

Partition Coefficient Calculation of Selected Terpenes and Low Molecular Weight Solvents Between Tall Oil Fatty Acid and Air and Polydimethyl Siloxane Oil and Air

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ABSTRACT: Headspace gas chromatography–mass spectrometry (GC–MS) has been applied to the analysis of the temperature-dependent tall oil fatty acid (TOFA)/air partition coefficient (k_1) and the polydimethyl siloxane oil/air partition coefficient (k_2) of selected terpenes and low molecular weight solvents. As expected, both the TOFA and the silicone oil are effective trapping media for the nonpolar terpenes, but they are also efficient traps for acetone, methanol, *n*-propanol, and *n*-butanol. However, several species of low and moderate molecular weight (less than 150 amu) aldehydes, ketones, and organic acids that might adversely affect its trapping capacity were detected in the TOFA. This article will report the empirically gathered data and the subsequent calculation of the partition coefficients for the terpenes: α - and β -pinene, limonene, and α -terpineol and the solvents: acetone, methanol, *n*-propanol, and *n*-butanol between 50 and 130°C.

Paper no. J9228 in *JAOCs* 77, 163–169 (February 2000).

KEY WORDS: Partition coefficient, partitioning, α -pinene, β -pinene, silicone oil, solvents, tall oil fatty acid, terpenes, TOFA.

For several years industry has been engaged in efforts to reduce the emission of volatile organic compounds (VOC) from exhaust stacks at both plant and research facility sites. In the forest products industry, the reduction of stack-released terpenes, particularly the mono-terpene α -pinene, from pine mill operations has required the installation of expensive, nonproductive, regenerative thermal oxidizers and electrostatic precipitators. The development of a more cost-effective means of reducing, either selectively or totally, VOC content from pine mill exhaust stacks would have a significant impact on the cost of manufacturing. Because terpenes in general are nonpolar, a method for removing them from the exhaust stream by using a clean, high-boiling, viscous oil was considered. This paper reports on the initial investigation of the partitioning of several select monoterpenes and low molecular weight alcohols in tall oil fatty acid (TOFA) and silicone oil media.

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Hydrocarbon oils solubilize nonpolar compounds, but the vapor pressure and flammability of most prohibit their use as VOC traps in hot turbulent systems such as a wood dryer exhaust stack. TOFA fractions extracted from pine trees have extremely low vapor pressures and a moderately high usable temperature range (<250°C) (1). Silicone oils also have extremely low vapor pressures and reasonably high usable temperature ranges (typically >250°C) (2). The latter property is evident in its use as the oil of choice for melting point apparatus. Both silicone oil and tall oil solubilize many nonpolar and some moderately polar compounds.

One measure of a compound's ability to trap and hold (solubilize) another compound is its partition function. The partition coefficient (k) describes the equilibrium distribution of the analyte between dissimilar phases (3). Most commonly, this property is used in chromatographic techniques to effect the separation of components in a complex mixture (4).

The partition coefficient is the proportionality constant between the concentration of component A in phase a and component A in phase b at constant temperature and pressure, or

$$k = \frac{[A]_a}{[A]_b} \quad [1]$$

Typically, k is found empirically since the partitioning effect is dependent on several thermodynamic properties including pressure, temperature, viscosity of both phases, molecular polarity, and molecular interactions. Tabulations of k for several compounds, including some terpenes, can readily be found in the bioscience literature but are primarily for the water/air interface (5). In this article, $[A]_a$ will refer to $[A]_m$, the liquid matrix phase, and $[A]_b$ will refer to $[A]_g$, the gas phase.

Headspace gas chromatography–mass spectrometry (GC–MS) sampling is a practical technique for collecting data required to calculate partition coefficients. In controlling both temperature and volume, headspace sampling provides a mechanism for the calculation of k for quantitative analysis. In order to evaluate $[A]_g$, a set of standards can be made in the headspace vial utilizing a full evaporative technique (FET) (6). In FET, the response attributable to a known quantity of totally evaporated solute is measured *via* the constant volume vial (22 mL) and GC–MS. By measurement of different quantitative levels, an external standard calibration curve can be

constructed. The sample preparation is critical in that both the volume of the headspace and the volume of the liquid matrix must be known.

