid color	Cloudiness	Particulate /deposit	Film/deposit on tube walls or in bottom of tube	Aluminum Corrosion	Copper Corrosion	Steel Corrosion	Copper plating
0	Water clear	Clear	No particulate/ no deposit	No film	Shiny	Shiny	Shiny	No copper plating
1	Water clear	Faint; very light cloudiness	Faint; very small amount	Faint; very light film or deposit on walls and in bottom of tube	Dull; dark gray or dull with coating	Slightly dull; slightly darker color	Dull; slightly darker	Light plating or plating on edges of coupon
2	Water clear	Light cloudiness	Small amount	Light film or deposit on walls and in bottom of tube	Darker color; spot or stain on surface	Dull; darker color	Dull; dark gray	Plating on surface
3	Pale yellow	Cloudy; medium cloudiness	Medium amount	Medium Film or deposit on walls and in bottom of tube	Black (with spots)	Dull with stains, film or coating	Spots or coating on surface	Heavy copper plating
4	Yellow	Very cloudy; Heavy cloudiness	Large, heavy amount	Heavy film or deposit on walls and in bottom of tube; ring at liquid/gas interface	Black; corroded	Black	Black	---
5	Light orange	Extremely heavy cloudiness	Extremely heavy amount	Extremely heavy deposit and extremely heavy ring	---	---	---	---
6	Orange-brown	---	---	---	---	---	---	---

Table 3: Visual Observations and TAN for PAG (SHR1452)

Table 3: Visual Observations and Total Acid Number (TAN) for PAG SHR1452 (Lubricant 1) Unaged Lubricant TAN =0.03					
Test Number	Refrigerant	Odorant	Visual Observations		TAN
			Liquid	Metal coupons	mg KOH/g
1	R-32	H_2S Hydrogen Sulfide (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel with slight darkening; copper became mottled and bluish-purple in color (versus deep purple-brown color before aging); aluminum unchanged.	0.06
2	R-32	COS Carbonyl Sulfide (50 ppm)	Light cloudiness (versus very faint cloudiness for unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit.	Steel with faint darkening; copper and aluminum unchanged.	0.05
3	R-32	DMS Dimethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.05
4	R-32	MES Methyl Ethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.05
5	R-32	Control (No odorant)	Clear (versus very faint cloudiness for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.08
6	R-1234yf	DMS Dimethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged);; color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.08
7	R-1234yf	MES Methyl Ethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged);; color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.07
8	R-1234yf	TA Trimethyl Amine (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.15
9	R-1234yf	Control (No odorant)	Clear (versus very faint cloudiness for unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.25
10	R-290	DMS Dimethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel with slight darkening; copper and aluminum unchanged	0.03
11	R-290	MES Methyl Ethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel with slight darkening; copper and aluminum unchanged	0.04
12	R-290	TA Trimethyl Amine (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.05
13	R-290	EM Ethyl Mercaptan (60 ppm)	Faint to light cloudiness (versus very faint cloudiness for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); faint white deposit on tube wall.	Steel with slight darkening; copper became bluish-purple; aluminum unchanged.	0.06
14	R-290	Control (No odorant)	Clear (versus very faint cloudiness for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel with faint darkening; copper and aluminum unchanged.	0.03

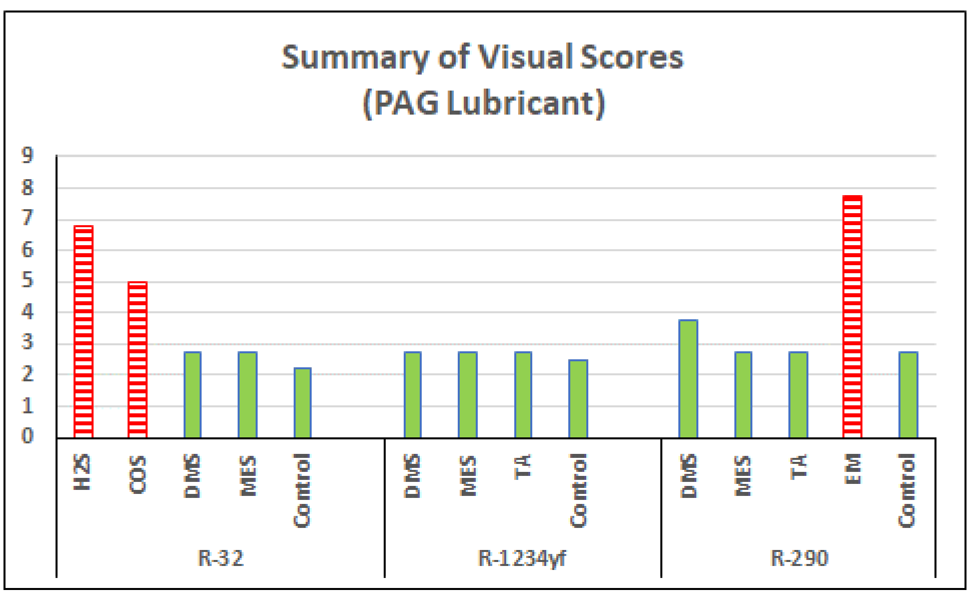
Note: Text is highlighted when the total visual score or TAN of the test sample is higher than double the total visual score or TAN of the control.

Table 4: Summary of Visual Scores for PAG (SHR1452)

Table 4: Summary of Visual Scores for PAG SHR1452 (Lubricant 1)									
Test Number	Lubricant	Refrigerant	Odorant	Visual Scores					Total Score
				Color	Cloudiness and/or deposit	Steel	Copper	Aluminum	
1	PAG	R-32	H_2S	2.25	0.5	1.0	3.0	0	6.8
2			COS	2.50	2.0	0.5	0	0	5.0
3			DMS	2.25	0.5	0	0	0	2.8
4			MES	2.25	0.5	0	0	0	2.8
5			Controls	2.25	0	0	0	0	2.3
6	PAG	R-1234yf	DMS	2.25	0.5	0	0	0	2.8
7			MES	2.25	0.5	0	0	0	2.8
8			TA	2.25	0.5	0	0	0	2.8
9			Controls	2.50	0	0	0	0	2.5
10	PAG	R-290	DMS	2.25	0.5	1.0	0	0	3.8
11			MES	2.25	0.5	0	0	0	2.8
12			TA	2.25	0.5	0	0	0	2.8
13			EM	2.25	2.5	1.0	2.0	0	7.8
14			Controls	2.25	0	0.5	0	0	2.8

Note: Text is highlighted when the total visual score of the test sample is higher than double the total visual score of the control.

Figure 1: Summary of Visual Scores for PAG (SHR1452)



Note: The red bars indicate that the total visual score of the test sample is higher than double the total visual score of the control.

Table 5: Visual Observations and TAN for POE (LM6228A)

Table 5: Visual Observations and Total Acid Number (TAN) for POE (LM6228A) (Lubricant 2) Unaged Lubricant TAN =0.04					
Test Number	Refrigerant	Odorant	Visual Observations		TAN mg KOH/g
			Liquid	Metal coupons	
15	R-32	H_2S Hydrogen Sulfide (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel became light to medium brown; copper became mottled and faint blue in color (versus medium reddish-brown color before aging); aluminum unchanged	0.53
16	R-32	COS Carbonyl Sulfide (50 ppm)	Faint cloudiness (versus very faint cloudiness for unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit.	Steel with slight darkening; copper and aluminum unchanged.	0.22
17	R-32	DMS Dimethyl Sulfide (150 ppm)	Faint cloudiness (versus very faint cloudiness for unaged); color unchanged (color = 2.25); no deposit.	All metals unchanged.	0.28
18	R-32	MES Methyl Ethyl Sulfide (150 ppm)	Faint cloudiness (versus very faint cloudiness for unaged); color unchanged (color = 2.25); no deposit.	Steel with slight darkening; copper and aluminum unchanged.	0.17
19	R-32	Control (No odorant)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit.	Steel with faint darkening; copper and aluminum unchanged.	0.25
20	R-1234yf	DMS Dimethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color unchanged (color = 2.25); no deposit.	Steel with slight darkening; copper and aluminum unchanged.	0.08
21	R-1234yf	MES Methyl Ethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.5 versus 2.25 for unaged); no deposit.	Steel and copper with slight darkening; aluminum unchanged.	0.21
22	R-1234yf	TA Trimethyl Amine (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.07
23	R-1234yf	Control (No odorant)	Clear (versus very faint cloudiness for unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.09
24	R-290	DMS Dimethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color unchanged (color = 2.25); no deposit.	Steel with slight darkening; copper with medium darkening; aluminum unchanged	0.07
25	R-290	MES Methyl Ethyl Sulfide (150 ppm)	Very faint cloudiness (same as unaged); color unchanged (color = 2.25); no deposit	Steel with slight darkening; copper and aluminum unchanged.	0.09
26	R-290	TA Trimethyl Amine (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.10
27	R-290	Control (No odorant)	Clear (versus very faint cloudiness for unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit.	Steel with faint darkening; copper and aluminum unchanged.	0.10

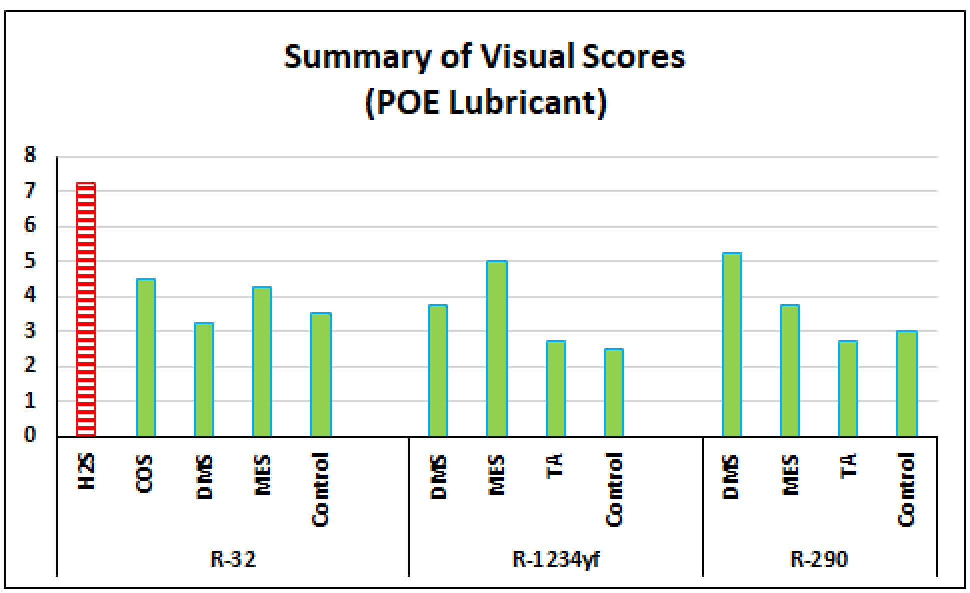
Note: Text is highlighted when the total visual score or TAN of the test sample is higher than double the total visual score or TAN of the control.

Table 6: Summary of Visual Scores for POE (LM6228A)

Table 6: Summary of Visual Scores for POE LM6228A (Lubricant 2)									
Test Number	Lubricant	Refrigerant	Odorant	Visual Scores					Total Score
				Color	Cloudiness and/or deposit	Steel	Copper	Aluminum	
15	POE	R-32	H_2S	2.25	0.5	1.5	3.0	0	7.3
16			COS	2.50	1.0	1.0	0	0	4.5
17			DMS	2.25	1.0	0	0	0	3.3
18			MES	2.25	1.0	1.0	0	0	4.3
19			Controls	2.50	0.5	0.5	0	0	3.5
20	POE	R-1234yf	DMS	2.25	0.5	1.0	0	0	3.8
21			MES	2.50	0.5	1.0	1.0	0	5.0
22			TA	2.25	0.5	0	0	0	2.8
23			Controls	2.50	0	0	0	0	2.5
24	POE	R-290	DMS	2.25	0.5	1.0	1.5	0	5.3
25			MES	2.25	0.5	1.0	0	0	3.8
26			TA	2.25	0.5	0	0	0	2.8
27			Controls	2.50	0	0.5	0	0	3.0

Note: Text is highlighted when the total visual score of the test sample is higher than double the total visual score of the control.

Figure 2: Summary of Visual Scores for POE (LM6228A)



Note: The red bar indicates that the total visual score of the test sample is higher than double the total visual score of the control.

Table 7: Visual Observations and TAN for PVE (LM6228B)

Table 7: Visual Observations and Total Acid Number (TAN) for PVE (LM6228B) (Lubricant 3) Unaged Lubricant TAN =0.01					
Test Number	Refrigerant	Odorant	Visual Observations		TAN mg KOH/g
			Liquid	Metal coupons	
28	R-32	H_2S Hydrogen Sulfide (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel became light to medium brown; copper became mottled and faint blue in color (versus medium reddish-brown color before aging); aluminum unchanged	0.09
29	R-32	COS Carbonyl Sulfide (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel with faint darkening; copper and aluminum unchanged.	0.03
30	R-32	DMS Dimethyl Sulfide (150 ppm)	Very faint cloudiness (same as unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit	All metals unchanged.	0.03
31	R-32	MES Methyl Ethyl Sulfide (150 ppm)	Very faint cloudiness (same as unaged); color unchanged (color = 2.0); no deposit	Steel with slight bluish-gray tint; copper and aluminum unchanged.	0.03
32	R-32	Control (No odorant)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.04
33	R-1234yf	DMS Dimethyl Sulfide (150 ppm)	Very faint cloudiness (same as unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit	Steel with slight darkening; copper and aluminum unchanged.	0.06
34	R-1234yf	MES Methyl Ethyl Sulfide (150 ppm)	Very faint cloudiness (same as unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit	Steel with slight darkening; copper with faint darkening; aluminum unchanged.	0.05
35	R-1234yf	TA Trimethyl Amine (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.07
36	R-1234yf	Control (No odorant)	Clear (versus very faint cloudiness for unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit.	All metals unchanged.	0.14
37	R-290	DMS Dimethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel with slight darkening; copper with faint darkening; aluminum unchanged.	0.02
38	R-290	MES Methyl Ethyl Sulfide (150 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 versus 2.0 for unaged); no deposit.	Steel and copper with slight darkening; aluminum unchanged.	0.01
39	R-290	TA Trimethyl Amine (50 ppm)	Very faint cloudiness (same as for unaged); color slightly darker (color = 2.25 to 2.5 versus 2.0 for unaged); no deposit.	Steel with slight darkening; copper and aluminum unchanged.	0.04
40	R-290	Control (No odorant)	Clear (versus very faint cloudiness for unaged); color slightly darker (color = 2.5 versus 2.0 for unaged); no deposit.	Steel with faint darkening; copper and aluminum unchanged.	0.01

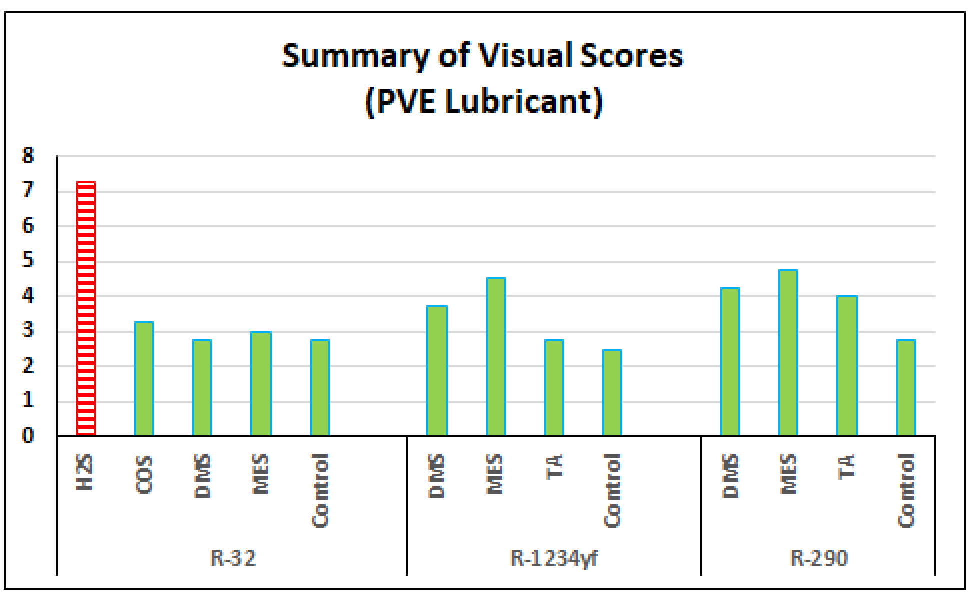
Note: Text is highlighted when the total visual score or TAN of the test sample is higher than double the total visual score or TAN of the control.

Table 8: Summary of Visual Scores for PVE (LM6228B)

Table 8: Summary of Visual Scores for PVE LM6228B (Lubricant 3)									
Test Number	Lubricant	Refrigerant	Odorant	Visual Scores					Total Score
				Color	Cloudiness and/or deposit	Steel	Copper	Aluminum	
28	PVE	R-32	H_2S	2.25	0.5	1.5	3.0	0	7.3
29			COS	2.25	0.5	0.5	0	0	3.3
30			DMS	2.25	0.5	0	0	0	2.8
31			MES	2.00	0.5	0.5	0	0	3.0
32			Controls	2.25	0.5	0	0	0	2.8
33	PVE	R-1234yf	DMS	2.25	0.5	1.0	0	0	3.8
34			MES	2.50	0.5	1.0	0.5	0	4.5
35			TA	2.25	0.5	0	0	0	2.8
36			Controls	2.50	0	0	0	0	2.5
37	PVE	R-290	DMS	2.25	0.5	1.0	0.5	0	4.3
38			MES	2.25	0.5	1.0	1.0	0	4.8
39			TA	2.50	0.5	1.0	0	0	4.0
40			Controls	2.25	0	0.5	0	0	2.8

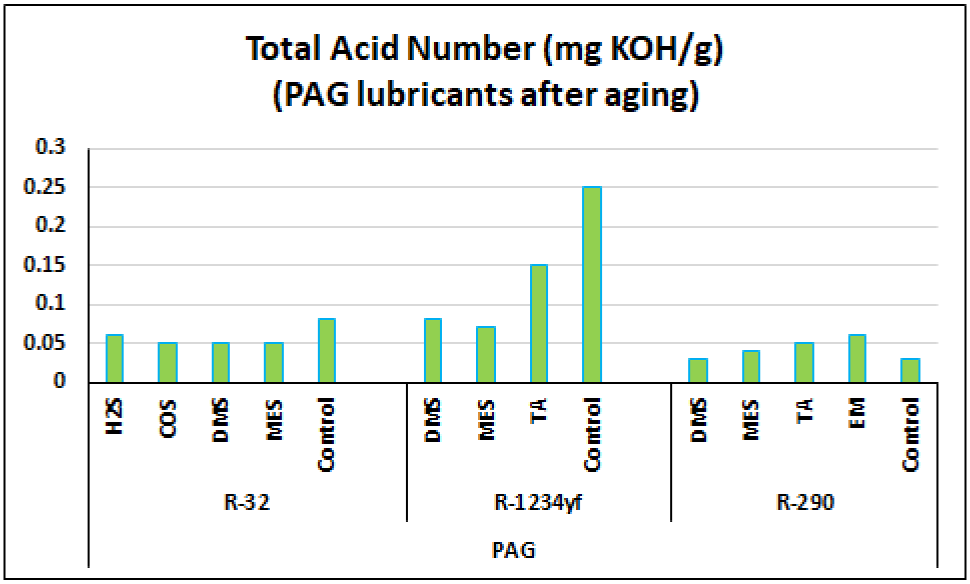
Note: Text is highlighted when the total visual score of the test sample is higher than double the total visual score of the control.

Figure 3: Summary of Visual Scores for PVE (LM6228B)



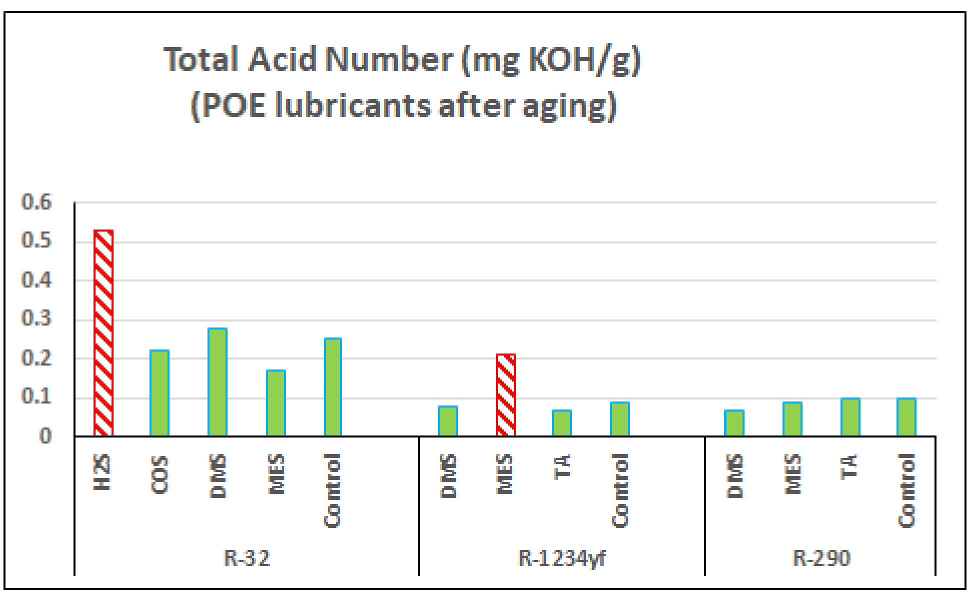
Note: The red bar indicates that the total visual score of the test sample is higher than double the total visual score of the control.

Figure 4: Total Acid Number (TAN) of PAG Lubricants After Aging



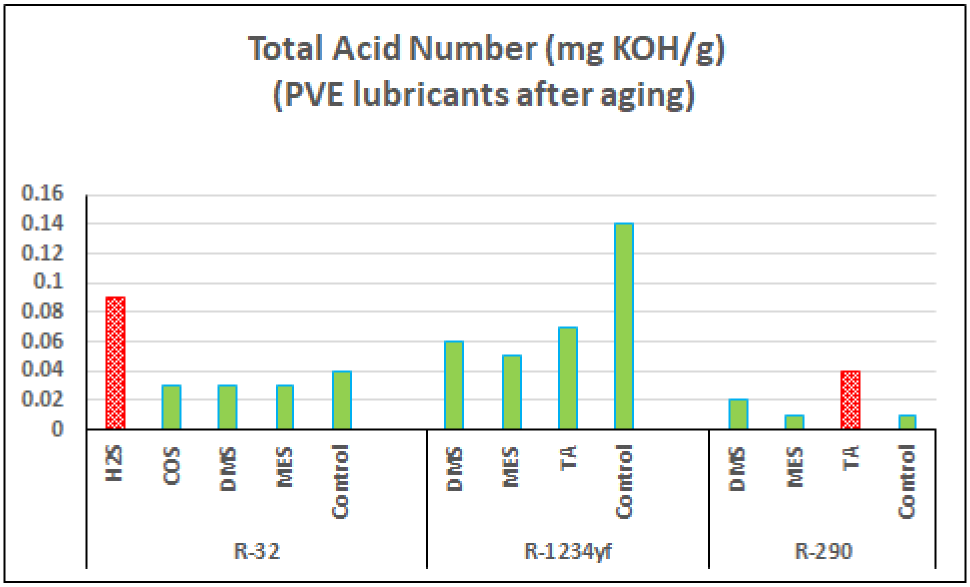
1. Note: The TAN of the aged controls is higher than the TAN of the lubricant with odorant for R-32/PAG and R-1234yf/PAG.

Figure 5: Total Acid Number (TAN) of POE Lubricants After Aging



Note: The red bars indicate that the TAN of the test sample is higher than double the TAN of the control.

Figure 6: Total Acid Number (TAN) of PVE Lubricants After Aging



Note: The red bars indicate that the TAN of the test sample is higher than double the TAN of the control.

