

Odor Threshold Studies Performed with Gasoline and Gasoline Combined with MTBE, ETBE and TAME

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EXECUTIVE SUMMARY

The Clean Air Act Amendments of 1990 require that gasoline sold in areas of non-attainment for carbon monoxide or ozone contain specified amounts of fuel oxygenates. Fuel oxygenates include, methyl-tertiary-butyl ether (MTBE), ethyl-tertiary-butyl ether (ETBE), and tertiary-amyl-methyl ether (TAME). These oxygenated compounds increase the oxygen content of fuels, producing a more complete combustion, resulting in a reduction in carbon monoxide emissions. Oxygenated compounds such as MTBE have been previously added to gasoline to enhance octane ratings. More recently, larger amounts of oxygenates, MTBE, in particular, have been added to fuels to meet Clean Air Act Amendment requirements. This study examines the effect of oxygenate addition on the odor of gasoline blends.

Three blends of gasoline (summer, winter and a "composite") were evaluated for their odor detection and recognition thresholds in air. These gasolines were also combined with the gasoline oxygenates MTBE, ETBE or TAME to evaluate the effect of the oxygenates on the gasolines' odor detection and recognition thresholds. Additionally, commercial grade MTBE (97% pure, obtained from ARCO Chemical Co.) was evaluated for its odor detection and recognition thresholds in air and water as well as its taste threshold in water. The detection threshold is defined as the minimum concentration at which 50 percent of a given population can differentiate between a sample containing the odorant and a sample of odor free air. The recognition threshold value is defined as the minimum concentration at which 50 percent of a given population can recognize or identify the odorant. These evaluations were conducted at TRC Environmental Corporation's (TRC's) Odor Laboratory in Windsor, Connecticut.

The average detection and recognition threshold values for commercial grade MTBE were determined to be 0.053 and 0.125 parts-per-million (ppm), respectively. The average detection and recognition threshold values for this MTBE in water were

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determined to be 0.045 and 0.055 ppm, respectively. In general, compounds with odor thresholds below 1 ppm are considered highly odorous. The panelists descriptions of MTBE's odor included alcohol, chemical, ether and butane. Finally, the average taste detection threshold value for this oxygenate was determined to be 0.039 ppm. The panelists found the taste of MTBE to be highly objectionable.

The average detection and recognition threshold values for the headspace vapor of the three gasoline blends are as follows: summer blend - 0.576 and 0.802 ppm, respectively; winter blend - 0.479 and 1.121 ppm, respectively; and "composite" blend - 0.474 and 0.765 ppm, respectively. In general, the panelists described all three blends as smelling like gasoline.

The average detection and recognition threshold values for the headspace vapor of the gasoline-oxygenate mixtures are as follows: summer blend + 3% MTBE (97% purity) - 0.5 and 0.696 ppm, respectively; summer blend + 11% MTBE (97% purity) - 0.275 and 0.710 ppm, respectively; summer blend + 15% MTBE (97% purity) - 0.264 and 0.686 ppm, respectively; summer blend + 15% MTBE (99% purity) - 0.113 and 0.358 ppm, respectively. The odors associated with these mixtures included organic volatile, gasoline, ether, car exhaust, sweet gasoline and gasoline with ether. The summer blend of gasoline was also mixed with 15% ETBE (99% purity) and also with 15% TAME (94% purity). The average detection and recognition threshold values for these mixtures are 0.064 and 0.139 ppm (summer blend + ETBE) and 0.114 and 0.207 ppm (summer blend + TAME). The odors the panelists associated with these mixtures included ether, gasoline, chemical with gasoline, cleaning fluid and natural gas.

The winter and composite gasolines were each mixed with 15% MTBE (97% purity), respectively. The average detection and recognition threshold values for these mixtures were 0.219 and 0.398 ppm (winter blend + MTBE) and 0.085 and 0.185 ppm (composite blend + MTBE), respectively. The odor of the winter gasoline - MTBE

ES-2

mixture was associated with gasoline, chemical and ether by the panelists. The odor of the "composite" gasoline - MTBE mixture was associated with gasoline, gasoline with ether, and permanent marker by the panelists.

ES-3

Section 1

INTRODUCTION

The Clean Air Act Amendments of 1990 require that gasoline sold in areas of non-attainment for carbon monoxide or ozone contain specified amounts of fuel oxygenates. Fuel oxygenates include, methyl-tertiary-butyl ether (MTBE), ethyl-tertiary-butyl ether (ETBE), and tertiary-amyl-methyl ether (TAME). These oxygenated compounds increase the oxygen content of fuels, producing a more complete combustion, resulting in a reduction in carbon monoxide emissions. Oxygenated compounds such as MTBE have been previously added to gasoline to enhance octane ratings. More recently, larger amounts of oxygenates, MTBE, in particular, have been added to fuels to meet Clean Air Act Amendment requirements. This study examines the effect of oxygenate addition on the odor of gasoline blends. A commercial blend of MTBE (97% purity, obtained from ARCO Chemical Co.) was also evaluated for its odor detection and recognition thresholds in air and water as well as its taste threshold in water. MTBE (99% purity) and ETBE (99% purity) were also supplied by ARCO Chemical Company. TAME (94% purity) was obtained by API from Aldrich Chemical Company and supplied to TRC through API's chemical repository, Experimental Pathology Laboratories, Inc. (Herndon, VA). The gasoline blends were furnished through Experimental Pathology Laboratories, Inc., Herndon, VA (summer blend - API Reference Fuel 91-01), and Sun Co., Inc., Marcus Hook, PA (winter blend and "composite" sample). The Reid Vapor Pressure (RVP) for the gasoline blends (in psi) are 8.5, for the summer blend; 12.3 for the winter blend; and 7.9 for the "composite sample".