In the calculation of k from a set of standards, the concentration of the analyte in the liquid matrix, $[A]_m$, does not need to be known. Since the total molar quantity of analyte is known in the standard $[A]_o$, and $[A]_g$ can be directly calculated from the external calibration curve, $[A]_m$ can be calculated by rearranging the volume-adjusted concentration equation (7),

$$[A]_o V_o = [A]_m V_m + [A]_g V_g \quad [2]$$

At temperatures less than the boiling point of the liquid matrix, the volume of the original sample (V_o) will be very nearly the volume of the thermally equilibrated matrix (V_m). At thermal equilibrium, Equation 2 may be rewritten as

$$k = \frac{[A]_o}{[A]_g} - \frac{V_g}{V_m} \quad [3]$$

The original concentration in solution $[A]_o$ is typically the targeted quantity in unknowns. Since $V_o = V_m$ for many matrices and $[A]_g$ can typically be measured directly, Equation 3 can be used to solve for $[A]_o$. If solving for analyte concentration $[A]_g$ in the gas phase once k is known can be accomplished by rearranging Equation 3 to the following equation (8):

$$[A]_g = \frac{[A]_o}{k + (V_g/V_m)} \quad [4]$$

where $[A]_o$ = total concentration of analyte, $[A]_g$ = concentration of analyte in the gas phase, V_m = volume of liquid matrix, V_g = volume of gas, k = partition coefficient.

The partitioning of selected terpenes and low molecular weight alcohols in both TOFA and silicone oil was investigated. Previous investigations of the liquid/air partition coefficients of several terpenes had been reported for human blood, olive oil, and water at 37°C as a means of quantifying the percutaneous uptake of terpenes in man (9). The goal of the present project was to better understand the behavior of the selected terpenes and low molecular weight alcohols in an absorbing system and under controllable laboratory conditions.

EXPERIMENTAL PROCEDURES

A Hewlett-Packard 5971A gas chromatograph–mass spectrometer (Palo Alto, CA) with a Tekmar 7000 (Cincinnati, OH) headspace autosampler input was used to acquire the reported data. A temperature equilibration time of 20 min per sample was used at each analysis temperature. Vial pressure varied between 25 and 75 kPa above ambient pressure depending on the analysis temperature. Valve and transfer line temperatures were held at 185 and 200°C, respectively, and the helium carrier gas sweeping the sample into the gas chromatograph was 40 mL/min. The headspace gas injection volume was 1.0 mL.

The chromatographic separations were performed using a 30 m, 0.25 mm i.d., HP Innowax column (Hewlett-Packard) having a 0.5 μ m film thickness. The temperature program consisted of an initial oven temperature of 50°C, which was held for 3 min. After the 3-min hold time, the temperature was ramped at 15°C/min to 180°C and held for 1.0 min. A short column bake-out consisted of a 30°C/min temperature ramp to 250°C with a hold time of 1.0 min. A constant carrier gas flow was employed and held at 0.50 mL/min (25.6 cm/s).

TOFA. The headspace gases of a stock solution (Table 1, TOFA) of acetone (cat.# GC230-4, 99.9%; Burdick & Jackson, Muskegon, MI), methanol (cat.# GC010-4, 99.9%; Burdick & Jackson), *n*-propanol (cat.# 322-1, 99.5%; Burdick & Jackson), *n*-butanol (cat.# A383, 99.9%; Fisher, Pittsburgh, PA), α -pinene (cat.# 27,439-9, 99%; Aldrich, Milwaukee, WI), β -pinene (cat.# 11,208-9, 99 %; Aldrich), limonene (cat.# 18,316, 97%; Aldrich), and α -terpineol (cat.# 21,837-5, 98%; Aldrich) in TOFA (XTOL-100; Georgia-Pacific Resins Inc., Atlanta, GA) were sampled at 50, 70, 90, 110, 130, and 150°C. Three replicate samples were taken at each temperature.

Samples were prepared as follows: 5.00 mL (4.4305 g, density = 0.8861 g/mL) of the TOFA stock solution was added to each of 18 headspace vials. The total volume of each empty headspace vial was 22.00 \pm 0.01 mL capped.

Silicone oil. The headspace gases of a stock solution (Table 1, silicone oil) of acetone, methanol, *n*-butanol, α -pinene, β -pinene, limonene, and α -terpineol in silicone oil (Aldrich # 14-615-3, cas. # [63148-62-9]) were sampled at 50, 70, 90, 110, and 130°C. Four replicate samples were taken at each temperature.