Figure 7: Summary of Total Acid Numbers for All Three Lubricants

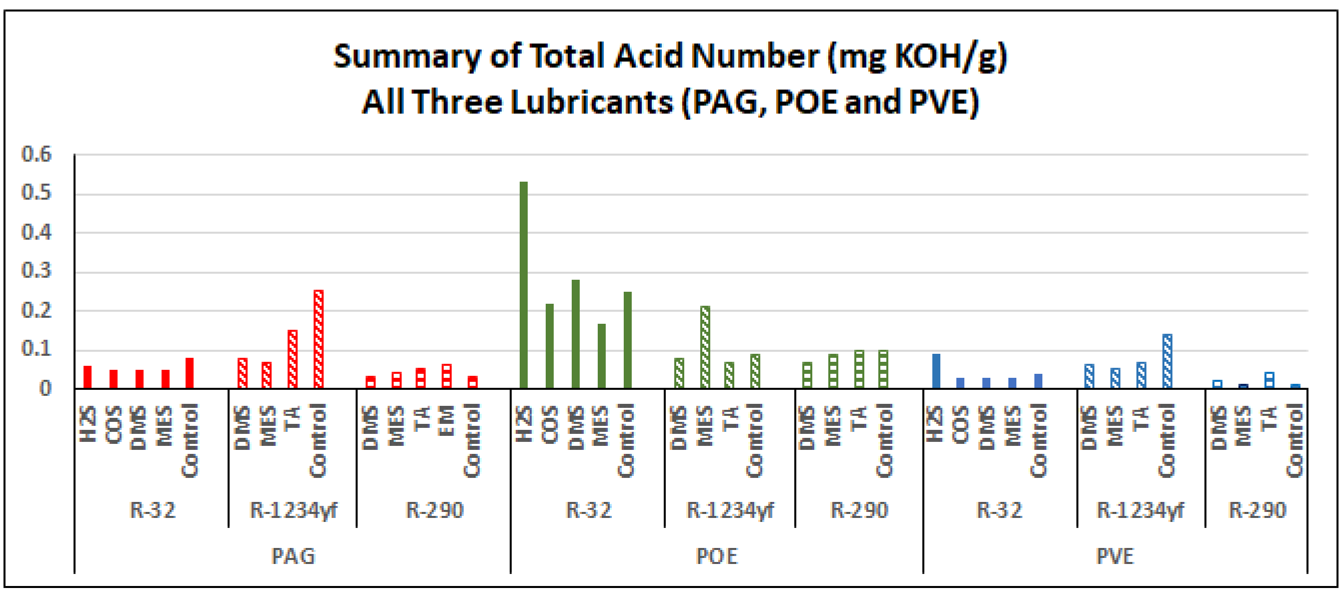


Table 9: Fluoride and Total Organic Acid (TOA) Concentrations for PAG Lubricants

Table 9: Ion Chromatograpy (IC) Results											
Test Number	Lubricant	Refrigerant	Odorant	Ion Concentrations, ppm							Total Organic Acids (TOA) ppm
				Fluoride	Chloride	Propa-noate	Penta-noate	Hexa-noate*	2-Ethyl-Hexanoate	Hepta-noate	
Lubricant 1	PAG SHR1452 Unaged	---	---	0	0	2	0	18	4	0	24
1	PAG	R-32	H_2S	3	0	0	0	143	5	16	164
2			COS	0	0	9	0	97	4	11	121
3			DMS	2	0	7	0	87	5	4	103
4			MES	1	0	9	0	140	6	11	166
5			Controls	0	0	6	0	90	9	6	111
6	PAG	R-1234yf	DMS	10	0	17	0	34	6	4	61
7			MES	7	0	12	0	35	1	7	55
8			TA	32	0	20	0	30	11	0	61
9			Controls	65	0	21	0	25	10	0	56
10	PAG	R-290	DMS	2	0	8	0	52	5	7	72
11			MES	2	0	11	0	53	3	10	77
12			TA	9	0	2	0	36	1	6	45
13			EM	1	0	10	0	41	4	11	66
14			Controls	0	0	10	0	51	8	8	77

* This compound may not be hexanoate but an unknown that showed up at the same retention time as hexanoate, but that has not been calibrated for the IC.

Figure 8: Total Organic Acids of PAG Lubricants After Aging

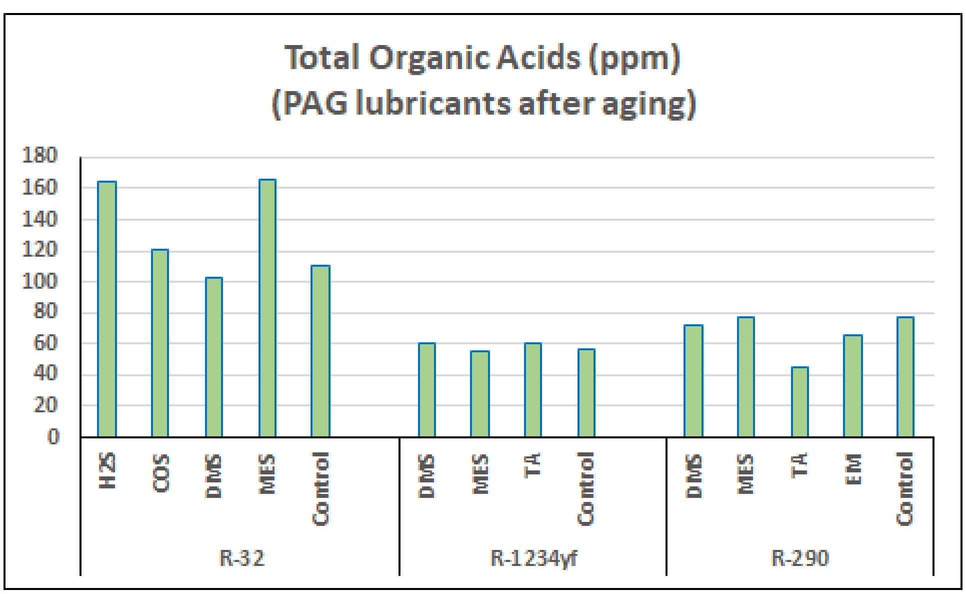


Table 10: Fluoride and Total Organic Acid (TOA) Concentrations for POE Lubricants

Table 10: Ion Chromatograpy (IC) Results											
Test Number	Lubricant	Refrigerant	Odorant	Ion Concentrations, ppm							Total Organic
				Fluoride	Chloride	Propa-noate	Penta-noate	Hexa-noate	2-Ethyl-Hexanoate	Hepta-noate	Acids (TOA) ppm
Lubricant 2	POE LM6228A Unaged	---	---	0	0	0	0	18	1	5	24
15	POE	R-32	H_2S	0	0	174	8	33	2	25	242
16			COS	0	0	67	4	69	3	15	158
17			DMS	0	0	80	0	114	3	11	208
18			MES	0	0	78	15	111	5	13	222
19			Controls	0	0	58	48	61	2	17	186
20	POE	R-1234yf	DMS	1	0	41	0	71	2	12	126
21			MES	1	0	56	7	70	2	19	154
22			TA	0	0	19	0	49	2	8	78
23			Controls	0	0	30	18	38	1	14	101
24	POE	R-290	DMS	1	0	21	4	71	1	1	98
25			MES	1	0	26	5	84	0	15	130
26			TA	0	0	35	1	24	2	9	71
27			Controls	0	0	48	26	58	1	14	147

Figure 9: Total Organic Acids of POE Lubricants After Aging

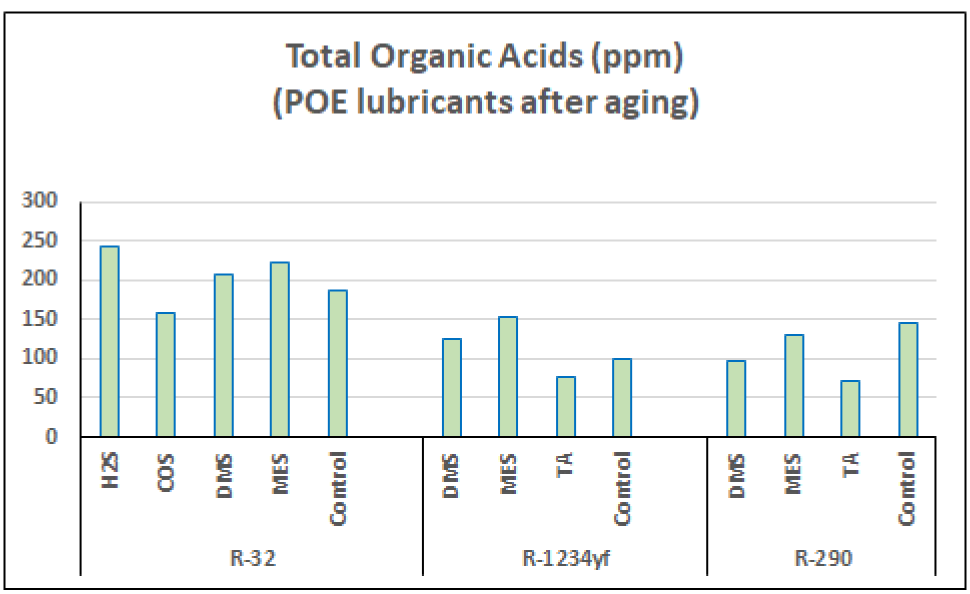
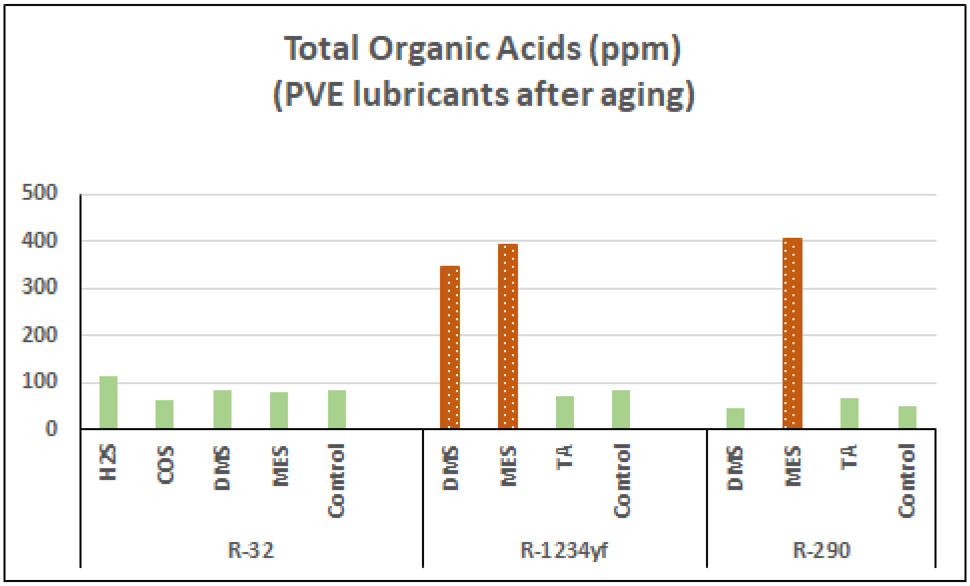


Table 11: Fluoride and Total Organic Acid (TOA) Concentrations for PVE Lubricants

Table 11: Ion Chromatograpy (IC) Results												
Test Number	Lubricant	Refrigerant	Odorant	Ion Concentrations, ppm								Total Organic Acids (TOA) ppm
				Fluoride	Chloride	Propa-noate	Buty-rate	Penta-noate	Hexa-noate *	2-Ethyl-Hexanoate	Hepta-noate	
Lubricant 3	PVE LM6228 B Unaged	---	---	0	0	0	0	0	25	2	6	33
28	PVE	R-32	H_2S	1	0	1	0	0	98	4	12	115
29			COS	0	0	0	0	0	51	2	10	63
30			DMS	1	0	1	0	0	69	2	12	84
31			MES	1	0	0	0	0	69	1	10	80
32			Controls	0	0	2	0	0	69	3	11	85
33	PVE	R-1234yf	DMS	19	0	0	325	0	22	0	0	347
34			MES	25	0	0	343	0	31	20	0	394
35			TA	35	0	6	0	0	36	10	17	69
36			Controls	0	0	24	0	0	38	16	5	83
37	PVE	R-290	DMS	1	0	3	0	0	42	0	1	46
38			MES	2	0	6	344	0	43	1	10	404
39			TA	7	0	26	0	0	34	1	7	68
40			Controls	1	0	1	0	0	36	8	4	49

Note: Text is highlighted when the TOA of the test sample is higher than double the TOA of the control.
* This compound may not be hexanoate but an unknown that showed up at the same retention time as hexanoate, but that has not been calibrated for the IC.

Figure 10: Total Organic Acids of PVE Lubricants After Aging



Note: The red bars indicate that the TOA of the test sample is higher than double the TOA of the control.

Figure 11: Summary of Total Organic Acids (TOA) for All Three Lubricants

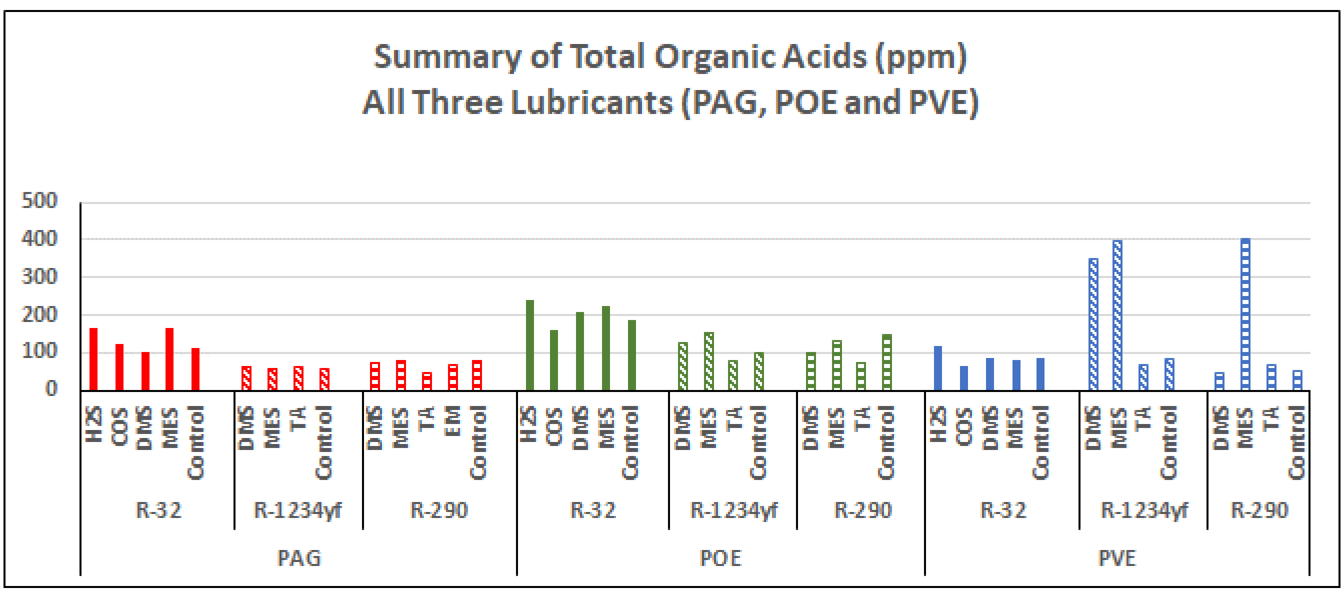


Table 12: Elemental Metal Concentrations by ICP for PAG Lubricants

Inductively Coupled Plasma (ICP) Results																	
Test Number	Lubricant	Refrigerant	Odorant	Metal Concentrations, ppm													
				Fe	Cr	Ni	Al	Pb	Cu	Sn	Si	Na	K	B	P	Zn	Ca
Lubricant 1	PAG SHR1452 Unaged	---	---	1	1	1	1	1	1	1	<1	1	2	2	4	1	1
1	PAG	R-32	H_2S	11	<1	<1	<1	<1	<1	<1	2	<1	<1	1	2	<1	<1
2			COS	6	<1	<1	<1	<1	1	<1	21	<1	1	4	3	1	1
3			DMS	4	<1	<1	<1	<1	2	1	<1	2	<1	2	3	<1	<1
4			MES	1	<1	<1	<1	<1	1	<1	<1	2	<1	2	1	<1	<1
5			Controls	7	1	1	1	1	2	1	15	1	3	8	4	2	6
6	PAG	R-1234yf	DMS	<1	<1	<1	<1	<1	<1	<1	1	3	<1	3	1	<1	<1
7			MES	<1	<1	<1	<1	<1	1	<1	2	2	<1	3	1	<1	<1
8			TA	<1	<1	<1	<1	<1	<1	<1	19	1	1	3	2	<1	<1
9			Controls	<1	<1	<1	<1	<1	<1	<1	32	1	2	6	2	<1	<1
10	PAG	R-290	DMS	<1	<1	<1	<1	<1	<1	<1	<1	1	<1	3	2	<1	<1
11			MES	<1	<1	<1	<1	1	<1	<1	<1	2	<1	2	2	<1	<1
12			TA	<1	<1	<1	<1	<1	<1	<1	4	<1	<1	<1	2	<1	<1
13			EM	<1	<1	<1	<1	<1	1	<1	<1	1	<1	3	2	<1	<1
14			Controls	<1	<1	<1	<1	<1	<1	<1	6	<1	1	1	2	<1	<1

Table 13: Elemental Metal Concentrations by ICP for POE Lubricants

Inductively Coupled Plasma (ICP) Results																	
Test Number	Lubricant	Refrigerant	Odorant	Metal Concentrations, ppm													
				Fe	Cr	Ni	Al	Pb	Cu	Sn	Si	Na	K	B	P	Zn	Ca
Lubricant 2	POE LM6228A Unaged	---	---	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	<1	1	<1	<1
15	POE	R-32	H_2S	<1	<1	<1	<1	<1	1	<1	8	<1	<1	<1	<1	<1	<1
16			COS	2	<1	<1	<1	<1	1	<1	14	<1	1	1	1	<1	<1
17			DMS	1	<1	<1	<1	<1	1	1	<1	2	<1	1	<1	<1	<1
18			MES	1	<1	<1	<1	<1	1	<1	<1	3	<1	1	<1	<1	<1
19			Controls	3	<1	<1	<1	<1	<1	<1	<1	<1	2	2	<1	<1	<1
20	POE	R-1234yf	DMS	<1	<1	<1	<1	<1	<1	<1	<1	2	<1	1	<1	<1	<1
21			MES	<1	<1	<1	<1	<1	<1	<1	<1	2	<1	1	<1	<1	<1
22			TA	<1	<1	<1	<1	<1	<1	<1	12	<1	1	<1	<1	<1	<1
23			Controls	<1	<1	<1	<1	<1	<1	<1	9	<1	<1	1	1	1	1
24	POE	R-290	DMS	1	<1	<1	<1	<1	<1	<1	11	1	<1	1	1	<1	1
25			MES	<1	<1	<1	<1	<1	<1	1	24	3	<1	1	<1	<1	<1
26			TA	<1	<1	<1	<1	<1	<1	<1	14	<1	<1	<1	<1	<1	<1
27			Controls	<1	<1	<1	<1	<1	<1	<1	2	<1	1	1	2	<1	<1

Table 14: Elemental Metal Concentrations by ICP for PVE Lubricants

Inductively Coupled Plasma (ICP) Results																	
Test Number	Lubricant	Refrigerant	Odorant	Metal Concentrations, ppm													
				Fe	Cr	Ni	Al	Pb	Cu	Sn	Si	Na	K	B	P	Zn	Ca
Lubricant 3	PVE LM6228B Unaged	---	---	<1	<1	<1	<1	<1	<1	1	<1	<1	1	<1	<1	<1	<1
28	PVE	R-32	H_2S	7	<1	<1	<1	<1	<1	<1	9	<1	<1	1	2	<1	<1
29			COS	1	<1	<1	<1	<1	1	<1	60	<1	1	2	<1	<1	<1
30			DMS	1	<1	<1	<1	<1	1	<1	<1	3	<1	1	<1	<1	<1
31			MES	1	<1	<1	<1	<1	1	1	<1	3	<1	1	<1	<1	<1
32			Controls	5	<1	<1	<1	<1	1	<1	<1	<1	1	3	1	<1	<1
33	PVE	R-1234yf	DMS	<1	<1	<1	<1	<1	<1	<1	43	2	<1	1	<1	<1	<1
34			MES	<1	<1	<1	<1	<1	<1	<1	30	1	<1	1	<1	<1	<1
35			TA	<1	<1	<1	<1	<1	<1	<1	21	<1	1	1	<1	<1	<1
36			Controls	<1	<1	<1	<1	<1	<1	<1	38	<1	1	2	<1	<1	<1
37	PVE	R-290	DMS	<1	<1	<1	<1	<1	<1	<1	5	1	<1	3	<1	<1	<1
38			MES	<1	<1	<1	<1	<1	<1	1	22	2	<1	3	2	<1	<1
39			TA	<1	<1	<1	<1	<1	<1	<1	16	<1	<1	<1	<1	<1	<1
40			Controls	<1	<1	<1	<1	<1	<1	<1	43	<1	<1	<1	1	<1	<1

5. DISCUSSIONS

Table 15 shows a summary of the compatibility test results of odorants with refrigerat/lubricant systems. The cells highlighted in green represent the refrigerant/lubricant/odorant systems with no significant compatibility concern, based on visual observations of the sealed tubes after aging, as well as TAN, TOA, fluoride ion concentrations and elemental metal concentrations. These systems include:

1. Dimethyl Sulfide at 150 ppm in R-32/PAG
2. Methyl Ethyl Sulfide at 150 ppm in R-32/PAG
3. Carbonyl Sulfide at 50 ppm in R-32/POE
4. Dimethyl Sulfide at 150 ppm R-32/POE
5. Methyl Ethyl Sulfide at 150 ppm in R-32/POE
6. Carbonyl Sulfide at 50 ppm in R-32/PVE
7. Dimethyl Sulfide at 150 ppm in R-32/PVE
8. Methyl Ethyl Sulfide at 150 ppm in R-32/PVE
9. Dimethyl Sulfide at 150 ppm in R-1234yf/PAG
10. Methyl/Ethyl Sulfide at 150 ppm in R-1234yf/PAG
11. Trimethyl Amine at 50 ppm in R-1234yf/PAG
12. Dimethyl Sulfide at 150 ppm in R-1234yf/POE
13. Trimethyl Amine at 50 ppm in R-1234yf/POE
14. Trimethyl Amine at 50 ppm in R-1234yf/PVE
15. Dimethyl Sulfide at 150 ppm in R-290/PAG
16. Methyl Ethyl Sulfide at 150 ppm in R-290/PAG
17. Trimethyl Amine at 50 ppm in R-290/PAG
18. Dimethyl Sulfide at 150 ppm in R-290/POE
19. Methyl/Ethyl Sulfide at 150 ppm in R-290/POE
20. Trimethyl Amine at 50 ppm in R-290/POE
21. Dimethyl Sulfide at 150 ppm in R-290/PVE

Table 15: Summary of Compatibility Test Results

Summary of Compatibility Test Results						
Refrigerant/ Lubricant	Odorant					
	Hydrogen Sulfide H_2S at 50 ppm	Carbonyl Sulfide COS at 50ppm	Dimethyl Sulfide DMS at 150 ppm	Methyl Ethyl Sulfide MES at 150 ppm	Trimethyl Amine TA at 50 ppm	Ethyl Mercaptan EM at 60 ppm
R-32/PAG	(Visuals)	(Visuals)			N/A	N/A
R-32/POE	(Visuals, TAN)				N/A	N/A
R-32/PVE	(Visuals, TAN)				N/A	N/A
R-1234yf/PAG	N/A	N/A				N/A
R-1234yf/POE	N/A	N/A		(TAN)		N/A
R-1234yf/PVE	N/A	N/A	(TOA)	(TOA)		N/A
R-290/PAG	N/A	N/A				(Visuals)
R-290/POE	N/A	N/A				N/A
R-290/PVE	N/A	N/A		(TOA)	(TAN)	N/A

Notes: N/A indicates that these tests were not included in the test matrix.

The cells highlighted in red represent the refrigerant/lubricant/odorant systems that may pose some compatibility concern based on visual observations, higher TAN and/or TOA than the controls. When the total visual score, TAN, or TOA of a test sample is higher than double the visual score, TAN, or TOA of the control, the test sample is highlighted as possibly causing concern. It should be noted that this criterion is subjective and selected mainly to provide ways of comparing and ranking the different odorants tested. Different applications require different criteria and the one chosen here may either be too lenient or too stringent for a particular application. The systems with compatibility concern include:

1. Hydrogen Sulfide at 50 ppm in R-32/PAG (due to changes in color and appearance of the steel and copper coupons).
2. Hydrogen Sulfide at 50 ppm in R-32/POE (due to changes in color and appearance of the steel and copper coupons, as well as higher TAN than the control).
3. Hydrogen Sulfide at 50 ppm in R-32/PVE (due to changes in color and appearance of the steel and copper coupons, as well as higher TAN than the control).
4. Carbonyl Sulfide at 50 ppm in R-32/PAG (due to cloudiness in the lubricant after aging).
5. Methyl Ethyl Sulfide at 150 ppm in R-1234yf/POE (due to higher TAN than the control).
6. Dimethyl Sulfide at 150 ppm in R-1234yf/PVE (due to higher TOA than the control).
7. Methyl Ethyl Sulfide at 150 ppm in R-1234yf/PVE (due to higher TOA than the control).
8. Trimethyl Amine at 50 ppm in R-290/PVE (due to higher TAN and TOA than the control).
9. Methyl Ethyl Sulfide at 150 ppm in R-290/PVE (due to higher TOA than the control)
10. Ethyl Mercaptan at 60 ppm in R-290/PAG (due to deposit on tube wall and change in color of the steel and copper coupons after aging).

6. CONCLUSIONS

In this research project, as part of a program undertaken by the Consumer Product Safety Commission (CPSC), different odorants (including Hydrogen Sulfide, Carbonyl Sulfide, Trimethyl Amine, Dimethyl Sulfide, Mehyl Ethyl Sulfide, and Ethyl Mercaptan, were tested for compatibility with refrigerant/lubricant mixtures, including three refrigerants (R-32, R-1234yf and R-290) each with three different lubricants (PAG, POE and PVE). The compatibility test results identified twenty-one refrigerant/lubricant/odorant systems with no significant compatibility concern, based on visual observations of the sealed tubes after aging, as well as TAN, TOA, fluoride ion concentrations and elemental metal concentrations. Ten refrigerant/lubricant/odorant systems were highlighted that may present some compatibility problems.

However, to fully evaluate candidate odorants for applications in refrigeration and air-conditioning (AC&R), additional analyses are needed, such as odorant toxicity evaluation, odorant threshold detection verification, refrigerant and odorant dispersion modeling and verification, evaluation of the impact of odorant addition on the AC&R equipment, odorant distribution evaluation within the equipment, and odorant effectiveness with time.

7. NOMENCLATURE

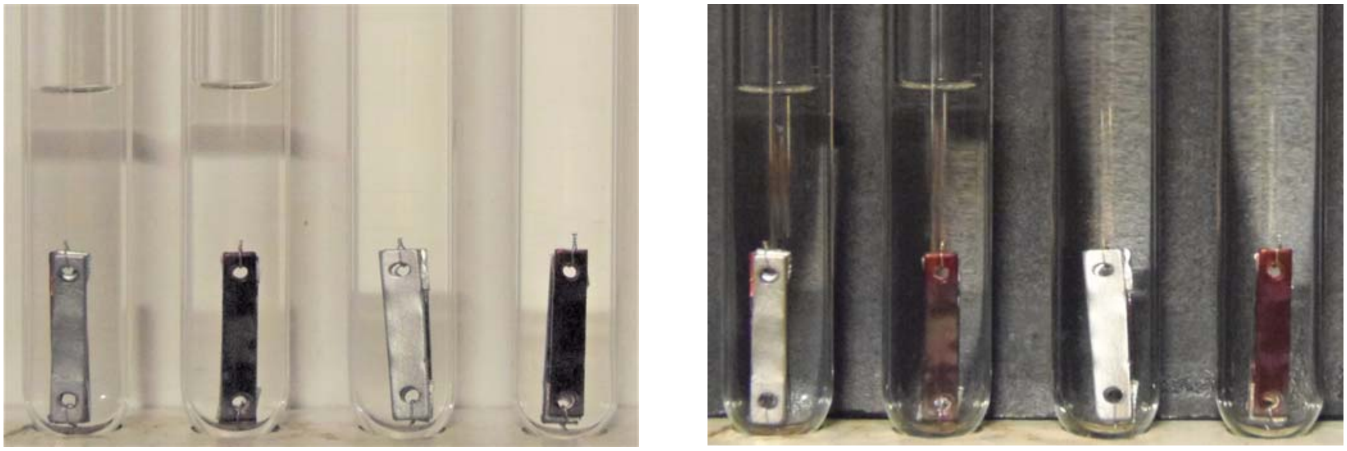
AC&R=	Air-Conditioning and Refrigeration
ASHRAE=	American Society of Heating, Refrigerating, and Air-Conditioning Engineers
DMS=	Dimethyl Sulfide

EM=	Ethyl Mercaptan
IC=	Ion Chromatography
ICP=	Inductively Coupled Plasma
MES=	Methyl Ethyl Sulfide
PAG=	PolyAlkylene Glycol lubricant
POE=	Polyol Ester lubricant
PVE=	Polyvinyl Ether lubricant
TA=	Trimethyl Amine
TAN=	Total Acid Number
TOA=	Total Organic Acid

8. REFERENCES

Forssell, E. W. 2020. "*1794-TRP, White Paper Investigation Relating to the Use of Odorants in Flammable Refrigerants"*. Final Report Draft – Rev 2" Prepared For ASHRAE, 1791 Tullie Circle NE Atlanta, GA 30329 USA.

9. APPENDIX A: PHOTOGRAPHS OF SEALED TUBES



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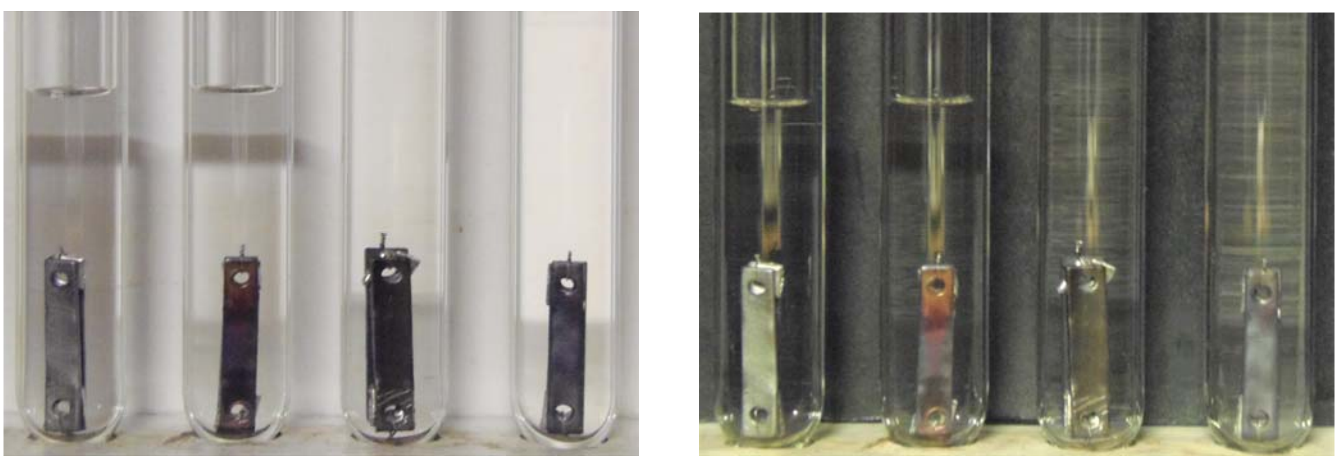
BEFORE AGING



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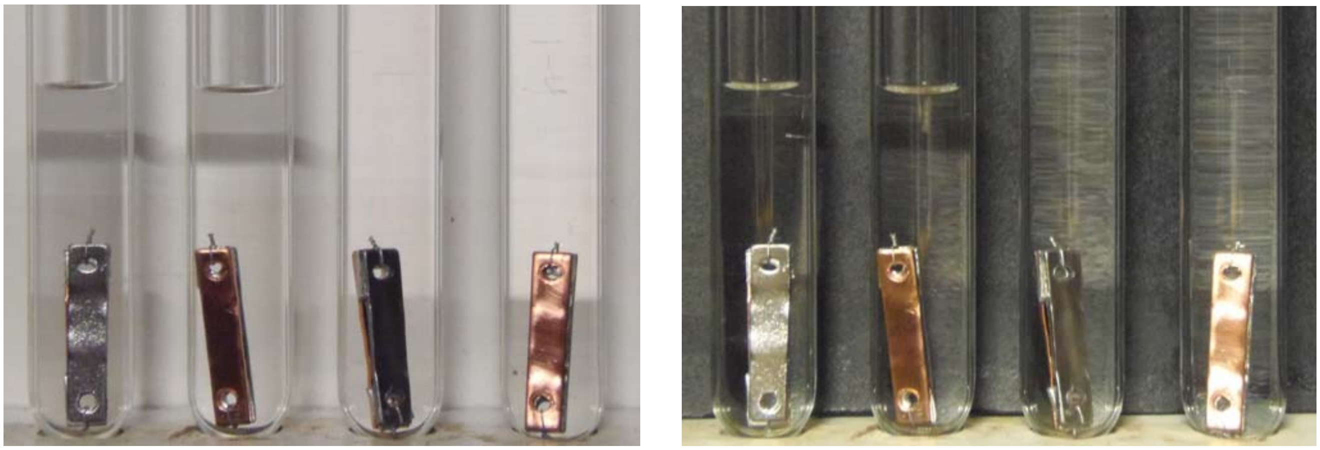
AFTER AGING

Figure 1: Photographs of Hydrogen Sulfide at 50 ppm in R-32/PAG



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BEFORE AGING

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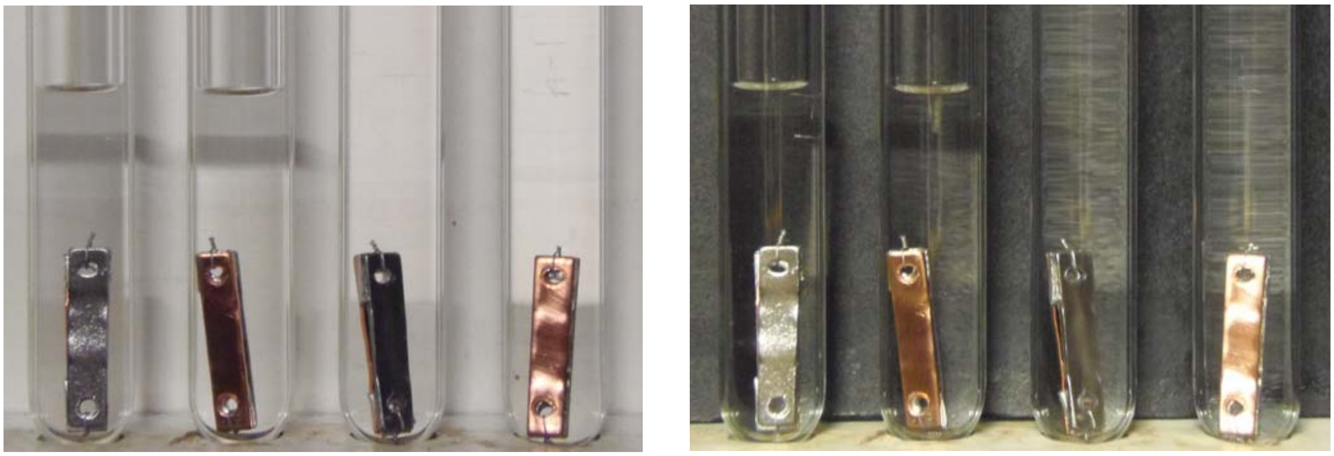
AFTER AGING

Figure 2: Photographs of Carbonyl Sulfide at 50 ppm in R-32/PAG
Note: One of the four sealed tubes broke during aging



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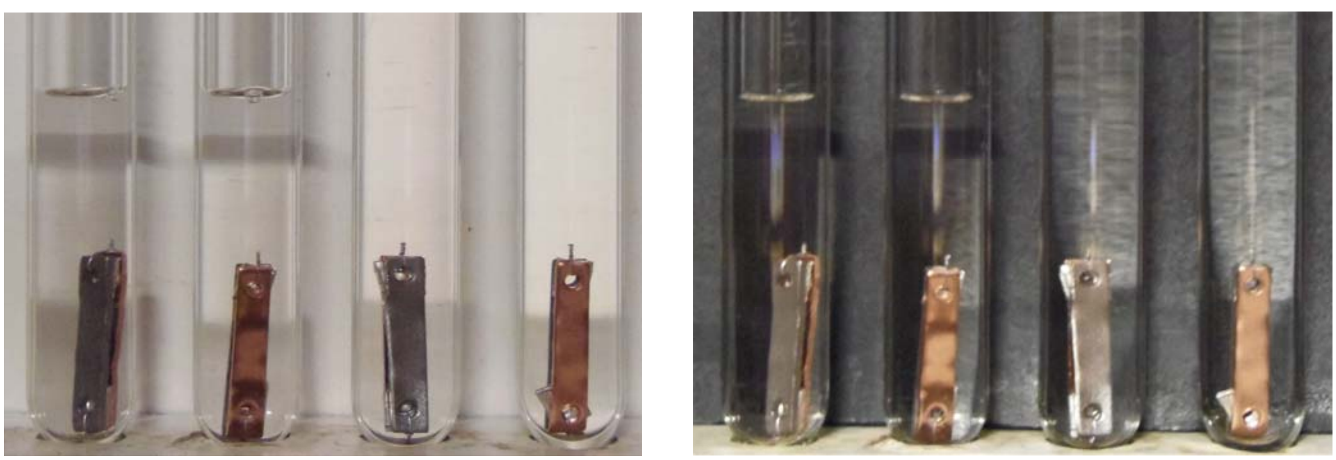
BEFORE AGING



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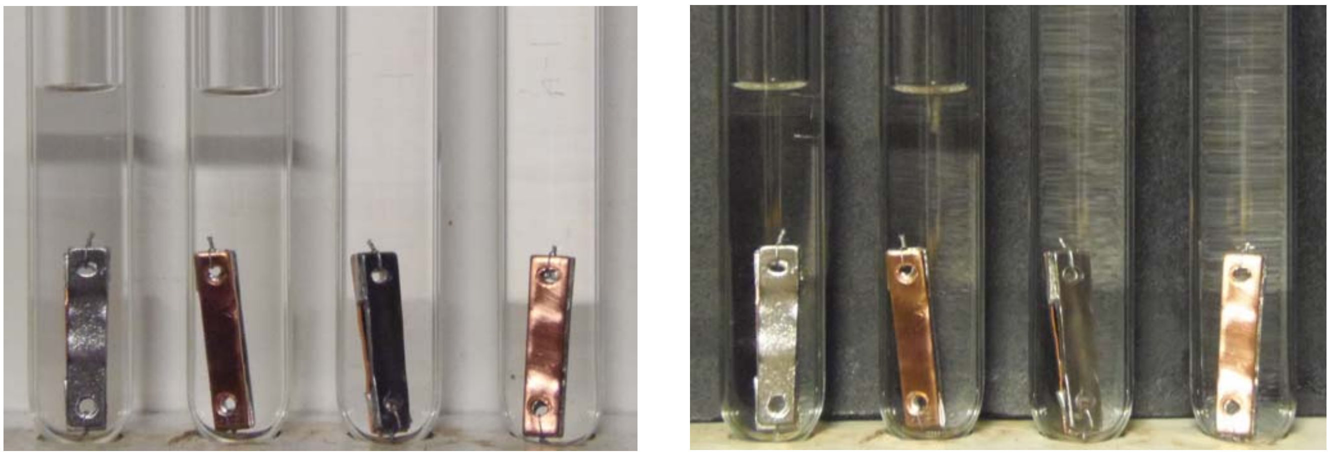
AFTER AGING

Figure 3: Photographs of Dimethyl Sulfide at 150 ppm in R-32/PAG



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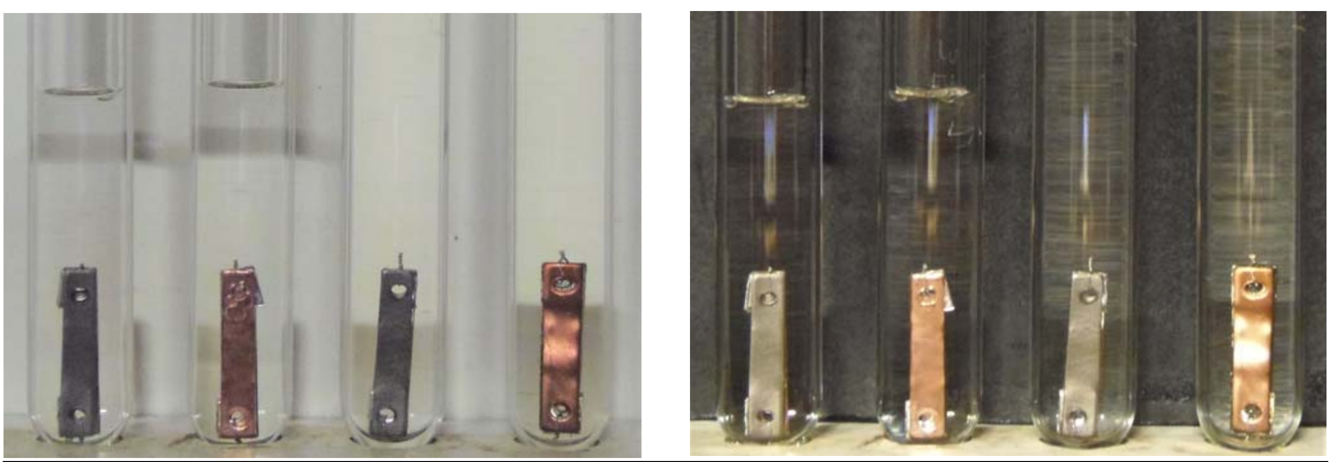
BEFORE AGING



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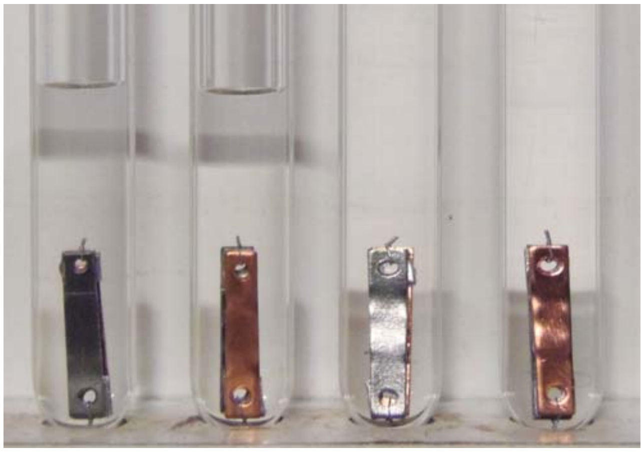
AFTER AGING

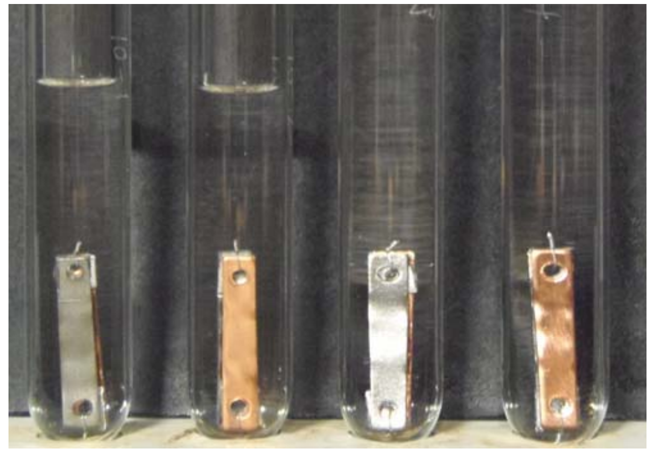
Figure 4: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-32/PAG

White background Black background
BEFORE AGING

White background Black background
AFTER AGING

Figure 5: Photographs of R-32/PAG (Control)
Note: One of the four sealed tubes broke during aging





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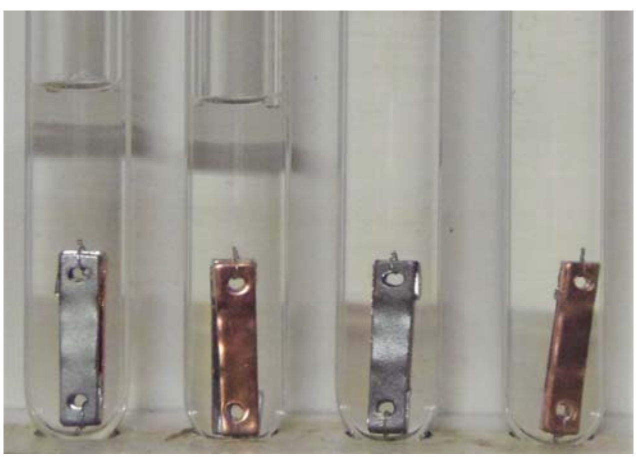
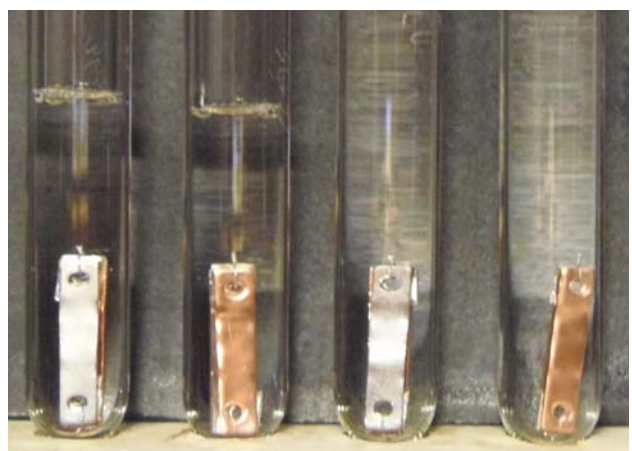
BEFORE AGING