Samples were prepared as follows: 5.00 mL (4.8171 g, density = 0.963 g/mL) of silicone oil stock solution (Table 1) was added to each of 20 headspace vials. The total volume of each empty headspace vial was 22.00 \pm 0.01 mL capped.

Standards were prepared as follows: Two or three levels of standards were prepared from a stock standard solution (Tables 2 and 3) made up with the appropriate analytes in diethyl ether. The concentrations of both the liquid stock standard solution and the prepared FET standards used to construct the calibration curve are listed in Tables 2 and 3.

TABLE 1
Analyte Concentrations for Tall Oil Fatty Acids (TOFA) and Silicone Oil

Analyte	TOFA (μ g/mL)	Silicone oil (μ g/mL)
Acetone	229	199
Methanol	219	234
<i>n</i> -Propanol	159	NA ^a
<i>n</i> -Butanol	170	240
α -Pinene	216	244
β -Pinene	245	255
Limonene	265	276
α -Terpineol	242	286

^aNA, not analyzed.

TABLE 2
Full Evaporative Technique (FET) Standard for TOFA Experiment^a

Analyte	Stock solution ($\mu\text{g/mL}$)	FET high ($\mu\text{g/mL}$)	FET low ($\mu\text{g/mL}$)
Acetone	94,924	8.63	2.16
Methanol	107,100	9.74	2.43
<i>n</i> -Propanol	106,061	9.65	2.41
<i>n</i> -Butanol	103,471	9.41	2.35
α -Pinene	96,555	8.78	2.20
β -Pinene	98,291	8.94	2.23
Limonene	121,316	11.03	2.76
α -Terpineol	103,056	9.37	2.34

^aFor abbreviation see Table 1.

TABLE 3
FET Full Standard for Silicone Oil Experiment^a

Analyte	Stock high ($\mu\text{g/mL}$)	FET high ($\mu\text{g/mL}$)	FET medium ($\mu\text{g/mL}$)	FET low ($\mu\text{g/mL}$)
Acetone	3090	15.5	3.10	0.62
Methanol	3410	14.0	2.81	0.56
<i>n</i> -Butanol	2820	12.8	2.56	0.51
α -Pinene	3360	15.3	3.06	0.61
β -Pinene	2600	11.8	2.37	0.47
Limonene	3620	16.5	3.29	0.66
α -Terpineol	3630	16.5	3.30	0.66

^aFor abbreviation see Table 2.

The calibration curves used in this study were constructed by averaging the response of four replicate injections of only the FET standards (far right columns in Tables 2 and 3).

Calculation of $[A]_g$ was made by direct correlation to the FET calibration curve, and $[A]_m$ was obtained by the rearrangement of Equation 2. Calculation of k was made using Equation 3. The relative standard deviation of the data for each temperature (three replicates for the TOFA experiment and four replicates for the silicone oil experiment) was less than 5.0% in all cases. Data were collected from 2.0 to 20.0 min. The 2-min delay was to avoid acquiring data during the air peak elution occurring at 1.6 min after injection. Void volume was noted at approximately 1.45 min.

RESULTS AND DISCUSSION

The eight compounds of interest, displayed in Figure 1, eluted as acetone ($t_R = 2.9$ min), methanol ($t_R = 3.9$ min), α -pinene ($t_R = 5.7$ min), *n*-propanol ($t_R = 5.9$ min), β -pinene ($t_R = 7.0$ min), *n*-butanol ($t_R = 7.4$ min), limonene ($t_R = 8.2$ min), and α -terpineol ($t_R = 13.3$ min). The tabulated data are listed in Tables 4, 5, and 6, and the plotted partition coefficient data with respect to temperatures between 50 and 150°C are exhibited in Figures 2, 3, 4, and 5.

Because the data reported in this paper were collected under the static conditions of the headspace oven and not under the dynamic environment of an exhaust stream, the reported partition coefficients (k) will be subject to the conditions of the experiment. However, the magnitude of the value should be an indication of the trapping efficiency over a range of experimental conditions (i.e., changes in pressure, viscosity, etc.). These would include those experienced in typical VOC emission sources since the intrinsic qualities of the oil that promote its capacity to trap compounds will be relatively unchanged. The large k values calculated for the various terpenes in the static headspace environment should also be relatively large under the dynamic conditions of a VOC emission source. Likewise, small headspace k values should also be reflected by small emission calculated k values. The implication is that the k values reported in this paper should be valid data that can be used to predict the trapping capacity of TOFA and/or silicone oil in the dynamic environments of VOC emission sources. Data acquisition was identical for both the TOFA and the silicone oil experiments. It should be noted that the reported k values are strictly thermodynamic in nature and do not reflect any kinetic behavior.