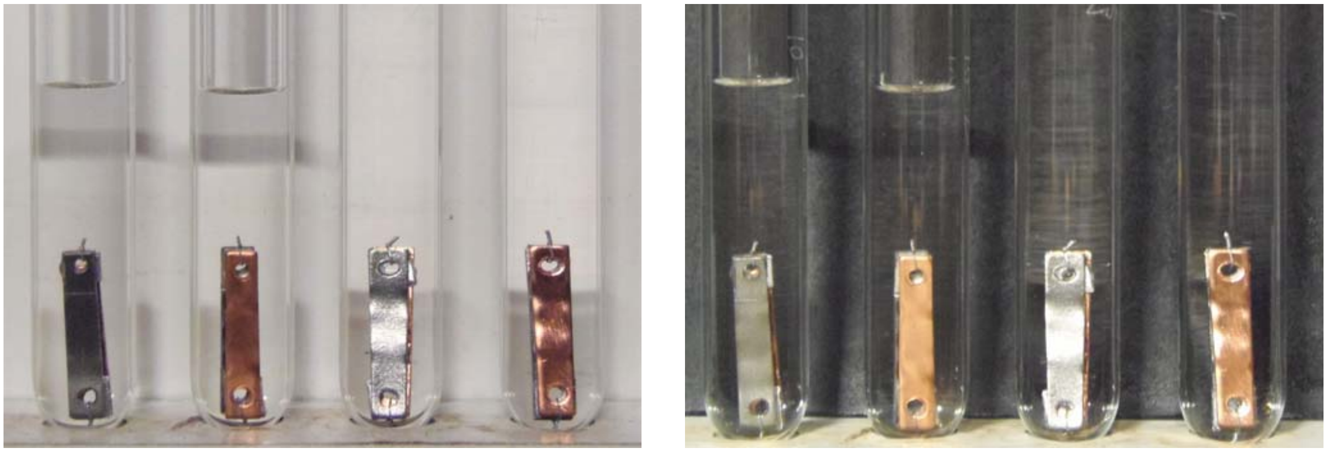




White background **Black background**

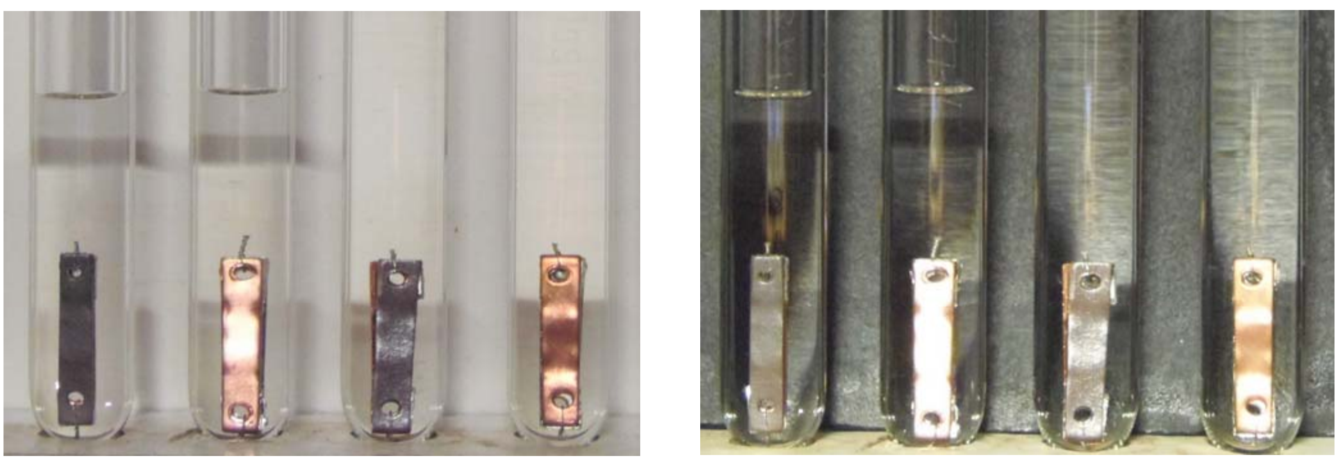
AFTER AGING

Figure 6: Photographs of Dimethyl Sulfide at 150 ppm in R-1234yf/PAG



White background **Black background**

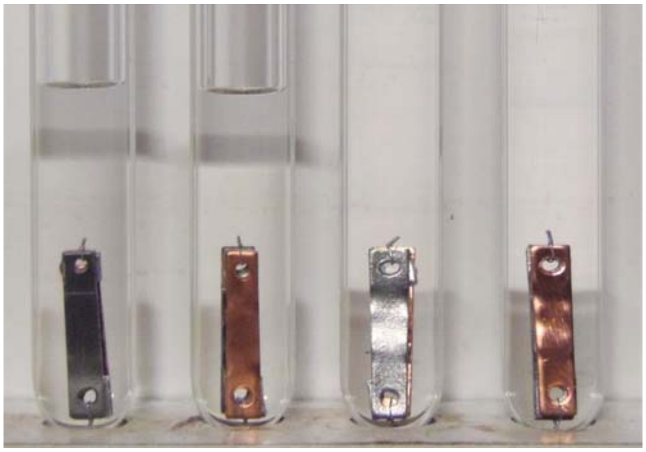
BEFORE AGING

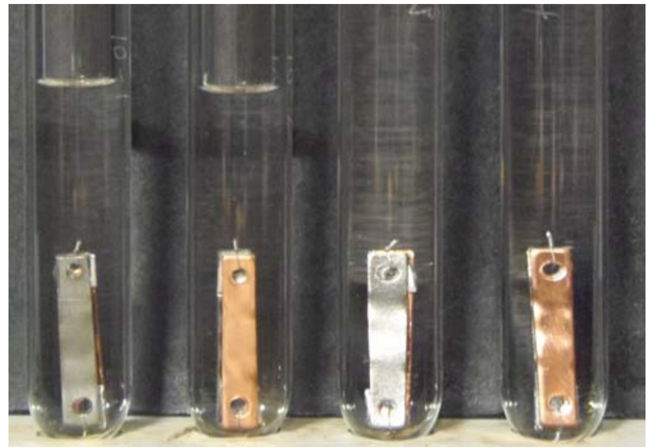


White background **Black background**

AFTER AGING

Figure 7: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-1234yf/PAG





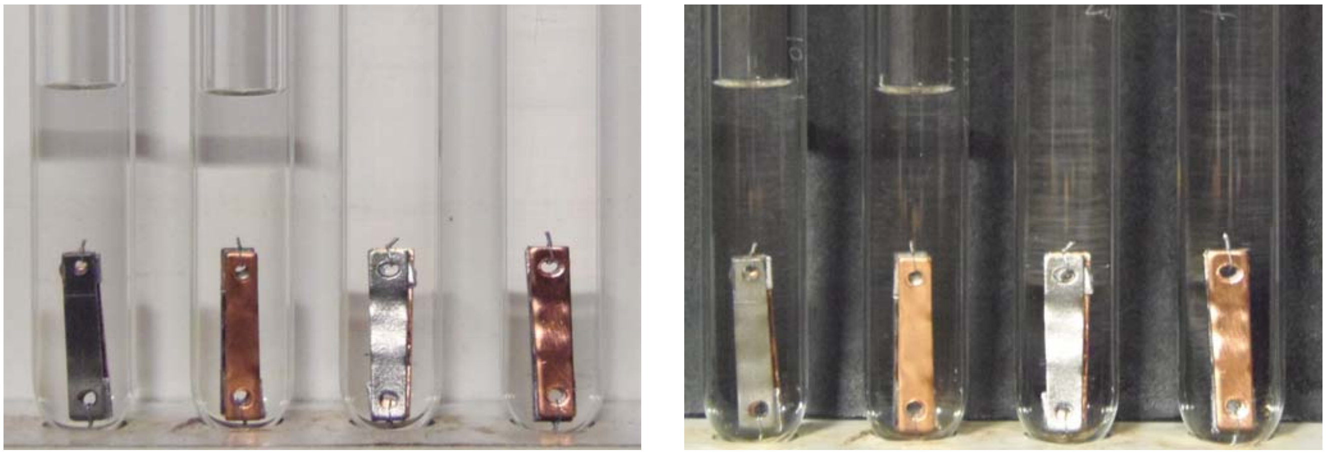
White background	**Black background**

BEFORE AGING

White background	**Black background**

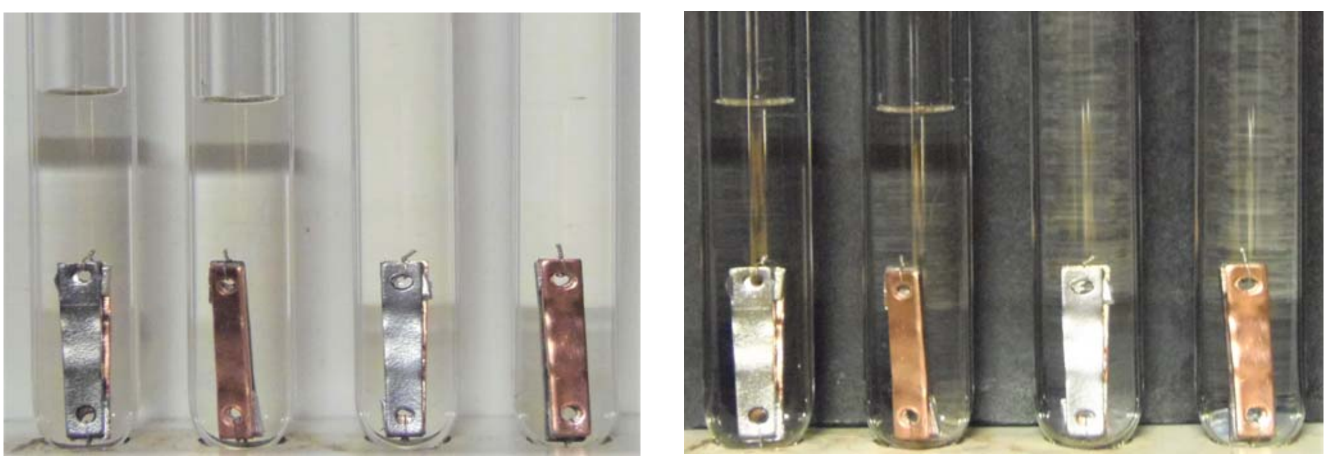
AFTER AGING

Figure 8: Photographs of Trimethyl Amine at 50 ppm in R-1234yf/PAG



White background **Black background**

BEFORE AGING



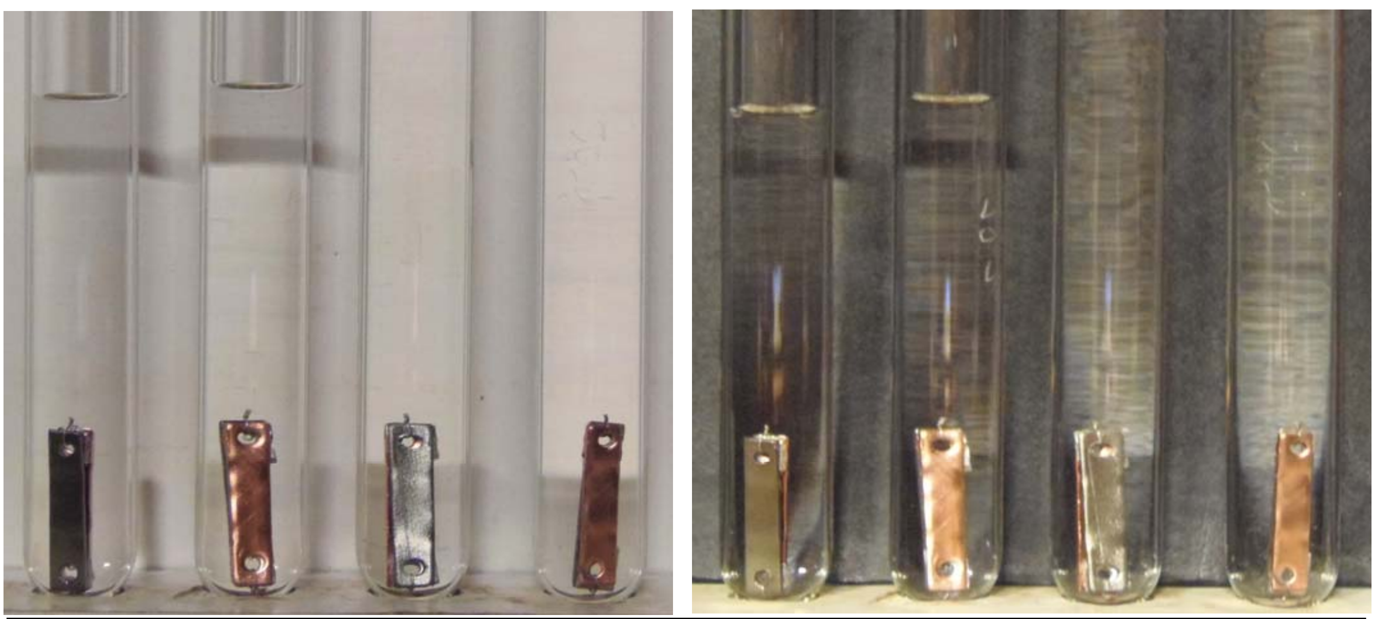
White background **Black background**

AFTER AGING

Figure 9: Photographs of R-1234yf/PAG (Control)

White background **Black background**

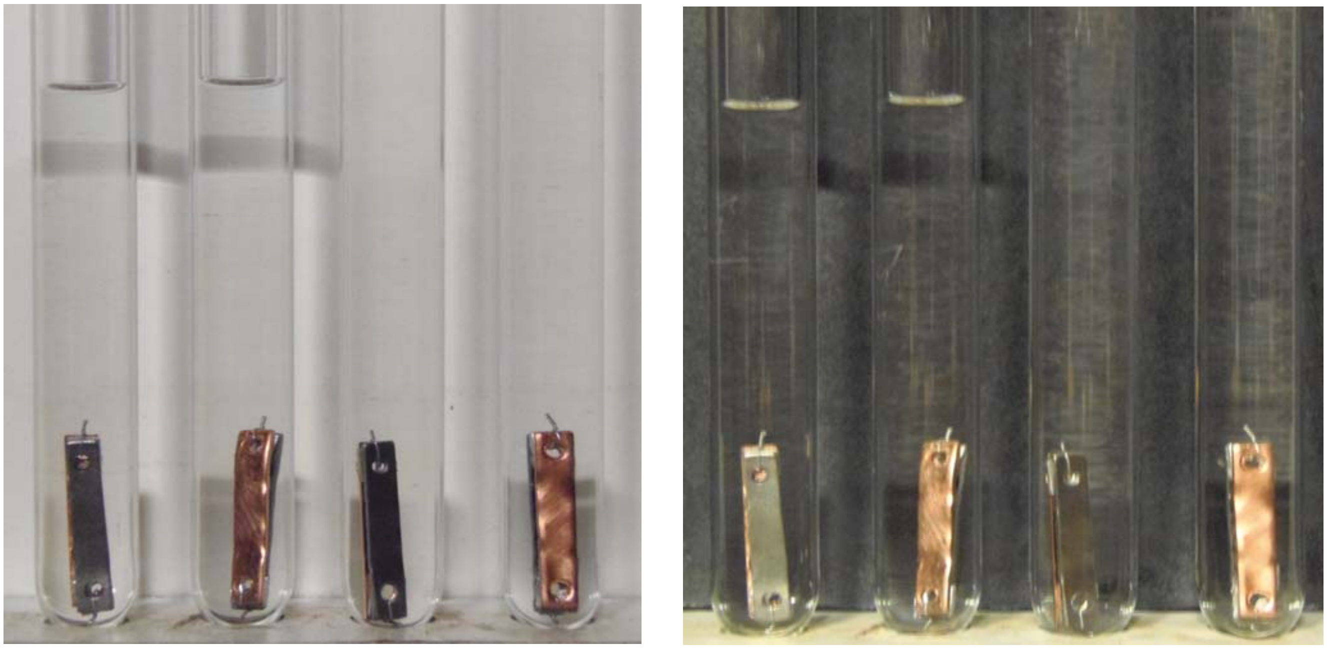
BEFORE AGING



White background **Black background**

AFTER AGING

Figure 10: Photographs of Dimethyl Sulfide at 150 ppm in R-290/PAG



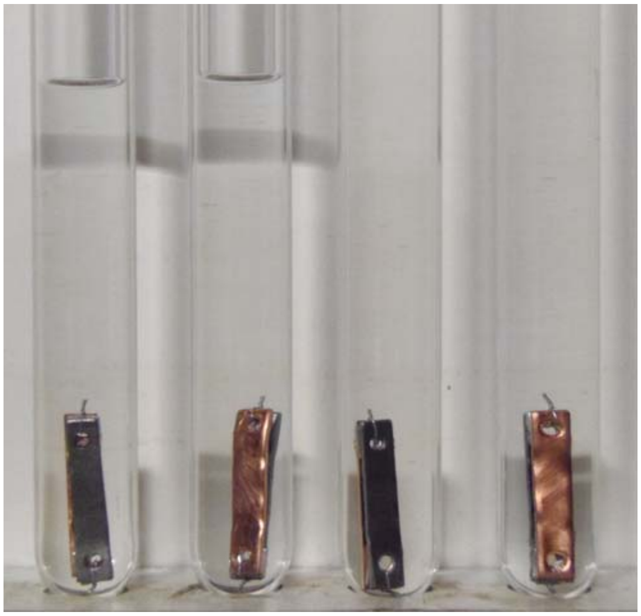
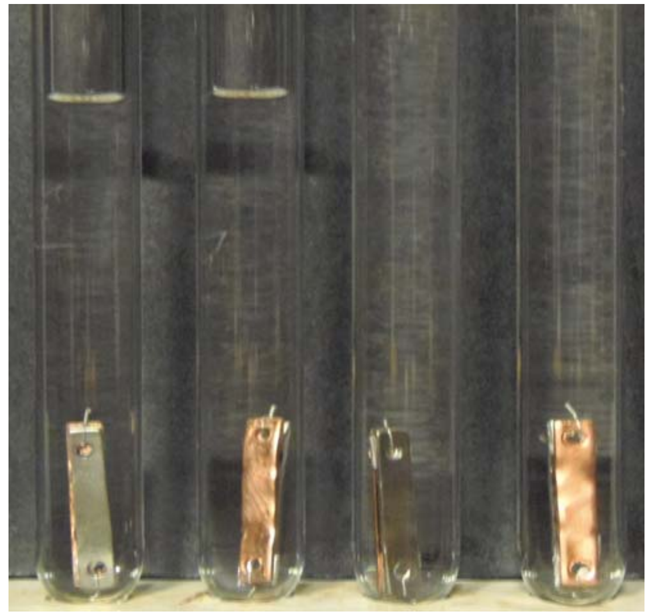
White background **Black background**

BEFORE AGING

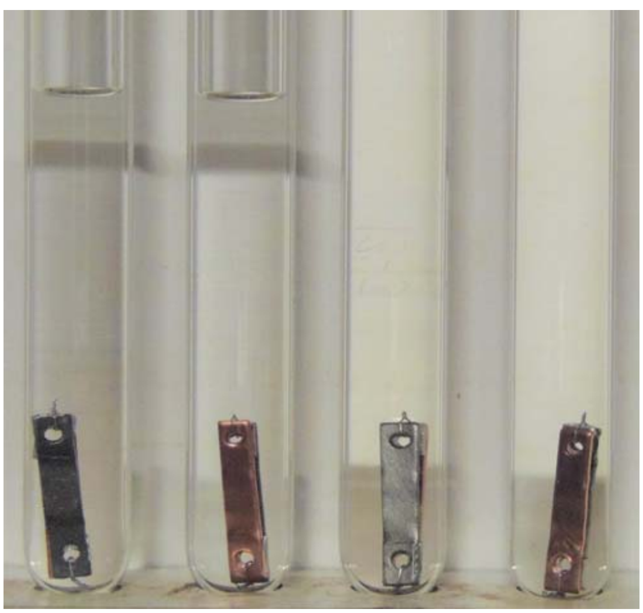
White background **Black background**

AFTER AGING

Figure 11: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-290/PAG

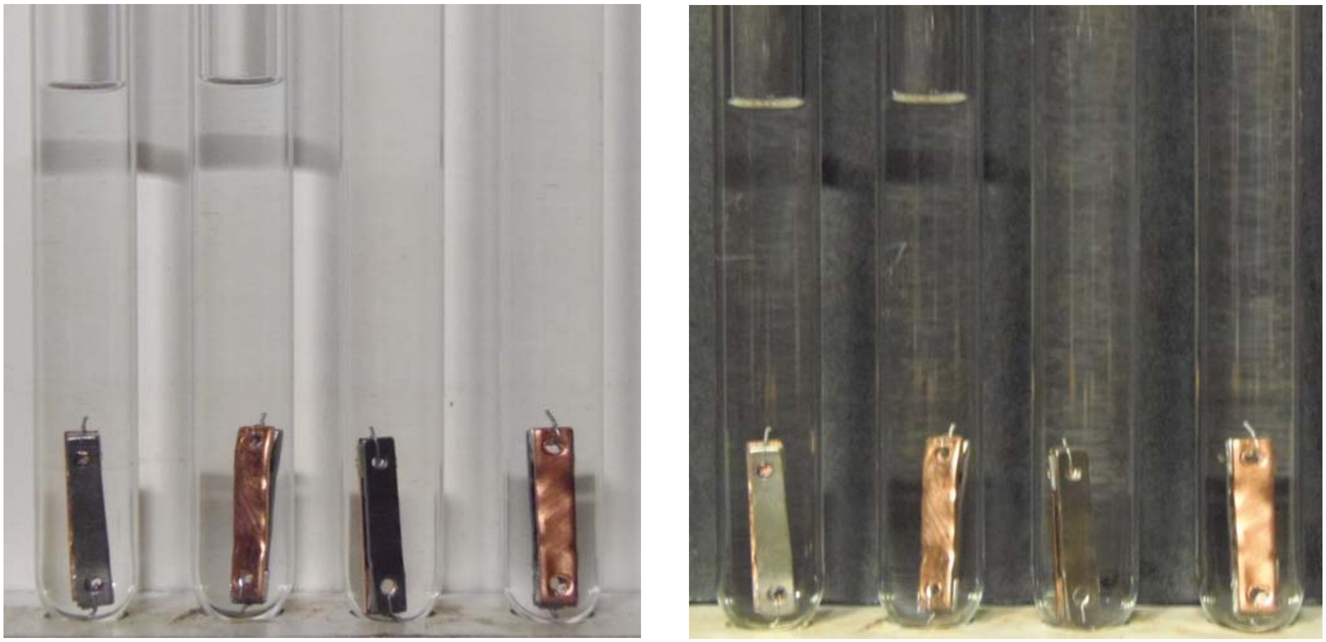
 

White background **Black background**
BEFORE AGING

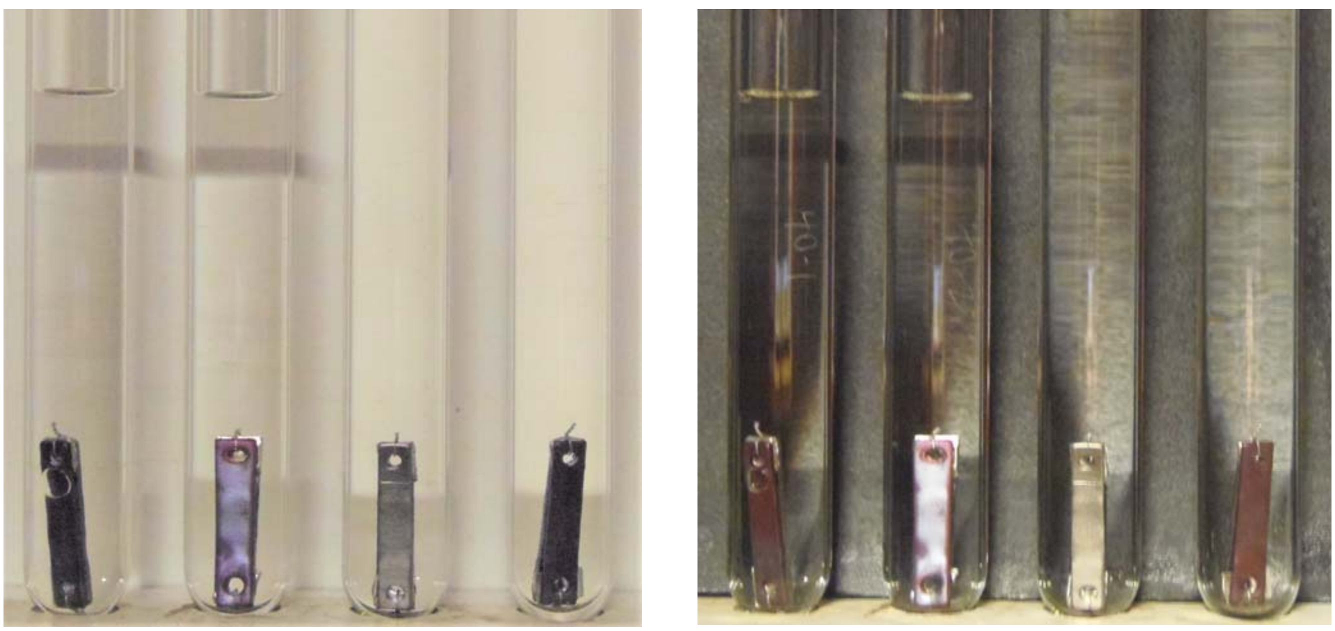
 

White background **Black background**
AFTER AGING

Figure 12: Photographs of Trimethyl Amine at 50 ppm in R-290/PAG

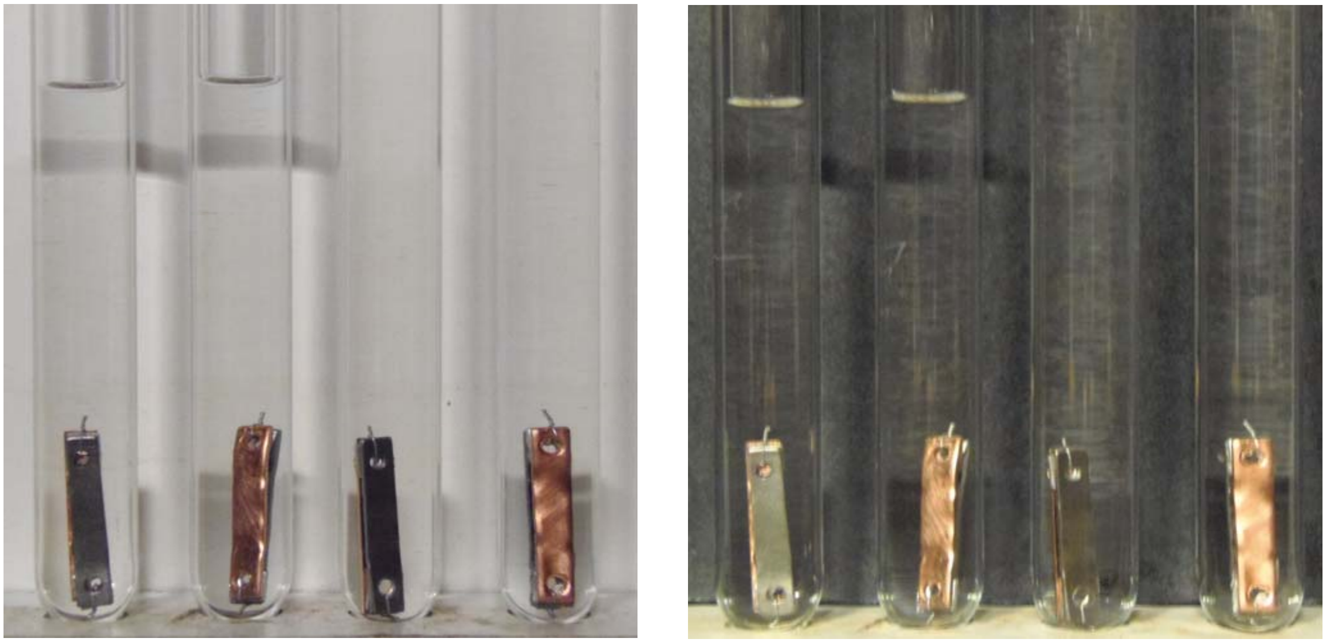


White background Black background
BEFORE AGING



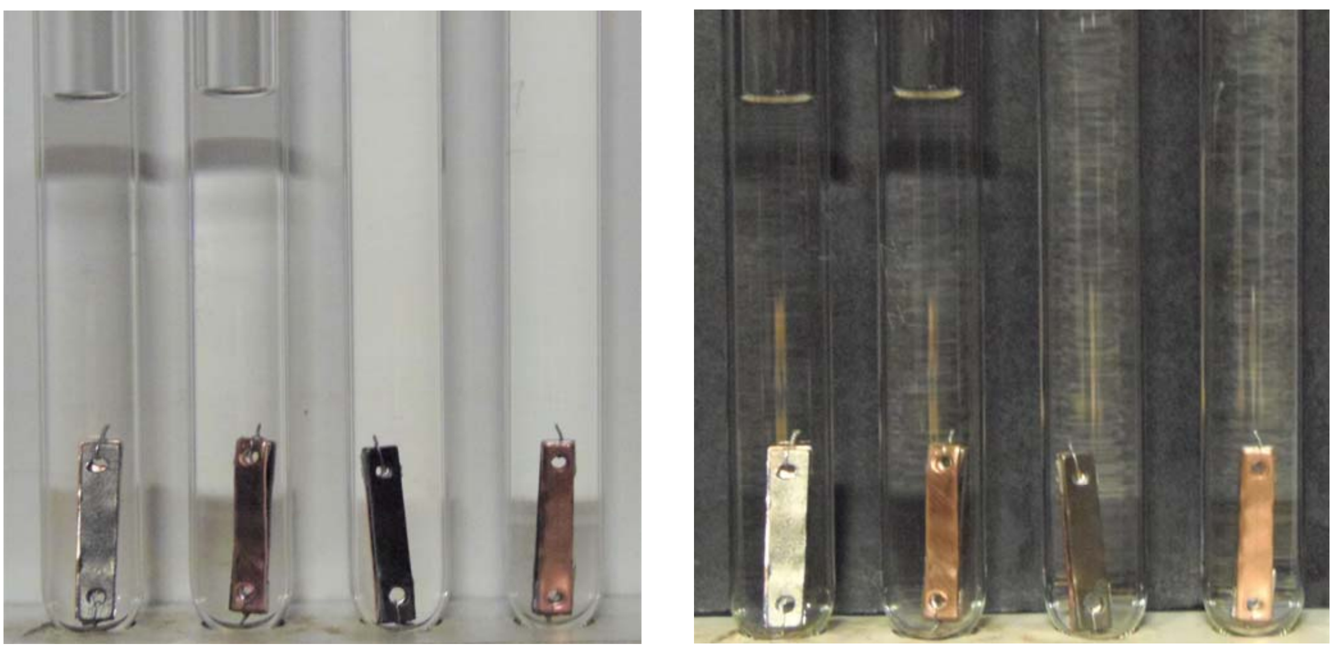
White background Black background
AFTER AGING

Figure 13: Photographs of Ethyl Mercaptan at 60 ppm in R-290/PAG



White background **Black background**

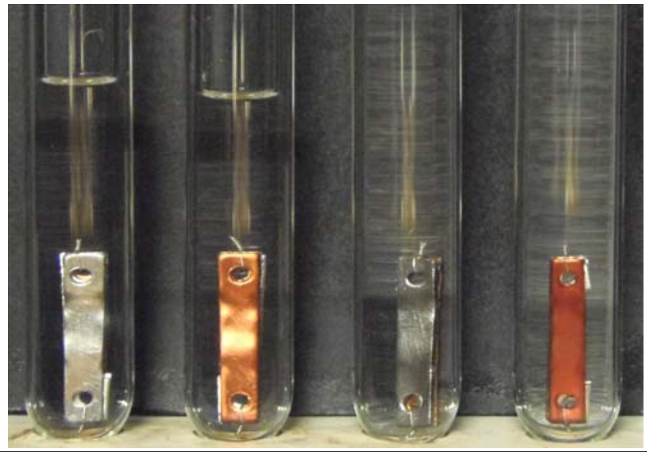
BEFORE AGING



White background **Black background**

AFTER AGING

Figure 14: Photographs of R-290/PAG (Control)



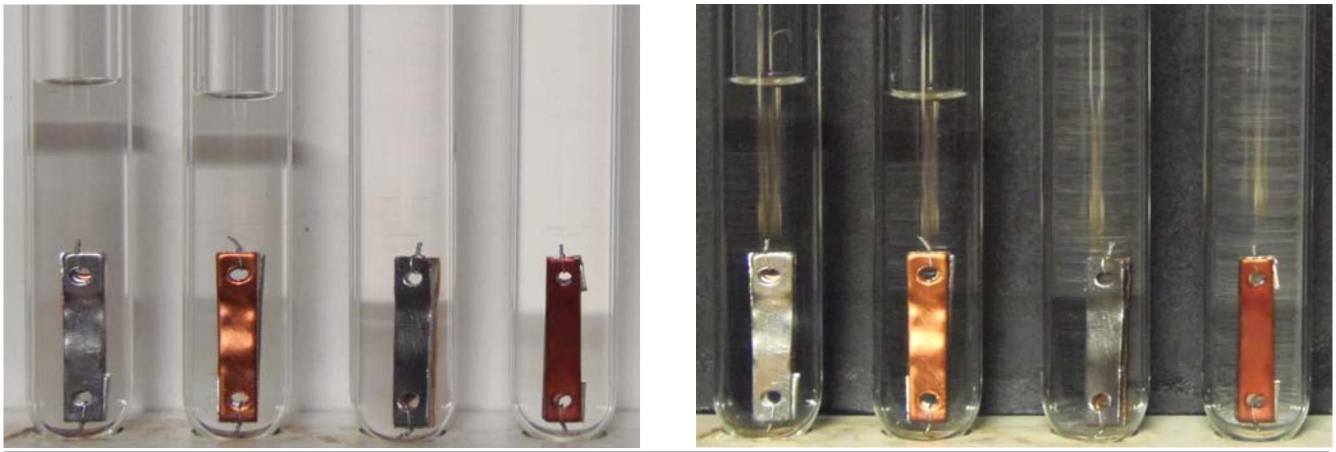
White background **Black background**

BEFORE AGING

White background **Black background**

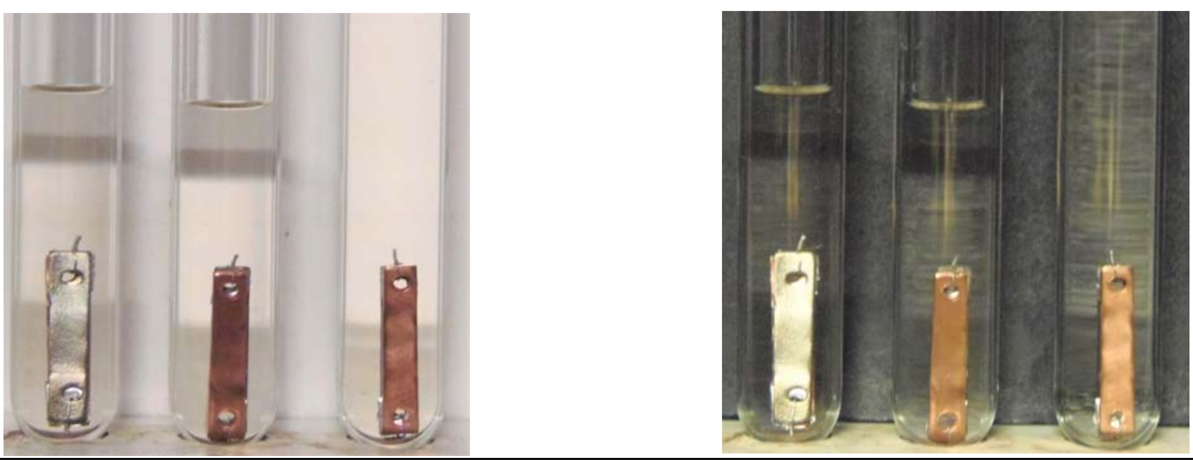
AFTER AGING

Figure 15: Photographs of Hydrogen Sulfide at 50 ppm in R-32/POE



White background **Black background**

BEFORE AGING



White background **Black background**

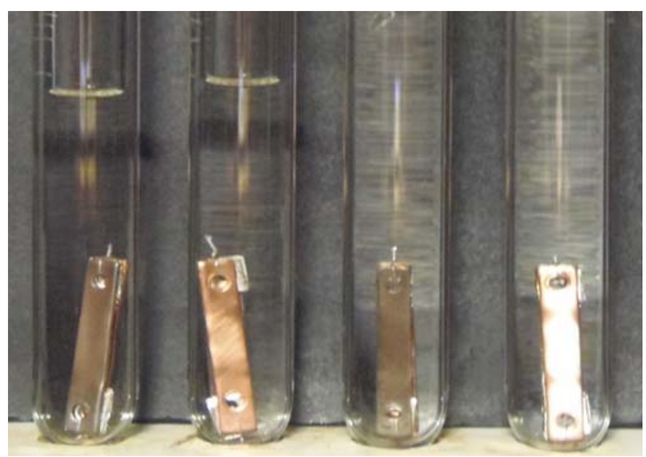
AFTER AGING

Figure 16: Photographs of Carbonyl Sulfide at 50 ppm in R-32/POE

Note: One of the four sealed tubes broke during aging


White background **Black background**

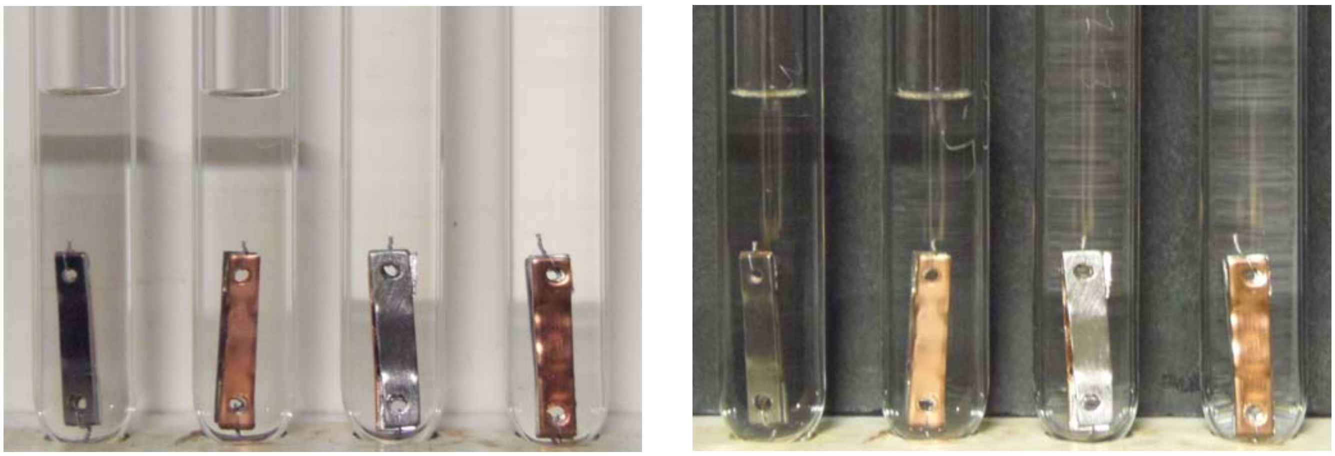
BEFORE AGING

White background **Black background**

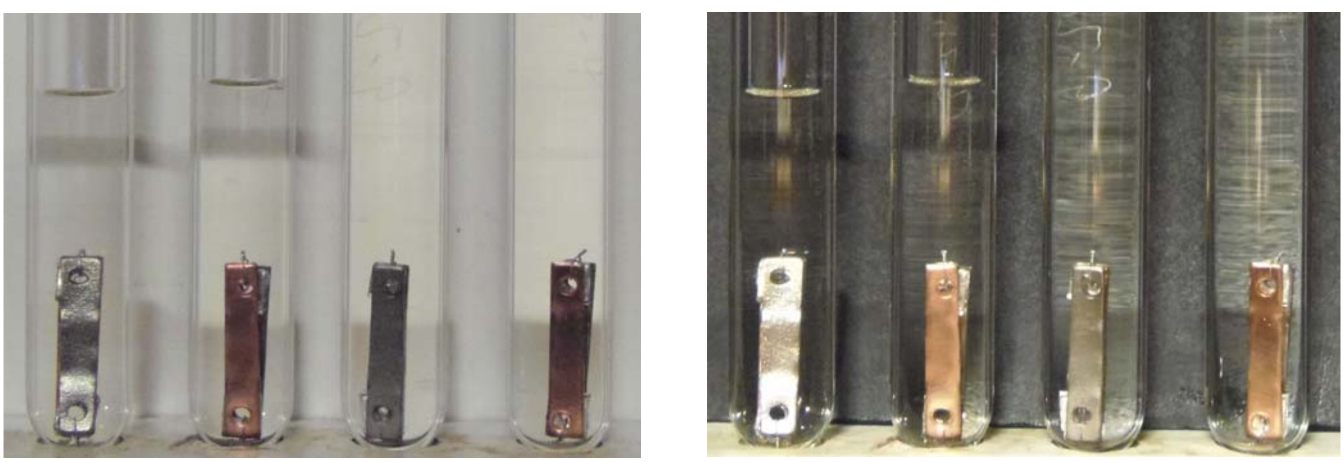
AFTER AGING

Figure 17: Photographs of Dimethyl Sulfide at 150 ppm in R-32/POE



White background **Black background**

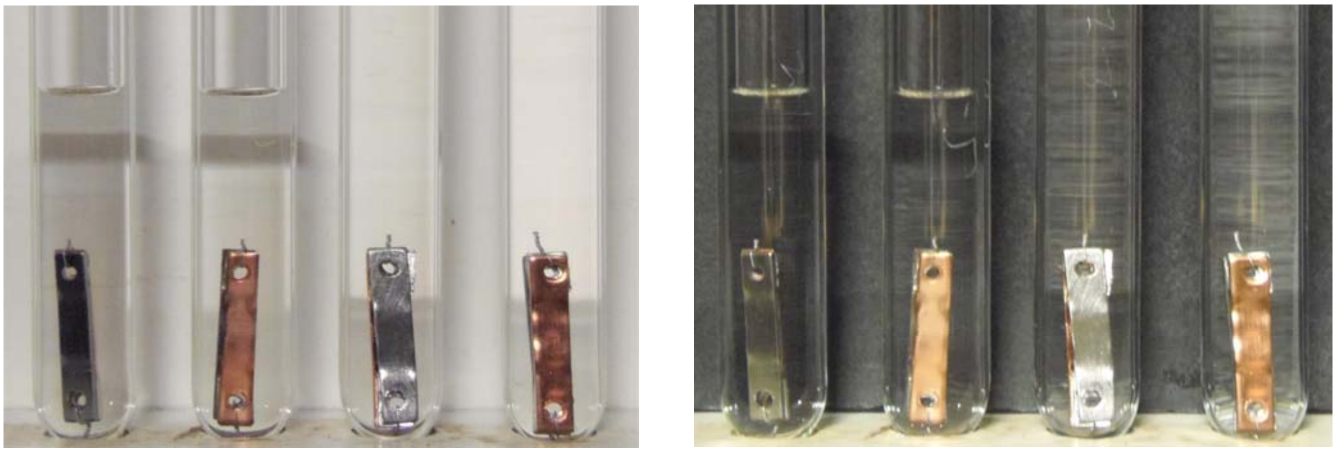
BEFORE AGING



White background **Black background**

AFTER AGING

Figure 18: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-32/POE



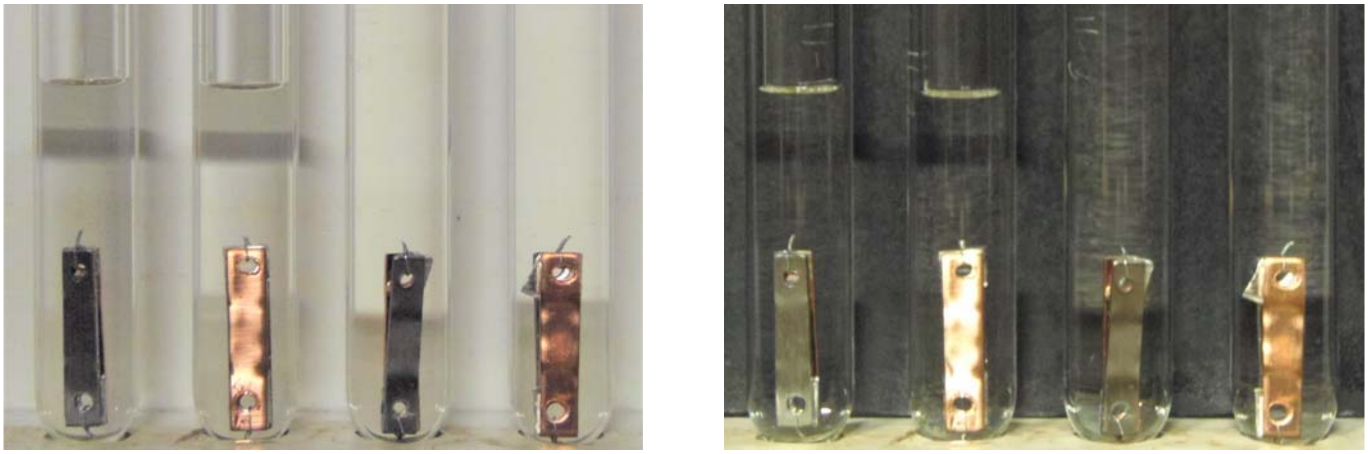
White background **Black background**

BEFORE AGING

White background **Black background**

AFTER AGING

Figure 19: Photographs of R-32/POE (Control)



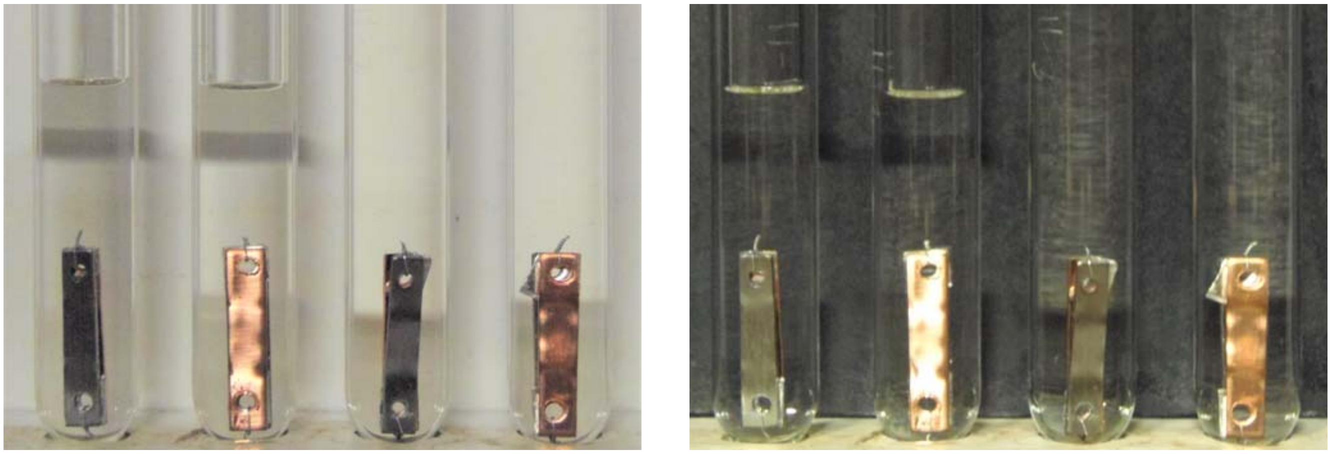
White background **Black background**

BEFORE AGING

White background **Black background**

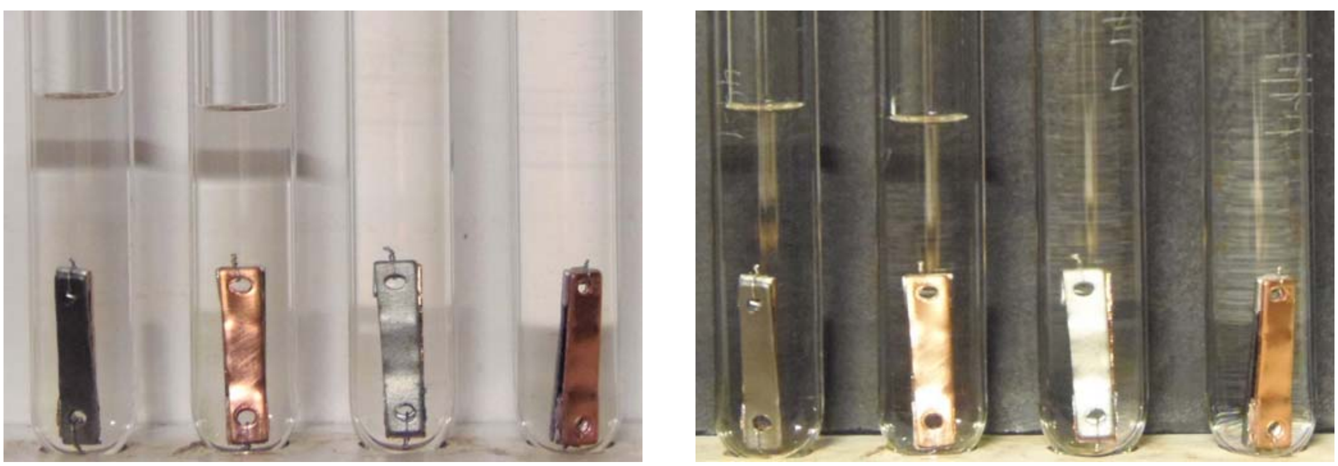
AFTER AGING

Figure 20: Photographs of Dimethyl Sulfide at 150 ppm in R-1234yf/POE



White background **Black background**

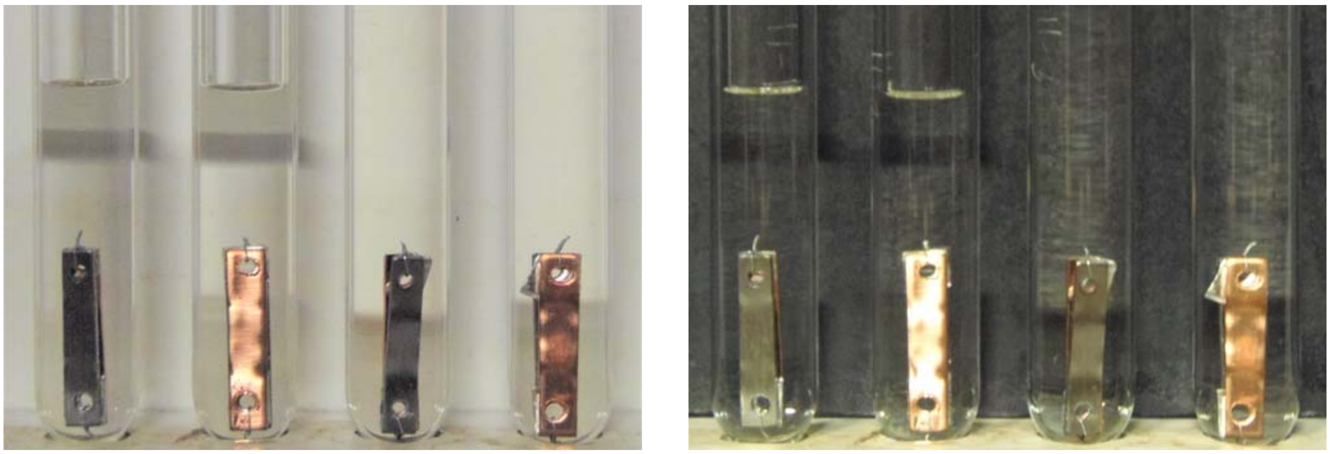
BEFORE AGING



White background **Black background**

AFTER AGING

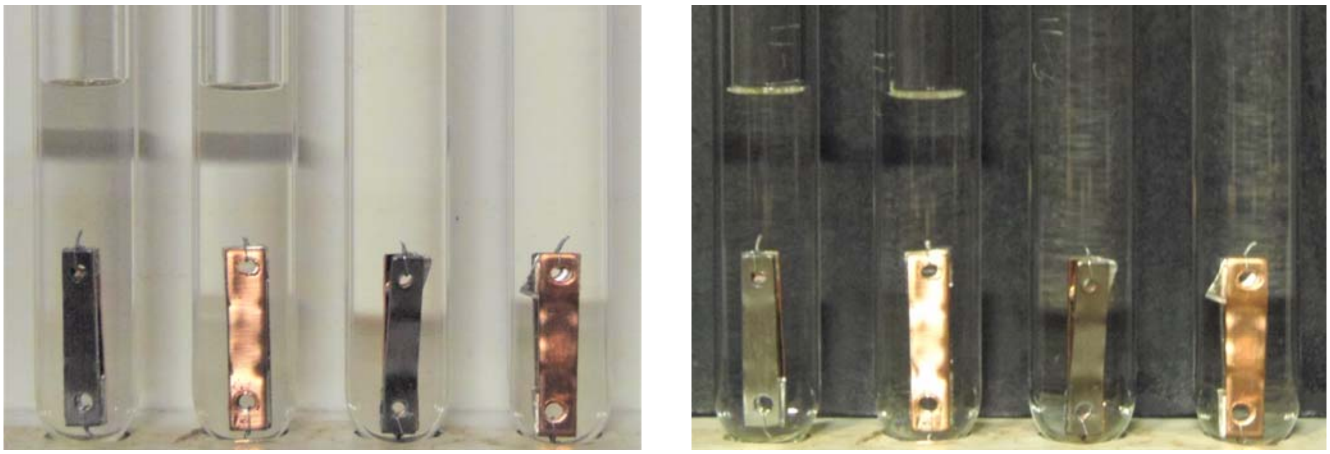
<u>Figure 21: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-1234yf/POE</u>



White background	BEFORE AGING	Black background

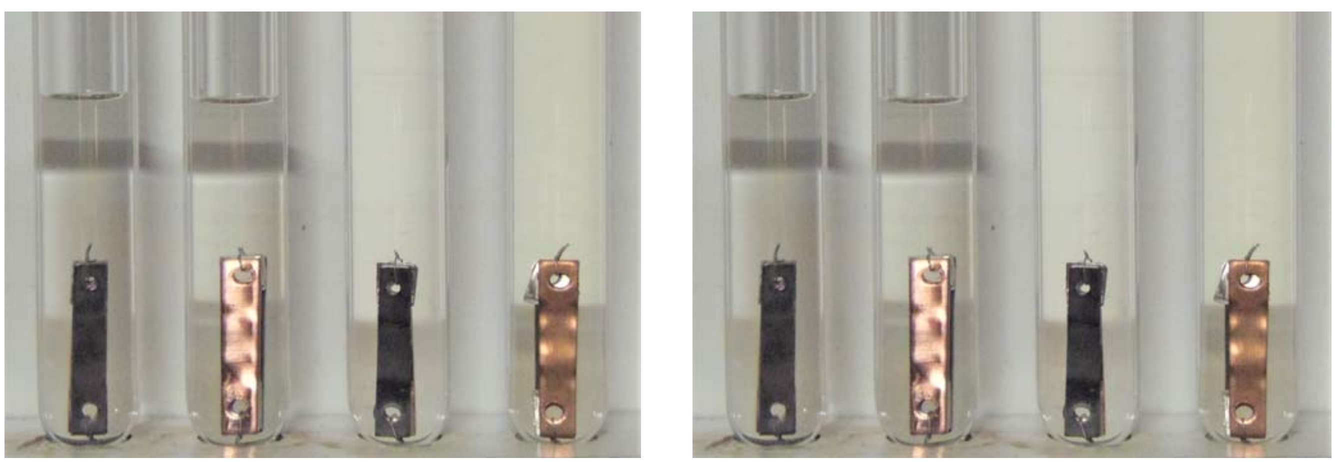
White background	AFTER AGING	Black background