TOFA. To establish a baseline from which the TOFA partition coefficients of the analytes of interest could be calculated, two high-temperature blanks (air and TOFA) were run at an equilibrium temperature of 170°C (same temperature at which the TOFA FET data were acquired). During the data collection phase, other oil blanks were collected at all analysis temperatures except 50°C. Several species of aldehydes, ketones, and organic acids were detected in the TOFA blanks.

TABLE 4
TOFA Oil/Air Interface Partition Coefficient for Selected Compounds^a

Compounds	Ret. time (min)	k @ 50°C ($\times 10^2$)	k @ 70°C ($\times 10^2$)	k @ 90°C ($\times 10^2$)	k @ 110°C ($\times 10^2$)	k @ 130°C ($\times 10^2$)	k @ 150°C ($\times 10^2$)
Acetone	2.9	1.14	0.634	0.431	0.265	0.186	0.156
Methanol	3.9	1.12	0.553	0.348	0.223	0.174	0.163
α -Pinene	5.7	30.9	12.4	6.32	3.11	1.57	1.01
<i>n</i> -Propanol	5.9	5.25	2.17	1.13	0.606	0.383	0.320
β -Pinene	7.0	34.9	17.9	8.81	4.50	2.30	1.51
<i>n</i> -Butanol	7.4	11.3	4.83	2.43	1.29	0.744	0.555
Limonene	8.2	75.7	29.4	12.6	6.04	2.90	1.74
α -Terpineol	13.3	161	145	145	51.7	19.0	10.5

^aThe data are background-corrected at all temperatures and reported as the mean of three replicates. The relative standard deviation was less than $\pm 5\%$ in all cases. Ret. time, retention time; for other abbreviation see Table 1.

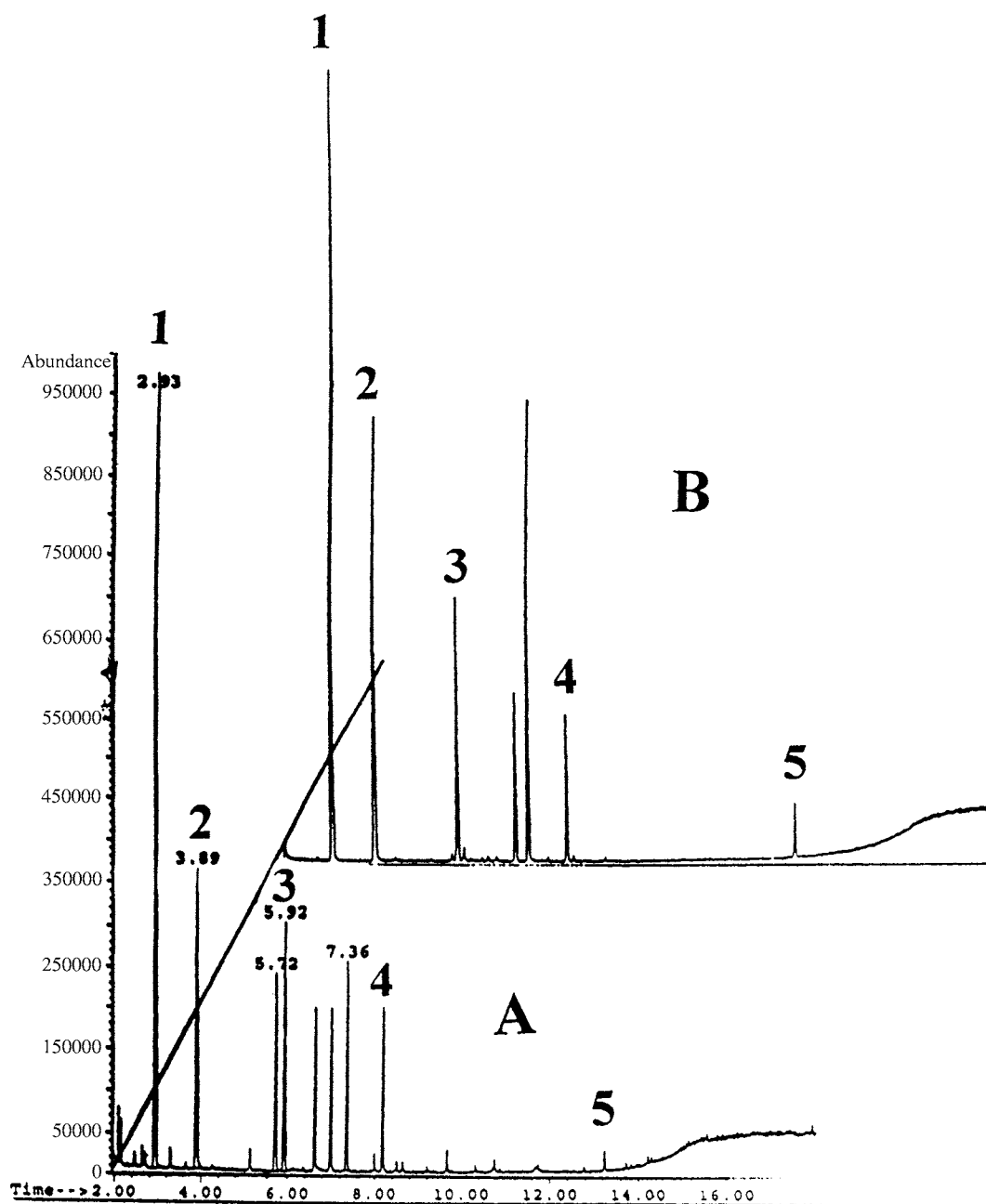


FIG. 1. (A) Representative gas chromatogram of a tall oil fatty acid (TOFA) sample at $T = 130^{\circ}\text{C}$; (B) representative silicone oil sample at $T = 90^{\circ}\text{C}$. (Ion abundance vs. time in minutes.)

These compounds are the result of oxidative fragmentation of specific unsaturated acids in the TOFA that occurred during the fractionation process at the time of manufacture. A tabulation of the identified species including their estimated quantities is listed in Table 5. When a compound of interest was detected in the blank, the concentration found in the blank was subtracted prior to the calculation of the partition coefficient. These calculations were done on the gas phase data. The error in this estimation is discussed later.

Carryover of α -terpineol was found to exist at both 110 and 130°C in the silicone oil experiments, but was not mea-

surable at the higher analysis temperatures in the TOFA experiments. Continual partitioning of α -terpineol probably occurred throughout the headspace valve and GC transfer line at all analysis temperatures but was not detected. It should be noted that the boiling point temperature was exceeded for all pertinent compounds in the valve and transfer areas of the headspace system except for α -terpineol. Owing to the relative inertness of the transfer system and to previous experimentation it is suggested that continual partitioning effects would be negligible for the compounds of interest.

Silicone oil. Figure 1B is the GC-MS total ion count chro-

TABLE 5
Detected Compounds in TOFA^a Blanks^b

Identified species	Quantification based on	Ret. time (min)	<i>k</i> @ 150°C	Est. [<i>A_m</i>] (μg/mL)	Est. [<i>A_o</i>] (μg/mL)
Heptane	α-Pinene	2.1	101	50	52
Acetaldehyde	Acetone	2.5	16	5	6
Octane	α-Pinene	3.3	101	26	27
Propanal	Acetone	3.8	15	2	2
Acetone		3	15	7	8
Methanol		3.9	16	2	2
Pentanal	α-Pinene	5.2	101	22	23
hexanal	α-Pinene	6.7	101	123	127
<i>n</i> -butanol		7.4	54	4	5
2-Pentyl furan	α-Pinene)	8.5	101	18	19
Pentanol	Limonene	8.7	174	24	25
Octanal	Limonene	9.2	174	10	11
2-Heptenal	Limonene	9.7	174	26	27
Nonanal	Limonene	10.3	174	16	16
Acetic acid	Limonene	11.2	174	23	23
Decanal	Limonene	12.76	174	16	16

^aTOFA XTOL (Georgia-Pacific Resins Inc., Atlanta, GA).^b[*A_m*], concentration of analyte in the liquid matrix; [*A_o*], concentration of analyte in the standard. For abbreviations see Tables 1 and 4.

matogram displaying the response of the silicone oil test solution mix at the experimental temperature of 90°C. Air and silicone oil blanks were taken prior to the start of the sample data collection. The equilibrium temperature for the blank acquisition was set at 180°C, the same temperature at which the silicone oil FET data were acquired, in order to establish a baseline of volatile components present as contaminants. Acetaldehyde and acetic acid were detected in the air blank. Oil blank data were also collected at 90 and 130°C. As was previously mentioned, carryover of α-terpineol was detected at both 110 and 130°C. This was not surprising since the headspace syringe valve and GC transfer temperatures were set at their usable maximum, which was 40°C less than the boiling point of α-terpineol. This allowed continual partitioning to occur throughout the headspace valve and GC transfer line at all the analysis temperatures but was only detected at the elevated temperature experiments. The error introduced by this partitioning effect was only partially corrected by averaging the carryover concentration and subtracting it from the [*A*]_g

calculation for each temperature. The error introduced by this partitioning effect may be significant, but at this time its extent is unknown.