Figure 22: Photographs of Trimethyl Amine at 50 ppm in R-1234yf/POE



White background **Black background**

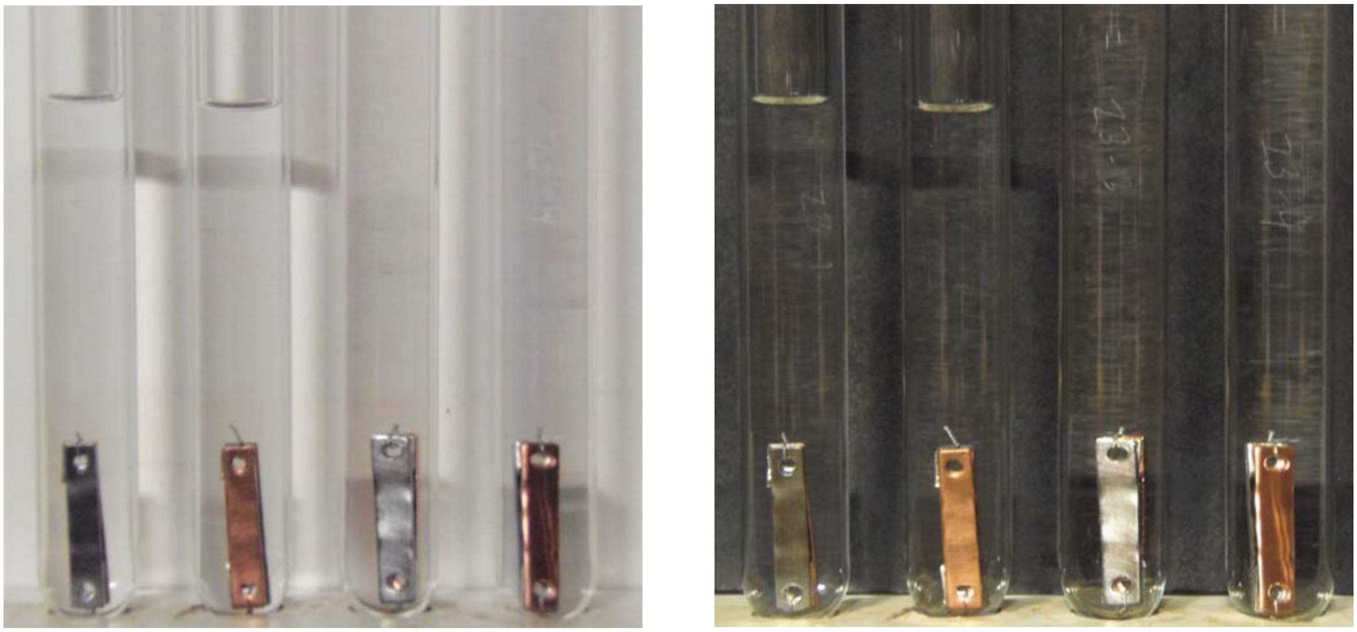
BEFORE AGING



White background **Black background**

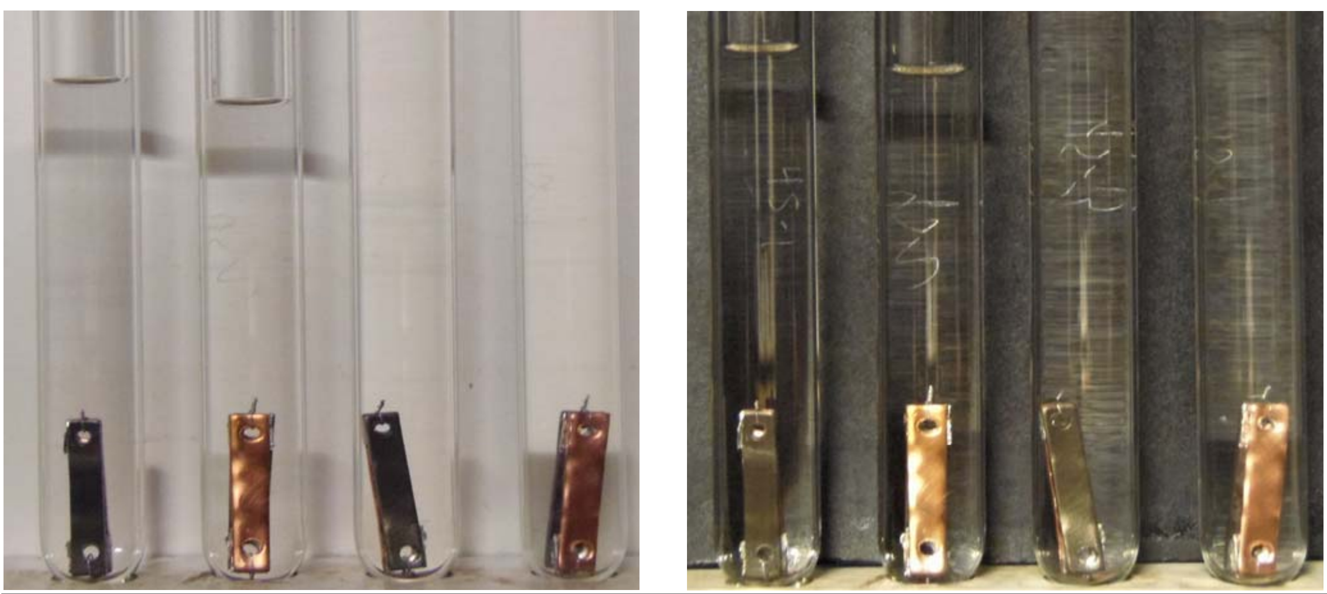
AFTER AGING

Figure 23: Photographs of R-1234yf/POE (Control)



White background **Black background**

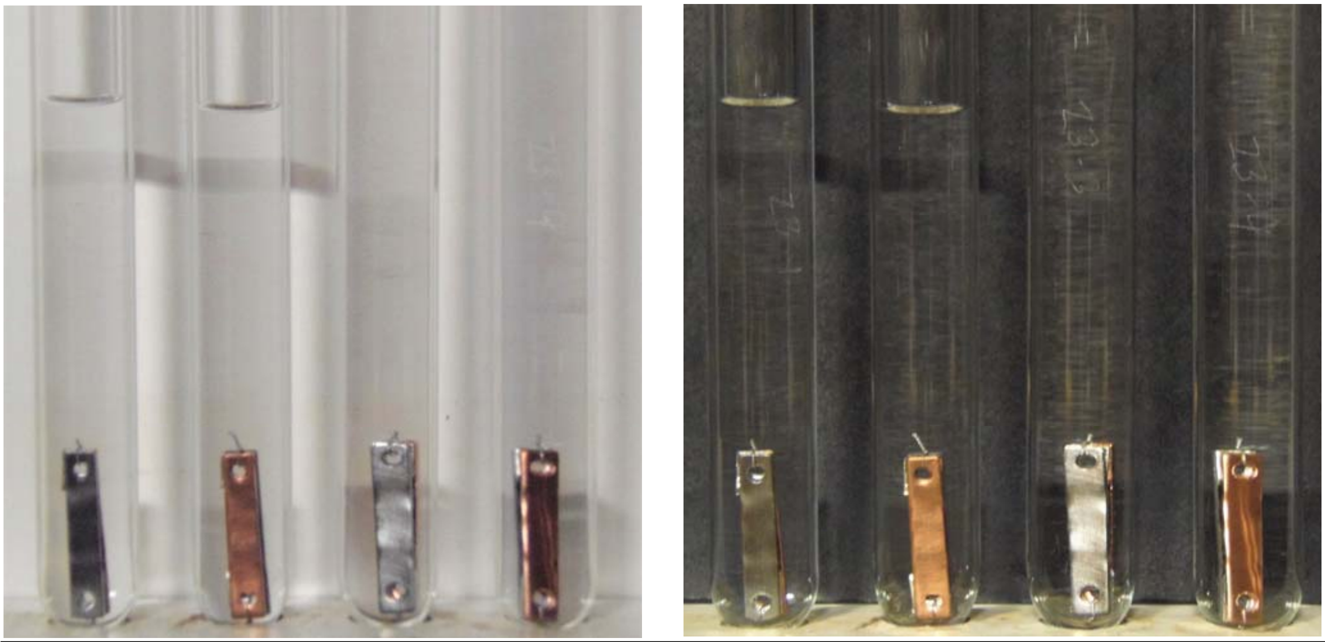
BEFORE AGING



White background **Black background**

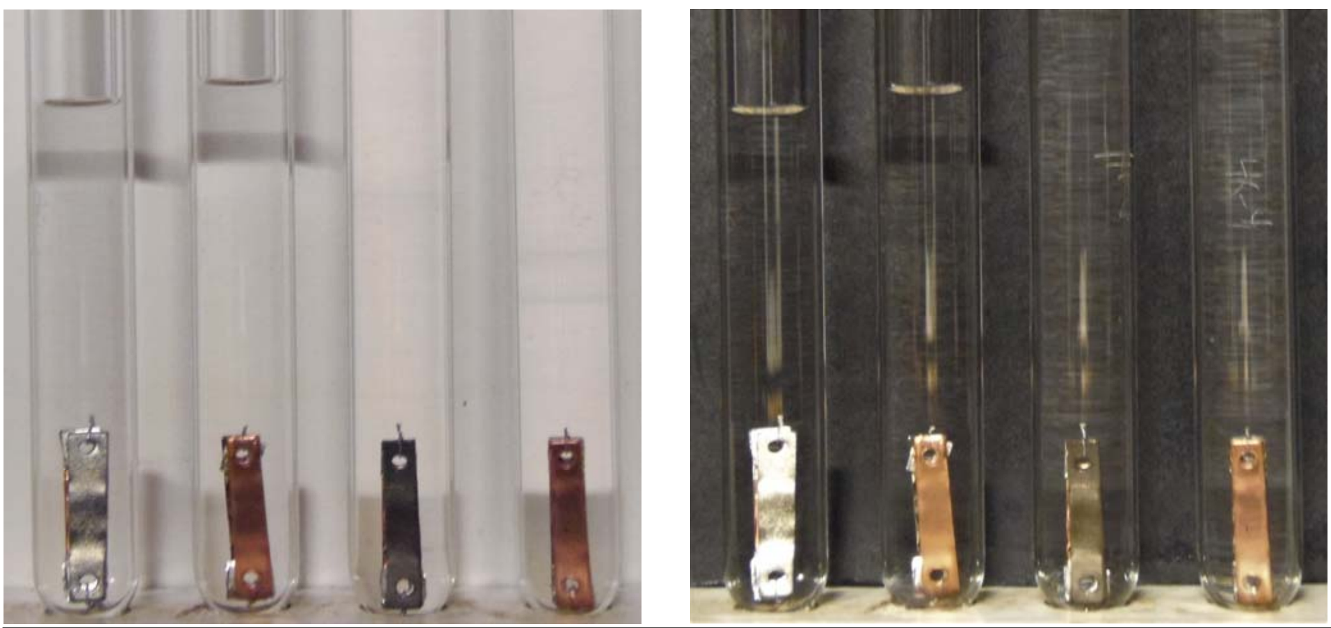
AFTER AGING

Figure 24: Photographs of Dimethyl Sulfide at 150 ppm in R-290/POE



White background **Black background**

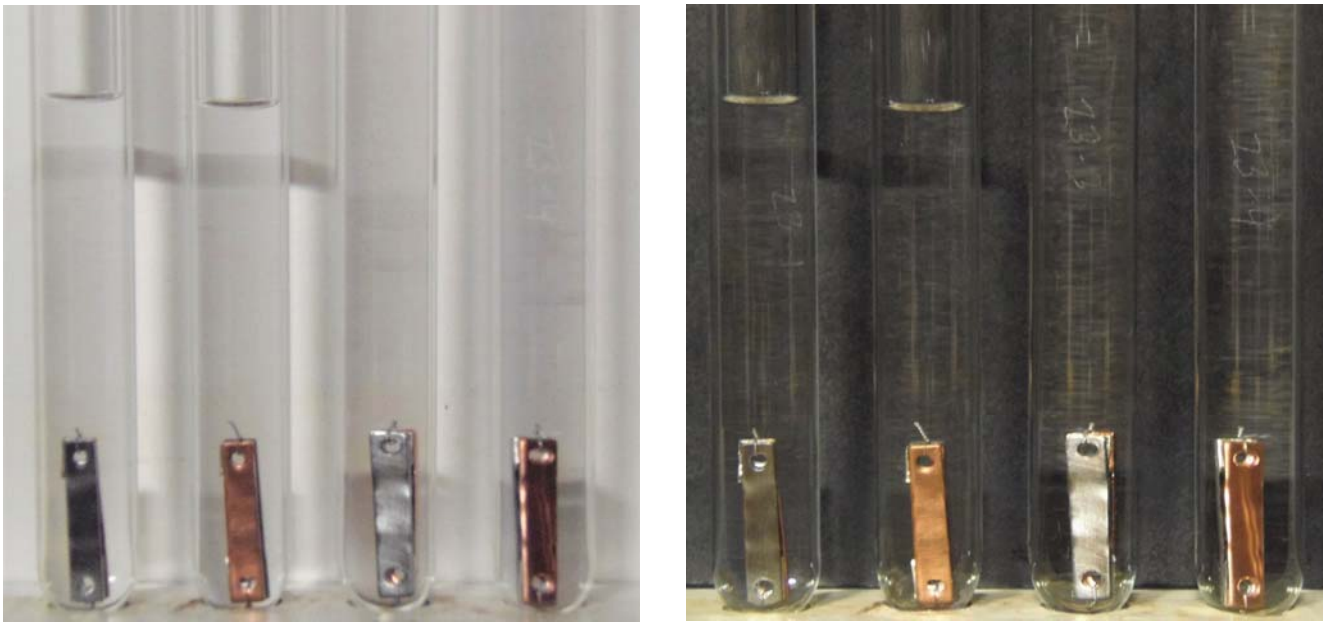
BEFORE AGING



White background **Black background**

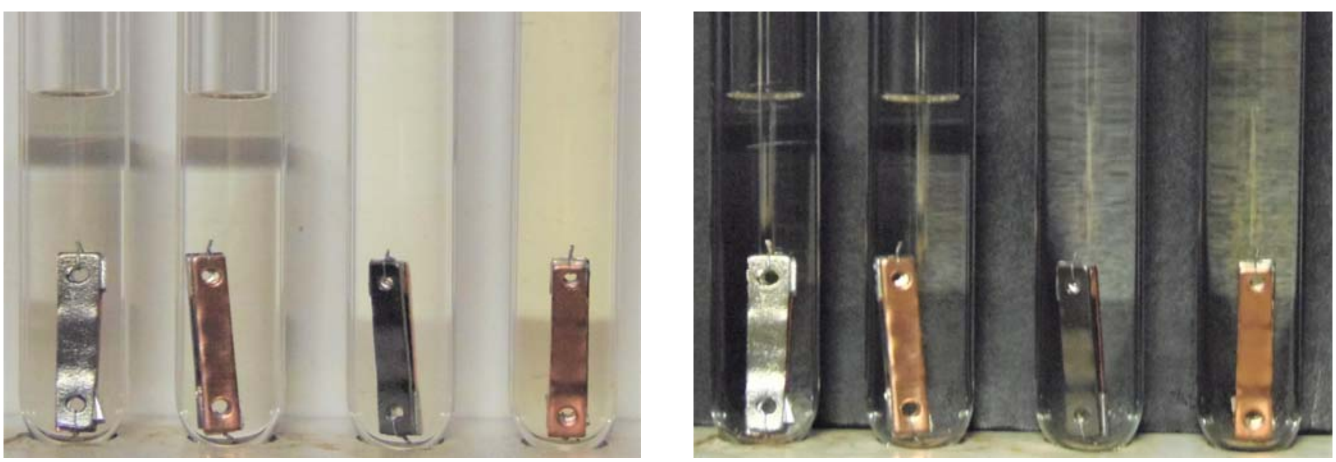
AFTER AGING

Figure 25: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-290/POE



White background **Black background**

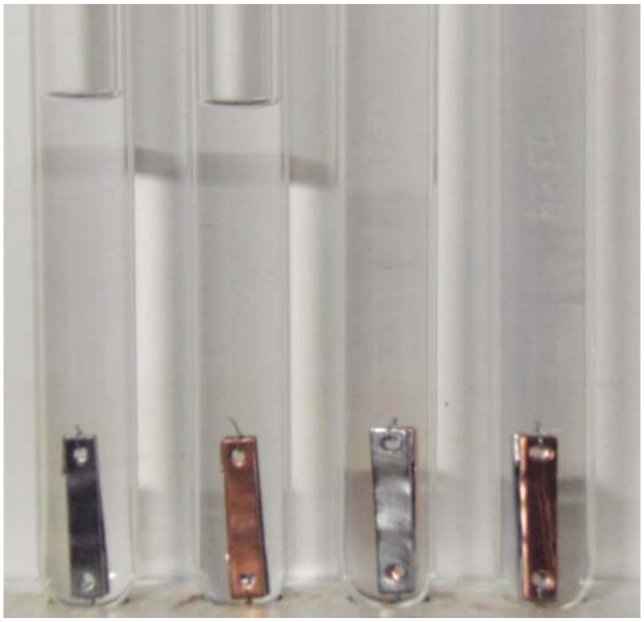
BEFORE AGING

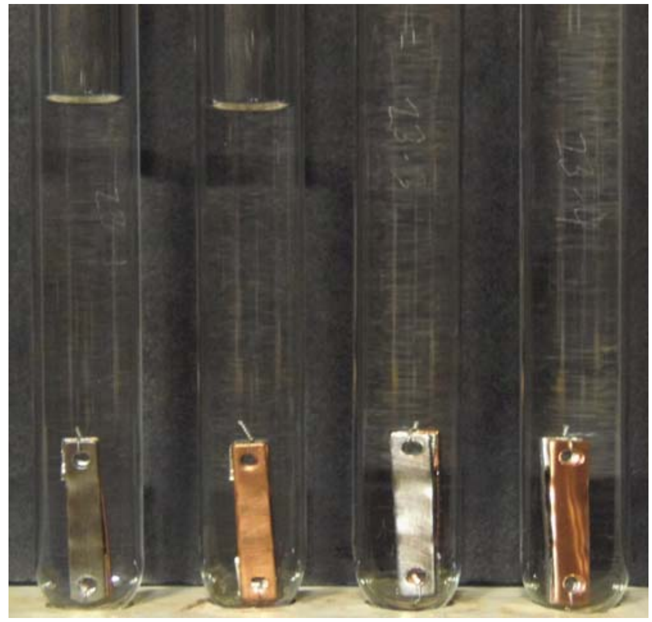


White background **Black background**

AFTER AGING

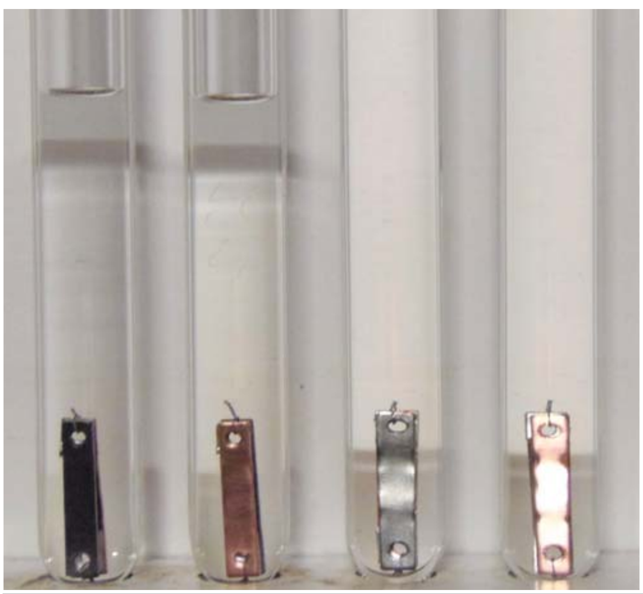
Figure 26: Photographs of Trimethyl Amine at 50 ppm in R-290/POE

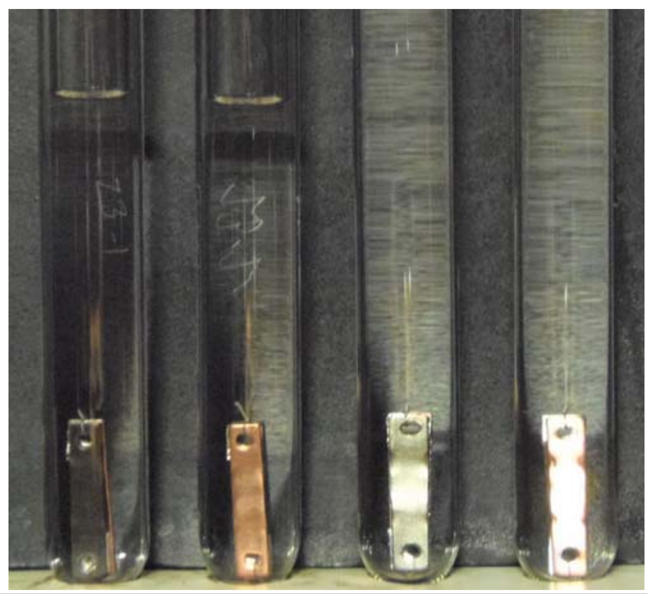




White background **Black background**

BEFORE AGING

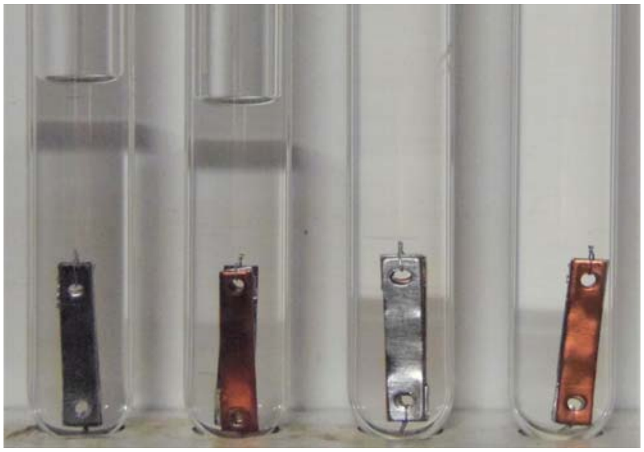
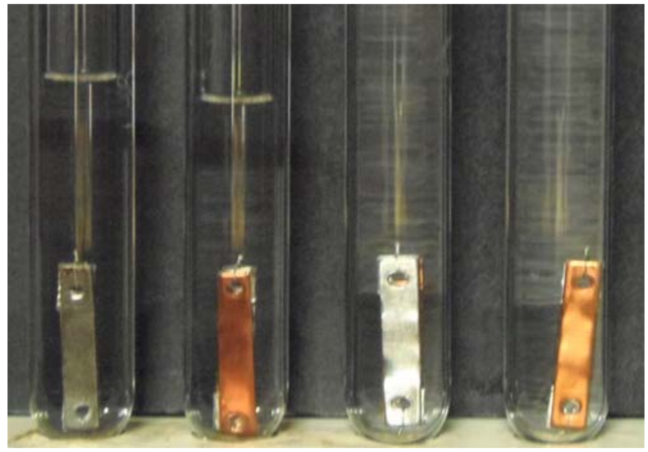




White background **Black background**

AFTER AGING

Figure 27: Photographs of R-290/POE (Control)