As expected, the data exhibit a nonlinear decay of the partition coefficient as the temperature increases for all compounds of interest and in all cases. The data also suggest that a practical limit at which these oils might be used as VOC trapping agents would not be much greater than the upper analysis temperature of 150°C for acetone and the alcohols. It is probably no greater than 200°C for the terpenes. Because the oils are essentially nonpolar, it is not surprising that the calculated partition coefficients are inversely proportional to the polarity of the species analyzed. The substantially increased capacity of TOFA as compared to silicone oil for the compounds tested was unexpected, but was demonstrated in every case for comparable quantities of oils. This is particularly evident for limonene and α-terpineol where the coefficients for limonene differed approximately 10:1 and progressively increased for α-terpineol from 8:1 at temperatures 50, 70, and 90°C to about 30:1 at the higher analysis temperatures. Note that at the lower temperatures the quantitation of α-terpineol in TOFA is questionable since it was so close to the practical quantitation limit of 18 ng/mL (0.018 μg/mL). The calculated coefficients for the low molecular weight solvents were not as great as anticipated in the TOFA experiments relative to the silicone oil, which may suggest that the carboxylate group may not be affecting the trapping capacity for these species to an appreciable extent even at the low temperatures examined.

Table 5 lists compounds identified in the TOFA that had the potential to interfere with the purpose of this study. Acetone, methanol, and butanol were detected, and their contribution in the gas phase was quantified. The quantity was subsequently subtracted from the quantified species in the prepared samples, and an estimated amount in the oil was calculated using the calculated partition coefficient at 150°C. The associated error in the correction of the background contribution was not thoroughly investigated but it is reasonable to assume the error is small, if not negligible, since the quantity in the prepared sample exceeds the estimated background contribution by a factor of 30 or more.

TABLE 6
Silicone Oil/Air Interface Partition Coefficient for Selected Compounds^a

Compounds	Ret. time (min)	<i>k</i> @ 50°C (× 10 ²)	<i>k</i> @ 70°C (× 10 ²)	<i>k</i> @ 90°C (× 10 ²)	<i>k</i> @ 110°C (× 10 ²)	<i>k</i> @ 130°C (× 10 ²)	<i>k</i> @ 150°C (× 10 ²)
Acetone	2.9	0.332	0.241	0.173	0.114	0.0834	NA
Methanol	3.9	0.241	0.203	0.174	0.137	0.116	NA
α-Pinene	5.7	8.25	4.13	2.05	1.04	0.583	NA
<i>n</i> -Propanol	5.9	NA	NA	NA	NA	NA	NA
β-Pinene	7.0	8.92	4.37	2.15	1.05	0.582	NA
<i>n</i> -Butanol	7.4	1.14	0.716	0.450	0.282	0.198	NA
Limonene	8.2	6.61	3.01	1.36	0.641	0.329	NA
α-Terpineol	13.3	18.97	7.52	3.02	1.30	0.618	NA

^aThe data are background-corrected at all temperatures and reported as the mean of four replicates. The relative standard deviation was less than ±5% in all cases. For abbreviations see Tables 1 and 4.

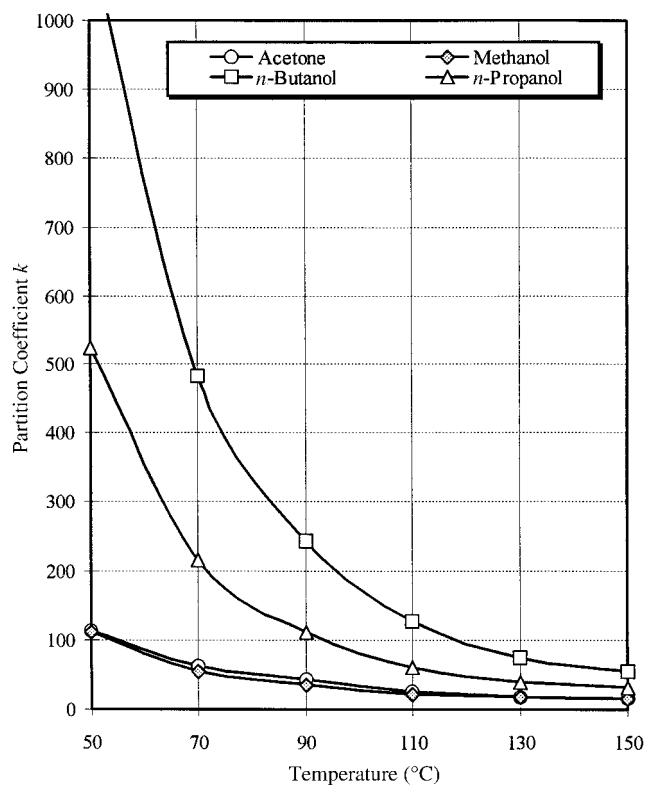


FIG. 2. Partition coefficients for acetone, methanol, *n*-propanol, and *n*-butanol in TOFA XTOL-100/air system. TOFA XTOL-100 (Georgia-Pacific Resins Inc., Atlanta, GA); for abbreviation see Figure 1.

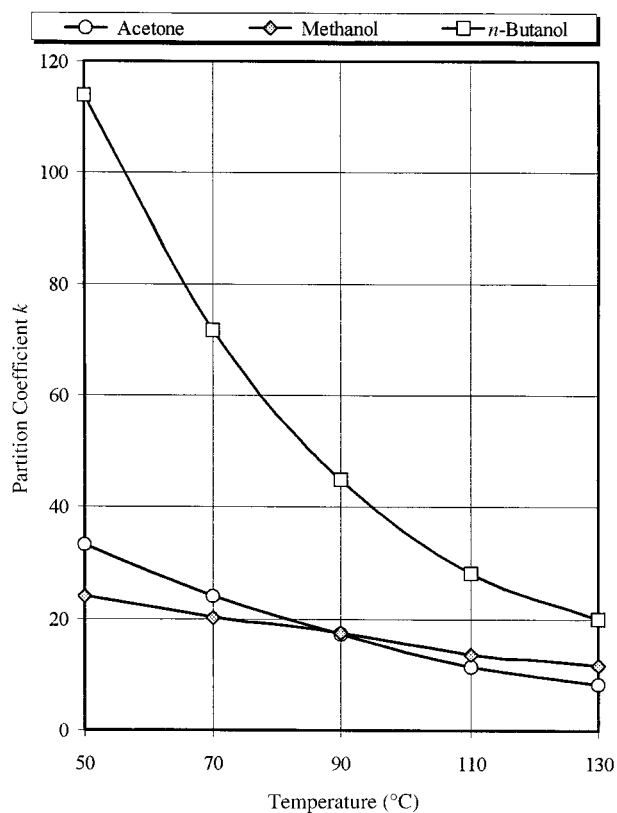


FIG. 4. Partition coefficient for acetone, methanol, and *n*-butanol in a silicone oil/air system.

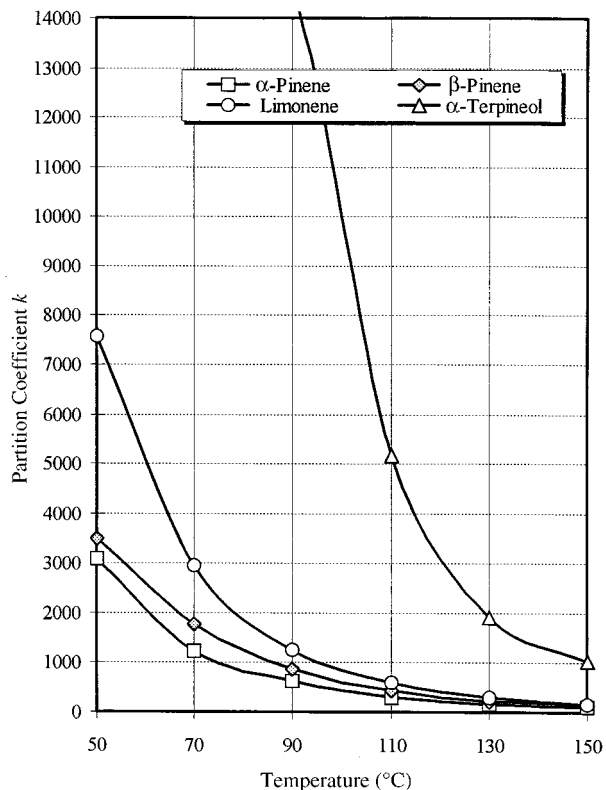


FIG. 3. Partition coefficients for α -pinene, β -pinene, limonene, and α -terpineol in a TOFA XTOL-100/air system. For abbreviations see Figures 1 and 2.