White background | Black background

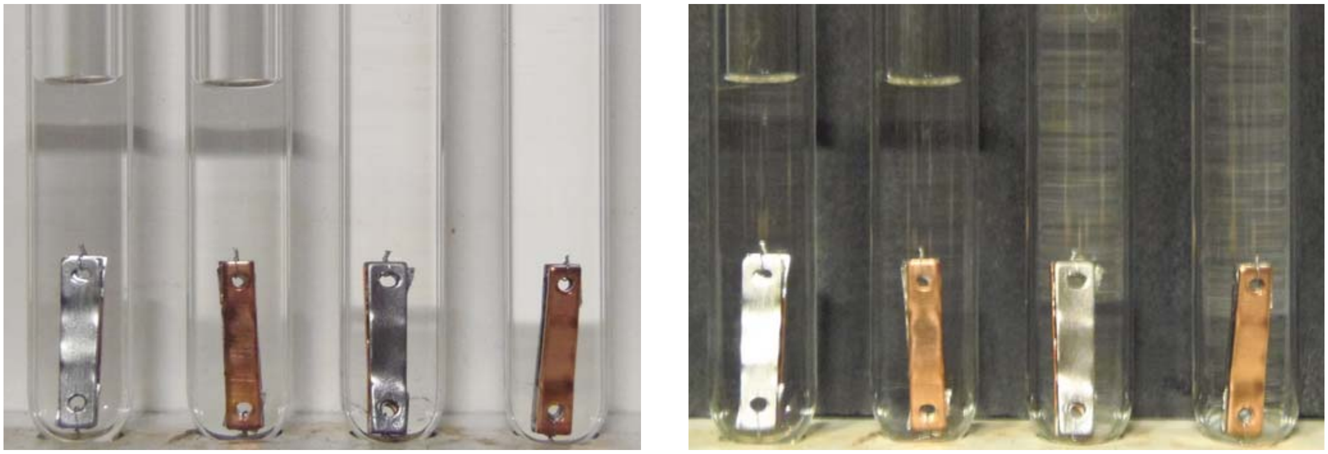
BEFORE AGING

White background | Black background

AFTER AGING

Figure 28: Photographs of Hydrogen Sulfide at 50 ppm in R-32/PVE



White background **Black background**

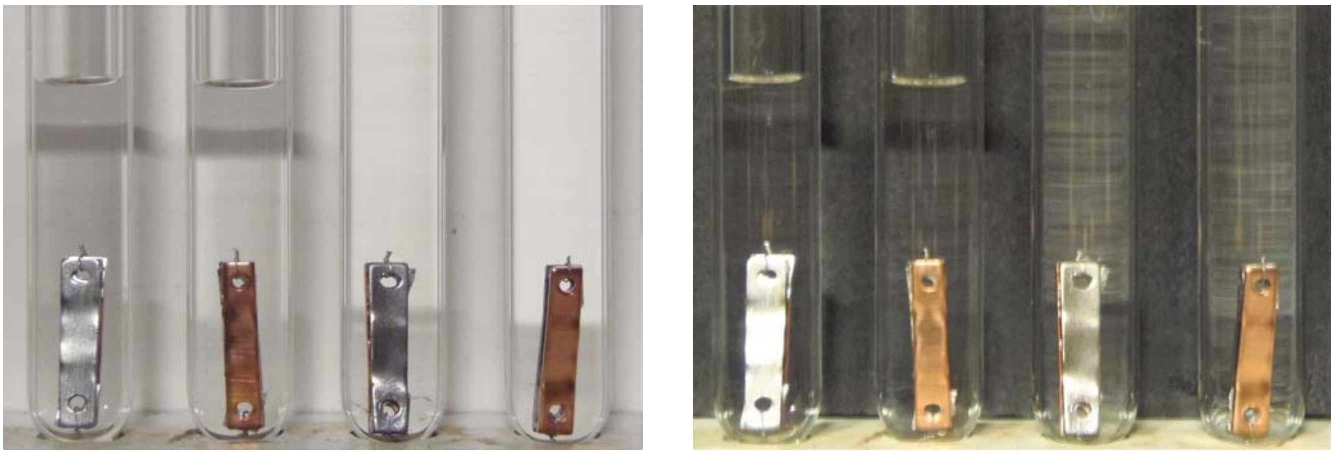
BEFORE AGING

White background **Black background**

AFTER AGING

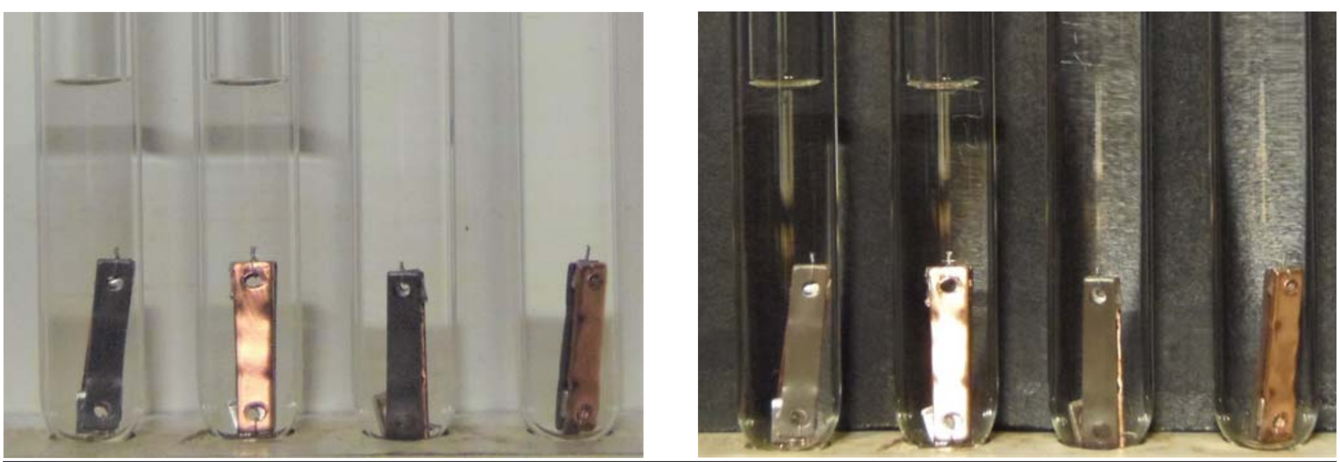
Figure 29: Photographs of Carbonyl Sulfide at 50 ppm in R-32/PVE

Note: One of the four sealed tubes broke during aging



White background **Black background**

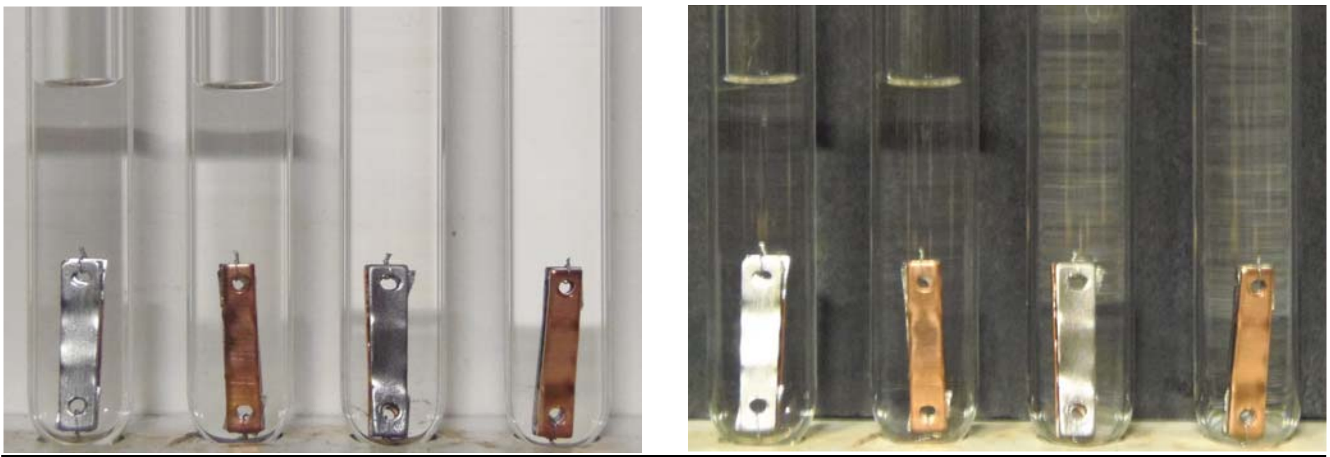
BEFORE AGING



White background **Black background**

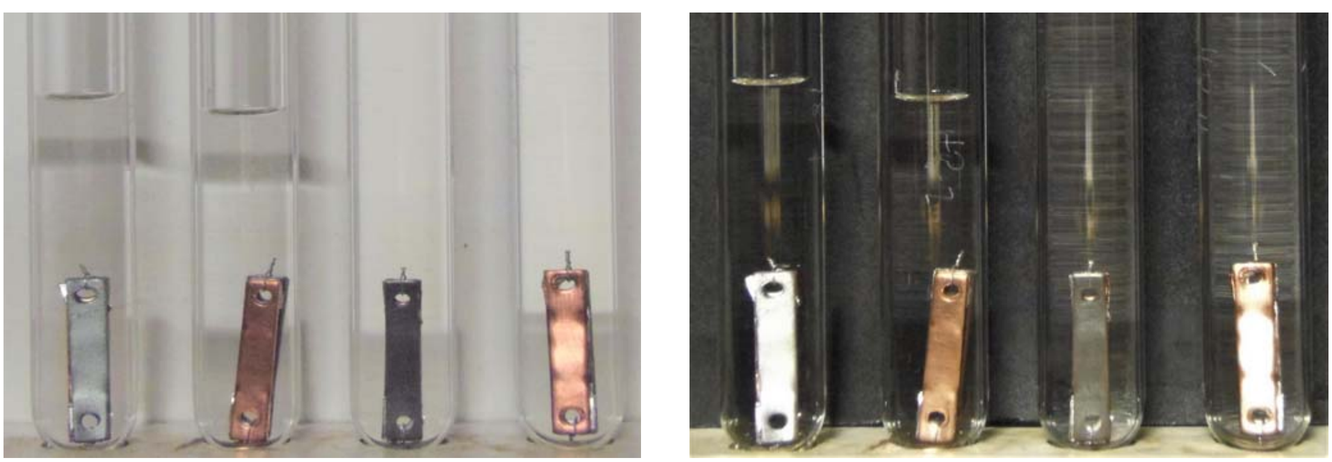
AFTER AGING

Figure 30: Photographs of Dimethyl Sulfide at 150 ppm in R-32/PVE



White background **Black background**

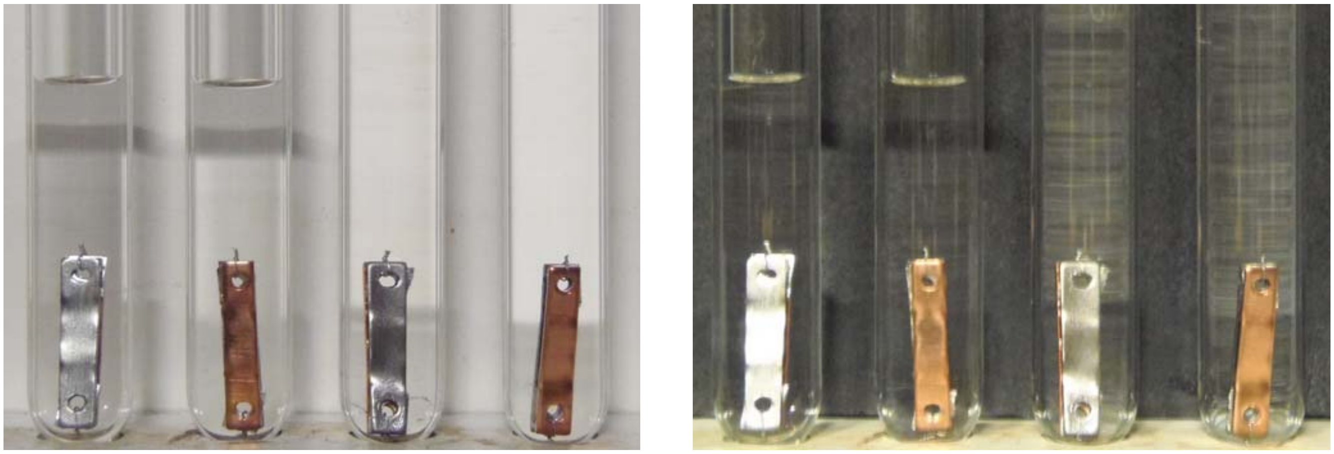
BEFORE AGING



White background **Black background**

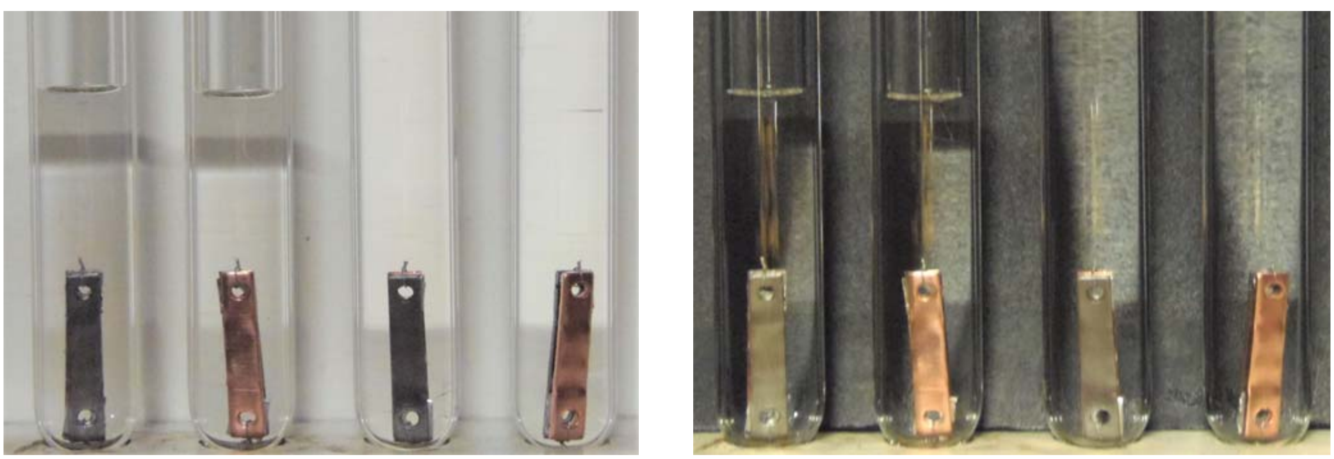
AFTER AGING

Figure 31: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-32/PVE



White background **Black background**

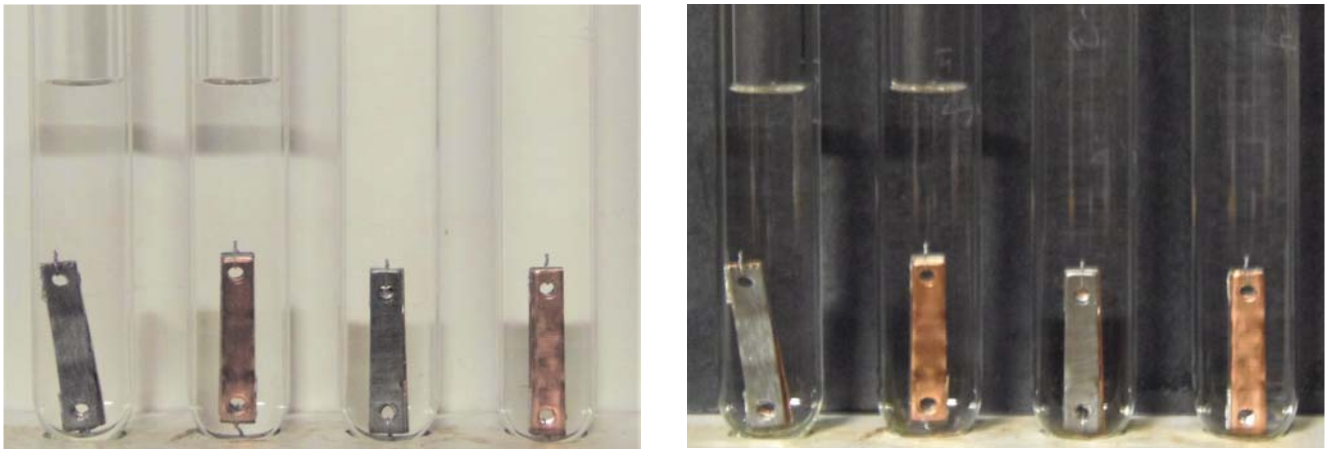
BEFORE AGING



White background **Black background**

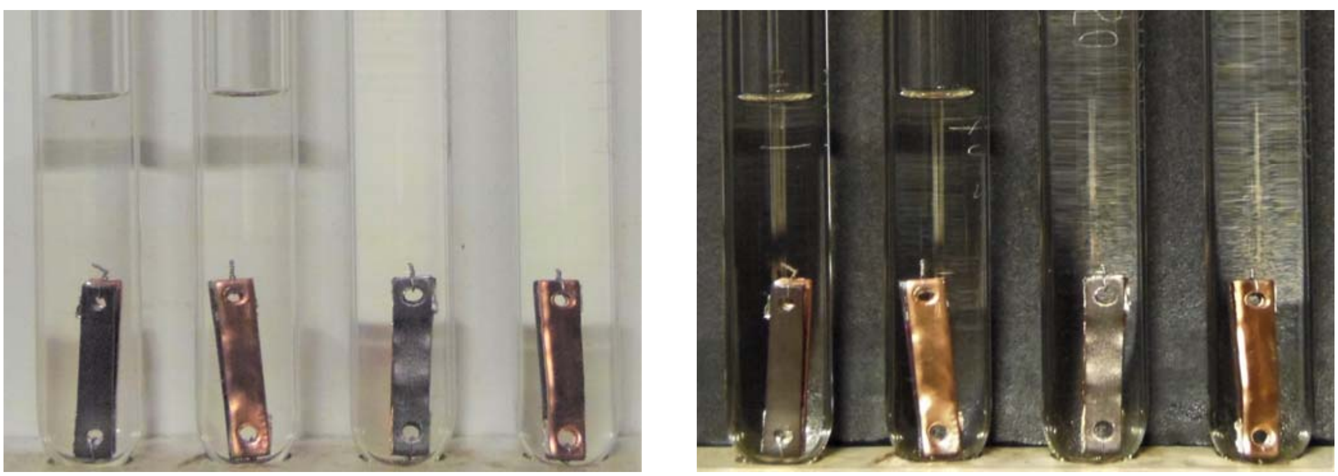
AFTER AGING

Figure 32: Photographs of R-32/PVE (Control)



White background **Black background**

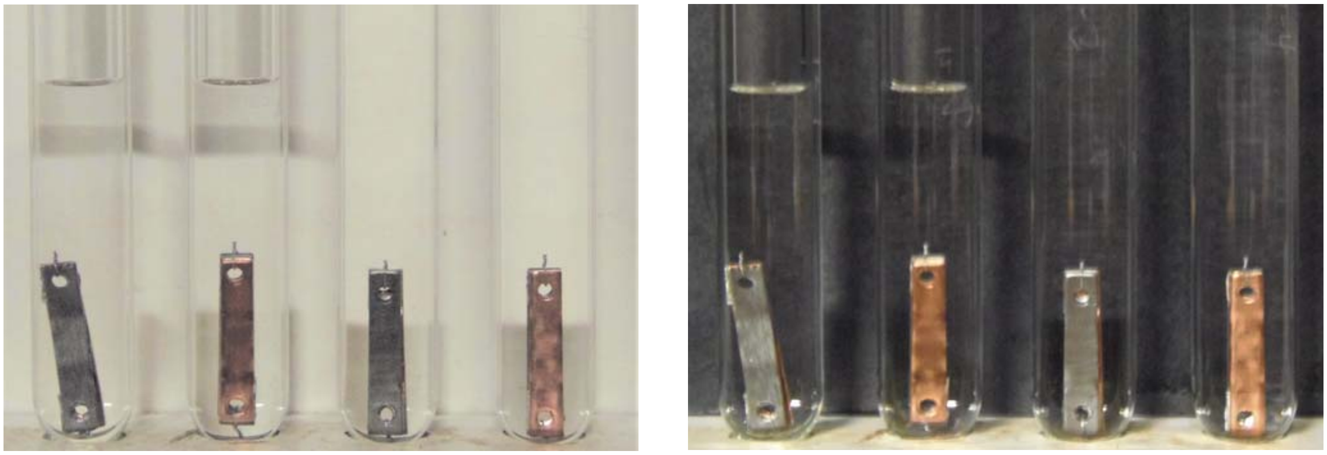
BEFORE AGING



White background **Black background**

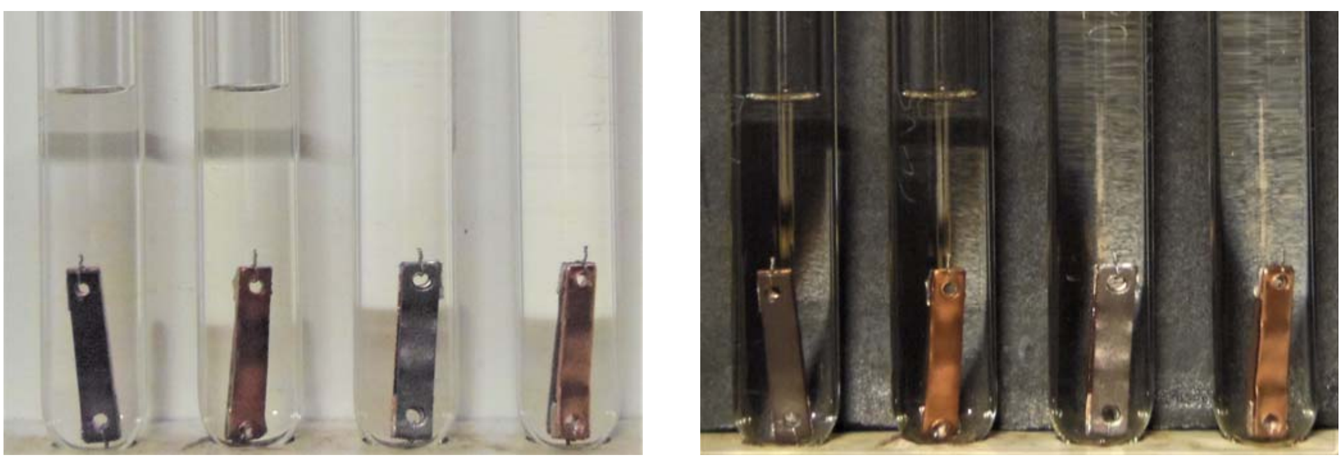
AFTER AGING

Figure 33: Photographs of Dimethyl Sulfide at 150 ppm in R-1234yf/PVE



White background **Black background**

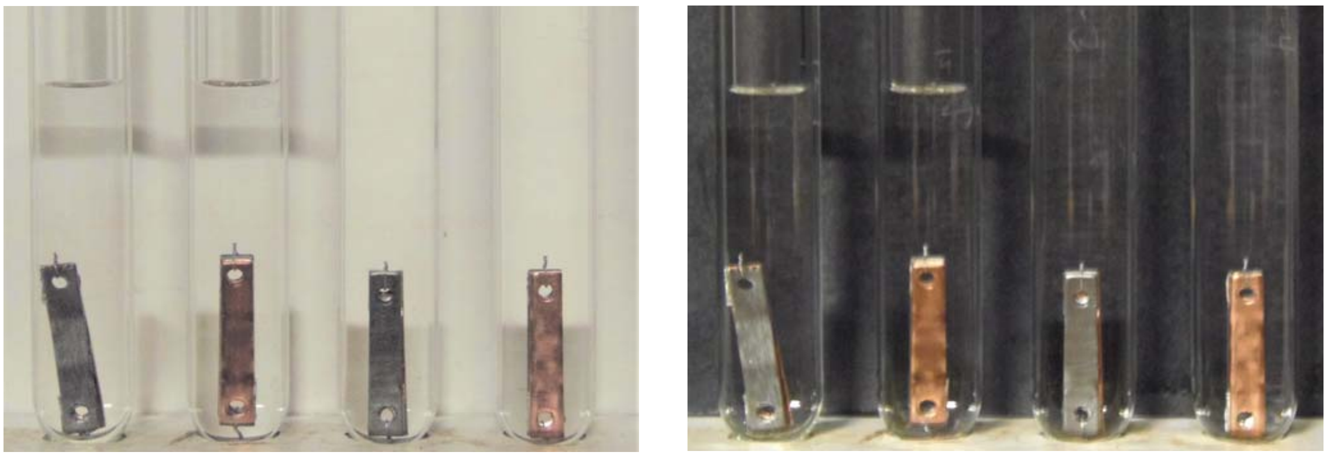
BEFORE AGING



White background **Black background**

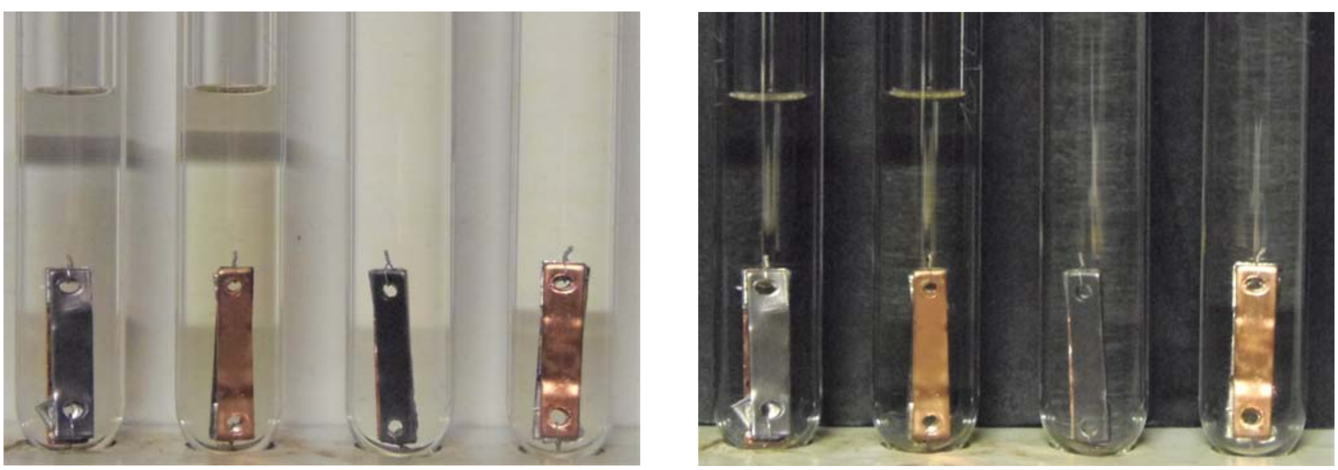
AFTER AGING

Figure 34: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-1234yf/PVE



White background **Black background**

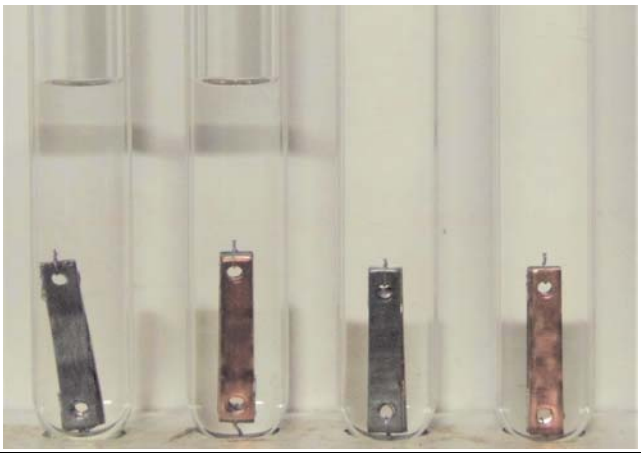
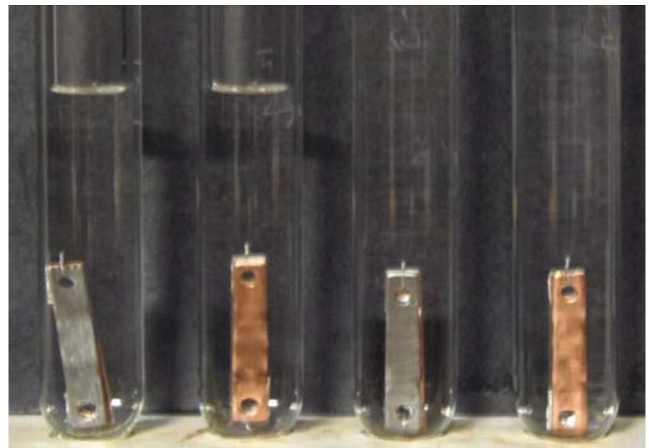
BEFORE AGING