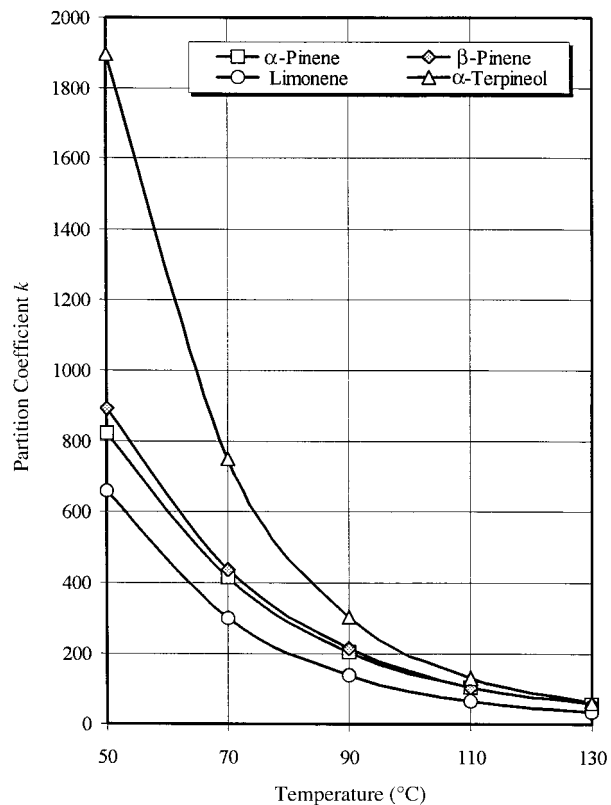


FIG. 5. Partition coefficients for α -pinene, β -pinene, limonene, and α -terpineol in a silicone oil/air system.

The original purpose of this study was to determine the efficacy of TOFA and silicone oil as VOC traps in industrial stacks. To do so, the partition coefficients of the named terpenes, alcohols, and acetone were calculated for TOFA and silicone oil systems. Although the partition coefficients clearly showed that TOFA or silicone oil could be used as trapping agents, some practical considerations preclude their use for trapping VOC from industrial emission sources. First, this experiment did not address a rate at which the species could be absorbed in a dynamic system. Although the terpenes are highly soluble in both TOFA and silicone oil, a certain contact time between oil and terpene would be required to effectively trap and remove the species from an exhaust stream. Second, TOFA is an extracted natural oil. Unfortunately, it contains several low molecular weight species, as evidenced in the background (e.g., Table 5), that would most likely contribute to the total VOC quantity. Even if a narrow fraction of TOFA could be obtained to reduce the background species, it contains a high percentage of long-chain unsaturated C₁₈ acids that can readily react in hot, moist environments resulting in the reformation of the very compounds removed in the initial clean-up. TOFA does not work because the low-weight molecular species are self-generating when exposed to the conditions of many industrial exhaust streams. Likewise, silicone oil is made up of a distribution of polydimethyl siloxanes and polydiphenyl siloxanes. This would mean a narrow fraction of the higher molecular weight species would have to be available which probably would add greatly to the cost and therefore exceed any current economic value for recovered VOC.

The partition coefficients obtained in this study indicate that both TOFA and silicone oil are reasonable media for trapping and subsequent speciation and quantitation of the non-polar and moderately polar compounds investigated. Although economic factors and interfering reactions currently

preclude their use as VOC trapping agents in large exhaust streams, obtaining the partition coefficients for these species is still fundamentally valid.

ACKNOWLEDGMENTS

I wish to thank Dr. David Valdez, Analytical Department Group Leader, Georgia-Pacific Resins, Inc. for the time allowed to complete this project, and Dr. Michael Hittmeier, Georgia-Pacific Building Products Director of Product Development for his invaluable advice and knowledge of wood extractives.

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[Received May 3, 1999; November 9, 1999]