White background **Black background**

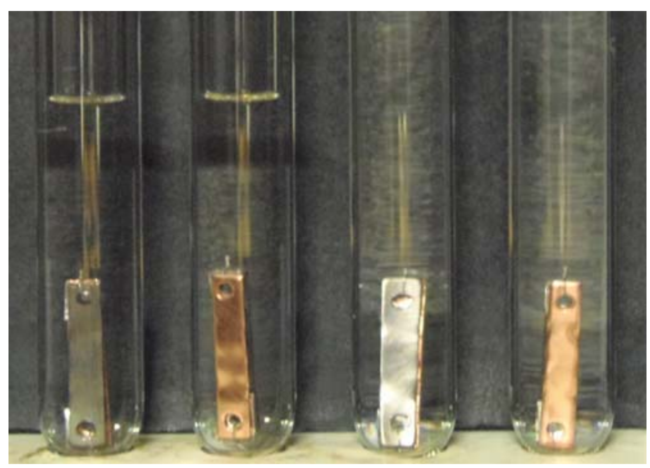
AFTER AGING

Figure 35: Photographs of Trimethyl Amine at 50 ppm in R-1234yf/PVE

White background **Black background**

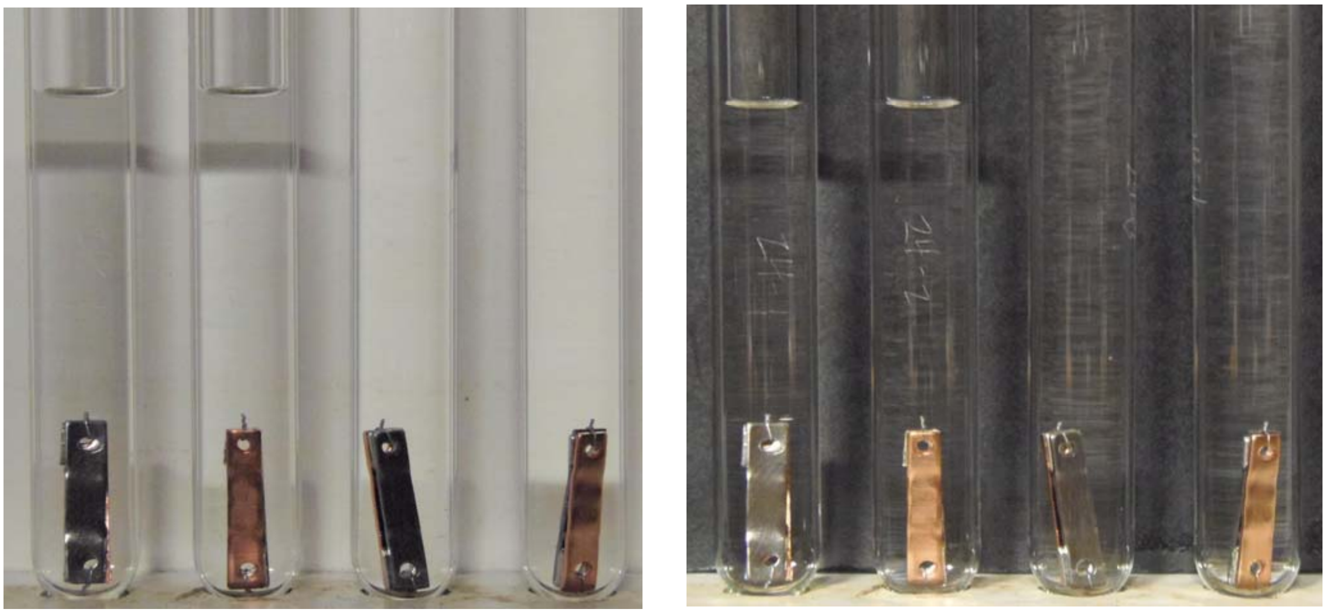
BEFORE AGING

White background **Black background**

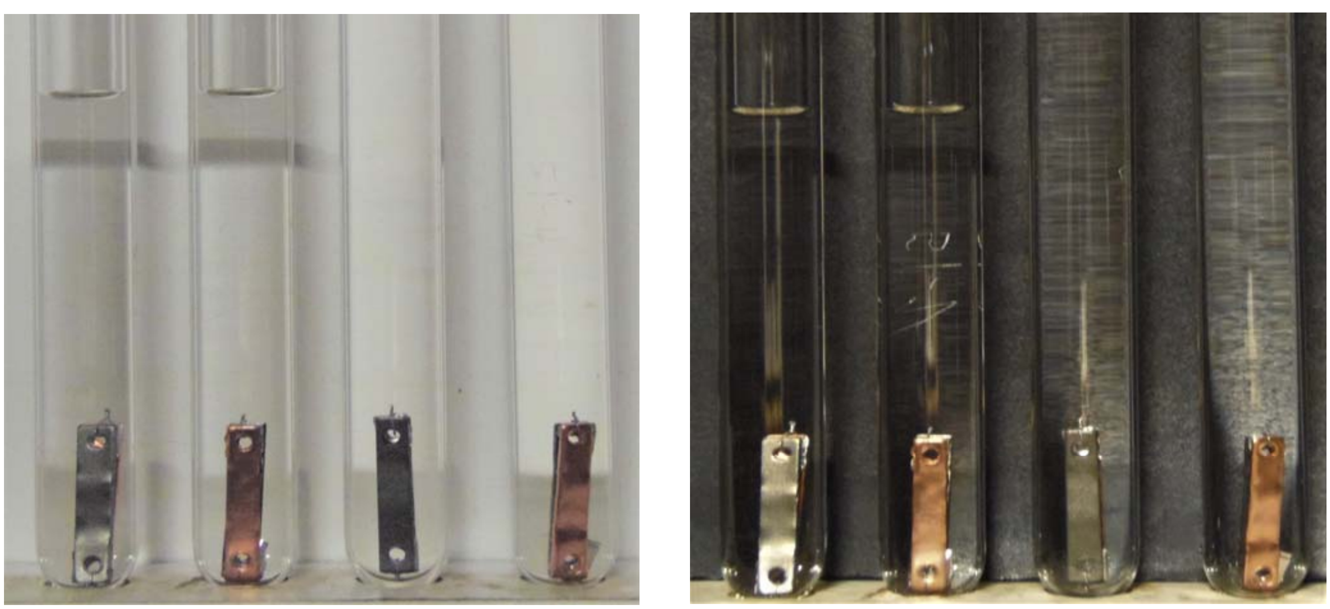
AFTER AGING

Figure 36: Photographs of R-1234yf/PVE (Control)



White background Black background

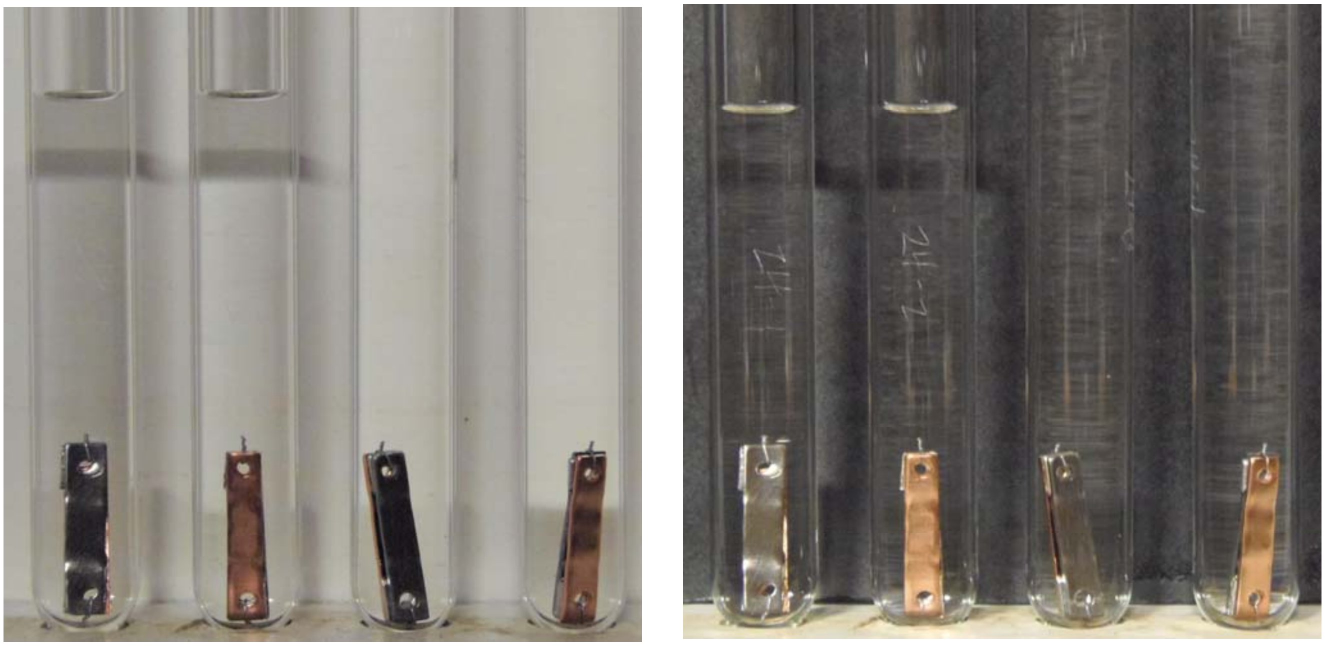
BEFORE AGING



White background Black background

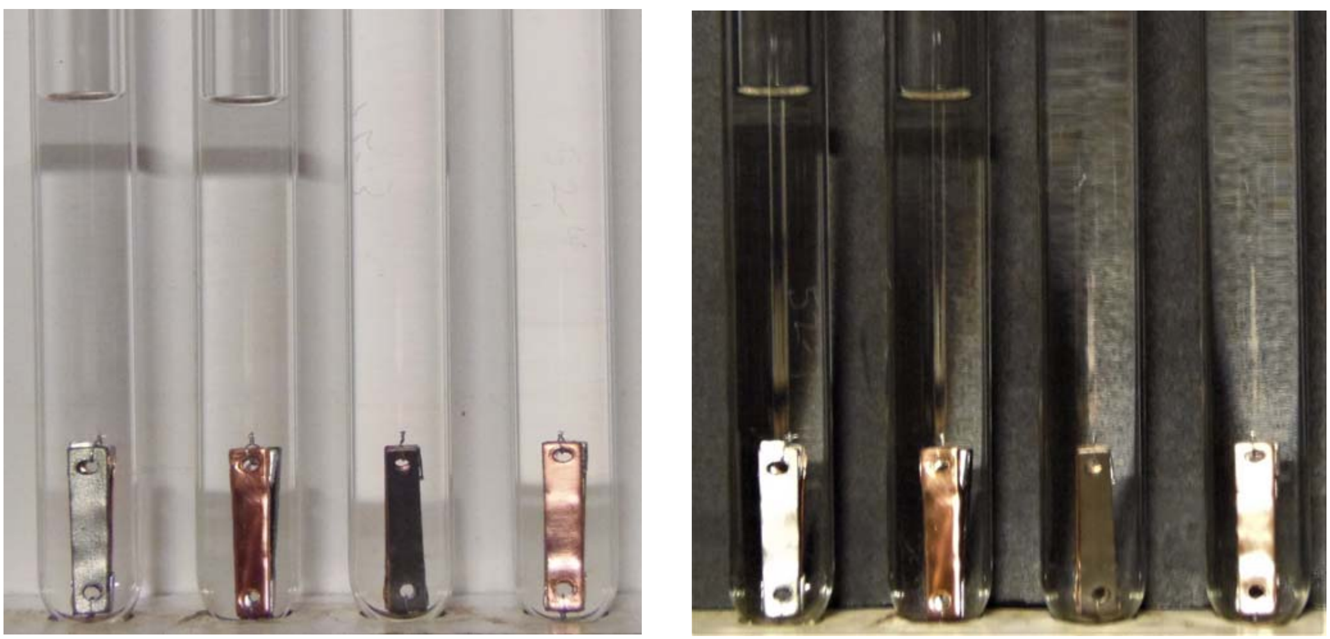
AFTER AGING

Figure 37: Photographs of Dimethyl Sulfide at 150 ppm in R-290/PVE



White background **Black background**

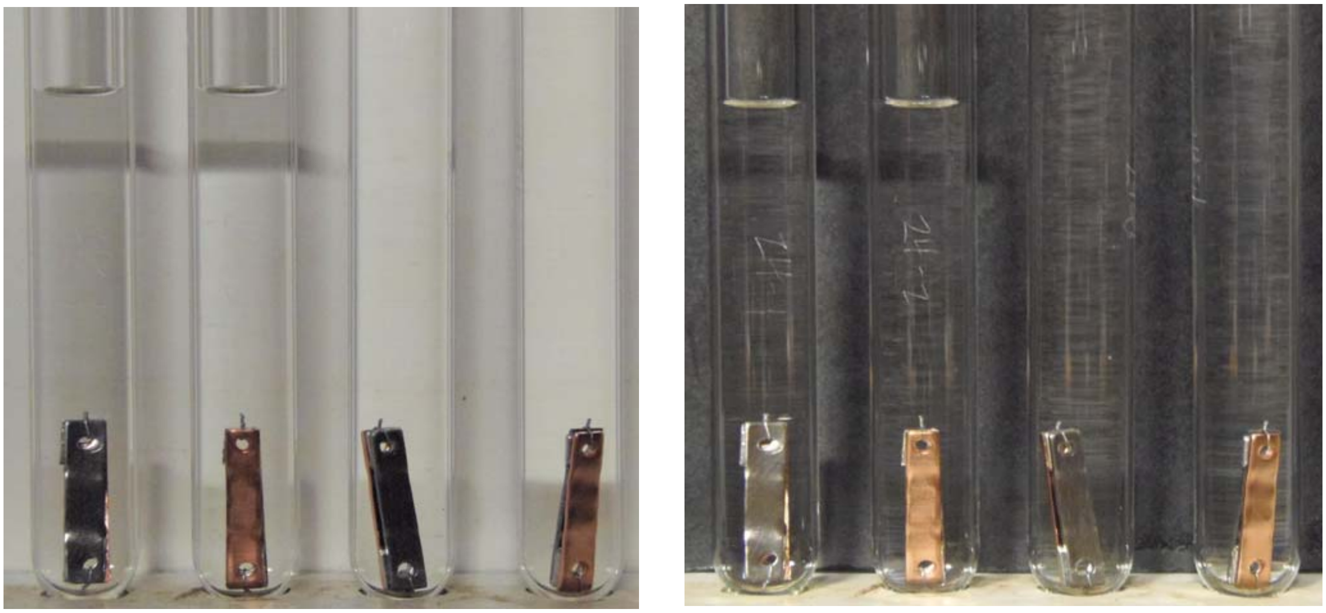
BEFORE AGING



White background **Black background**

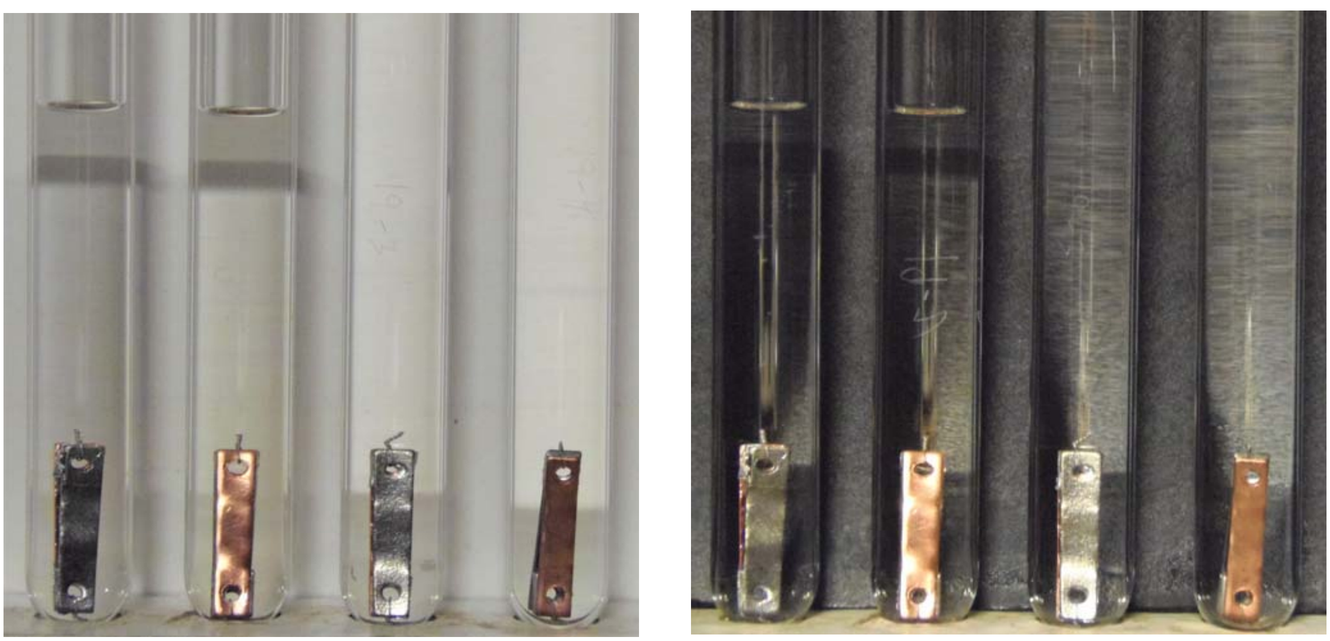
AFTER AGING

Figure 38: Photographs of Methyl Ethyl Sulfide at 150 ppm in R-290/PVE



White background **Black background**

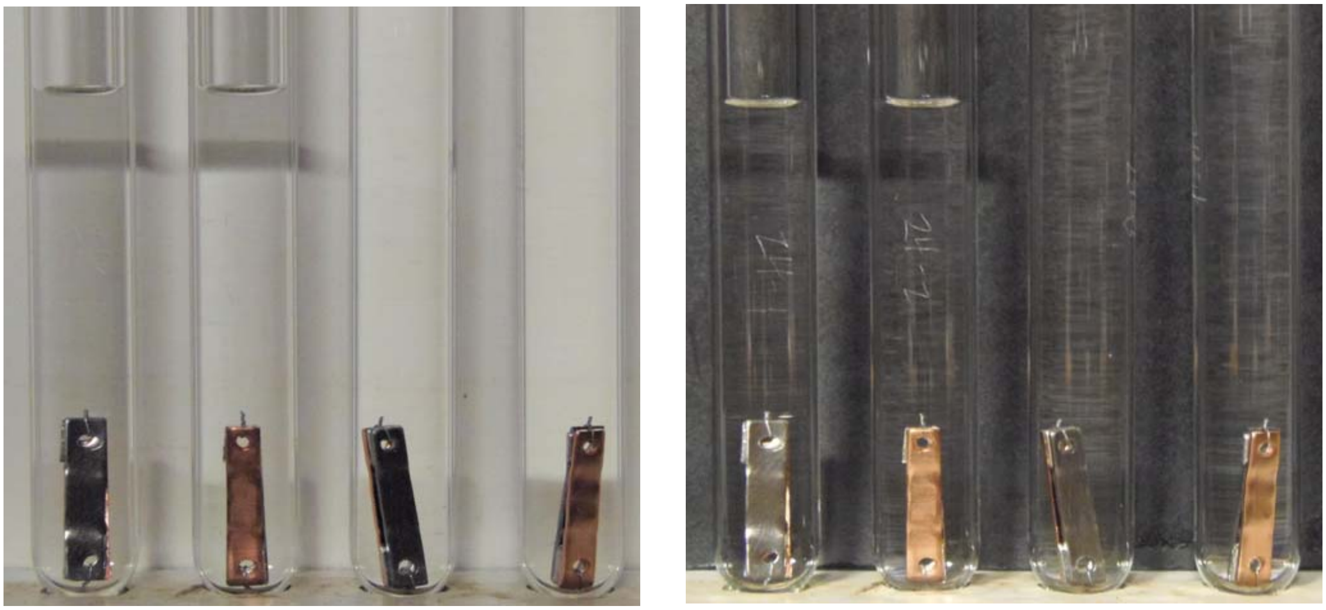
BEFORE AGING



White background **Black background**

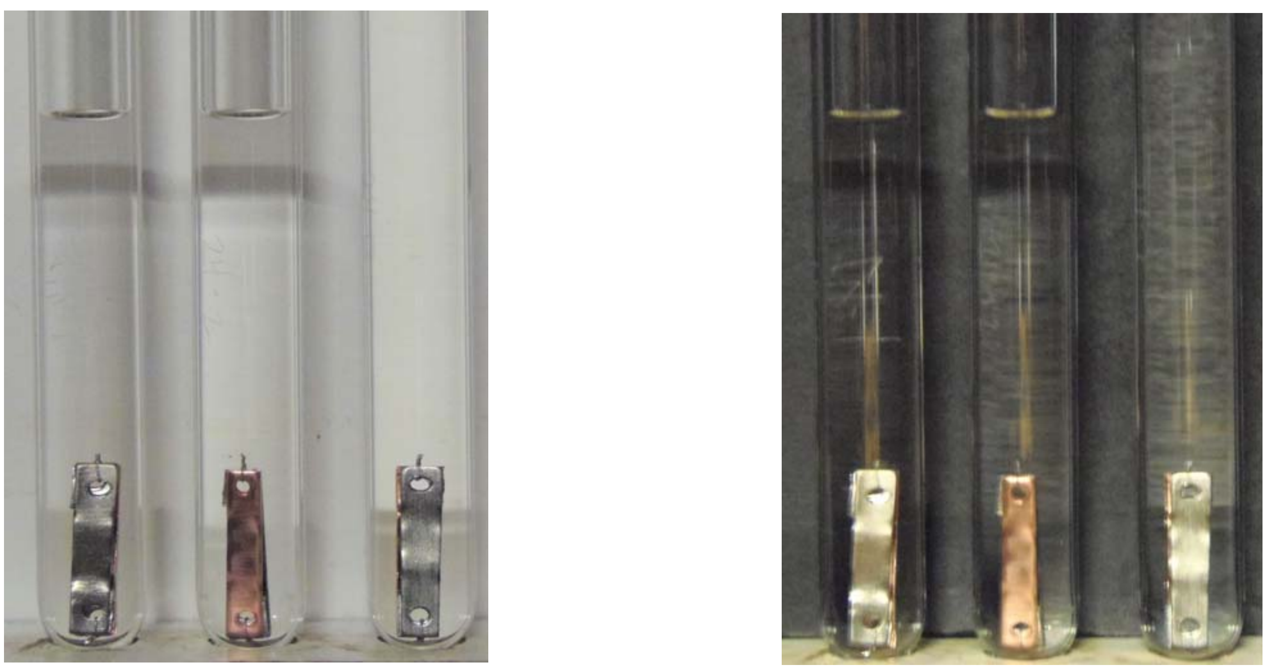
AFTER AGING

Figure 39: Photographs of Trimethyl Amine at 50 ppm in R-290/PVE



White background **Black background**

BEFORE AGING



White background **Black background**

AFTER AGING

Figure 40: Photographs of R-290/PVE (Control)
Note: One of the four sealed tubes broke during aging