Section 2

EXPERIMENTAL PROCEDURES

TASTE EVALUATION PROCEDURES

The taste threshold determinations met the criteria specified in *Review of Published Odor and Taste Threshold Values of Soluble Gasoline Components* (TRC, 1985).

These criteria are summarized as follows:

1. Panel selection of at least six per group;
2. Panel selection based on taste sensitivity;
3. Panel calibration;
4. A "sip" and "spit" presentation method;
5. Room temperature solutions;
6. Purified water as a diluent;
7. Rinse between stimuli;
8. Consideration of threshold type;
9. Staircase presentation series;
10. Forced-choice procedure;
11. Repeated trials;
12. Concentration step increasing by a factor of two or three.

TRC performed the taste threshold testing following the procedure in Standard Method 2160B for the Examination of Water and Wastewater (APHA et al., 1992). The taste threshold value of MTBE was determined by comparing this oxygenate with water. Aliquots of the MTBE solutions used for the aqueous odor testing were also used for the taste tests. The samples were presented to the panelists in a series of increasing concentrations, and each sample was paired with a water reference. Each panelist was required to sip the sample via straw, hold it inside the mouth for a few seconds and discharge it without swallowing. The panelist then compared the sample of oxygenate with the reference sample and indicated whether or not a flavor or aftertaste could be detected.

ODOR EVALUATION PROCEDURES

These studies were conducted in TRC's Odor Laboratory in Windsor, Connecticut. The odor threshold determinations met the criteria specified in *Review of Published Odor and Taste Threshold Values of Soluble Gasoline Components* (TRC, 1985).

These criteria are summarized as follows:

1. Panel selection of at least six per group;
2. Panel selection based on odor sensitivity;
3. Panel calibration;
4. Consideration of vapor modality (air and water);
5. Diluent in accord with compound;
6. Presentation mode that reduces ambient air intake;
7. Analytical measurement of odorant concentration;
8. Calibration of flow rate and face velocity (for olfactometers);
9. Consideration of threshold type (detection or recognition);
10. Ascending presentation series;
11. Repeated trials;
12. Forced-choice procedure;
13. Concentration step increasing by factor of two or three.

Threshold Determinations in Air Samples

Air samples of neat MTBE were produced by vaporizing a known volume of MTBE (0.6 μl) in a known volume of hydrocarbon-free air (0.400 ft^3) which was contained in a Tedlar® bag. The concentration in each sample bag was calculated according to the equation presented in Table 2-1 and expressed in parts-per-million (ppm). The average starting concentration of MTBE in the Tedlar® bag was calculated to be 11.16 ppm.

In contrast to the wholly vaporized MTBE samples, the headspace vapor samples from the summer, winter and "composite" gasolines as well as from the gasoline-oxygenate mixtures were generated by a mini-impinger system. Ten milliliters of gasoline or gasoline-oxygenate mixture were placed into a glass impinger. Carbon-filtered air was passed through an inlet tube over the headspace and the vapor was collected through an outlet tube into a Tedlar® bag. The resultant headspace vapor was diluted approximately 2000-fold prior to presentation to the odor panel. The

concentration (in ppm) of total hydrocarbons in the Tedlar® bags containing the diluted gasoline headspace vapor was approximated by using an Organic Vapor Analyzer (OVA) (Foxboro 128). The OVA was calibrated against a gaseous mixture of 45% butane, 45% pentane and 10% hexane. The Tedlar® bag containing the diluted gasoline headspace vapor was then connected to the sampling port of the OVA and a reading obtained.

The readings for each sample were recorded on the appropriate ED₅₀ evaluation forms (Appendices B and C). An API study of consumer gasoline vapor exposure during refueling demonstrated that approximately 80% of gasoline vapors are comprised of saturated C₄-C₆ compounds (Clayton Environmental Consultants, 1993).

The dilution-to-threshold (D/T) values used to calculate the threshold concentration levels were measured with a dynamic dilution triangle olfactometer (IITRI System, 1979 Model). The D/T value represents the ratio of the volume of odor-free air that must be added to the odorous sample to reach threshold. For example, a D/T of 100 means that 100 volumes of odor-free air must be added to one volume of odorous air to dilute it to threshold. The D/T ratio represents that dilution required for 50% of the panel to detect a difference between the odorous stimuli and the blank air.

On the triangle olfactometer, this is the point at which the panelist successively identifies the sniff port containing the odor. The olfactometer uses carbon-filtered air to make six simultaneous dilutions of the odorous air. A series of dilutions were presented in an ascending manner, each series representing approximately a three-fold concentration step. The dilution ratios, as determined by a soap film flow-meter, were approximately: 1/2411, 1/608, 1/175, 1/55, 1/24, 1/8. Each dilution level was presented by means of a cup containing three glass sniff ports. Two ports dispensed only carbon filtered air while the third dispensed the diluted odor. Flow rates from the sniffing ports were constant at 3 L/minute. Panelists chose which of the three ports differed from the other two, i.e., the odor. The olfactometer and its procedures meet

the requirements of ASTM Standard Practice E 679 (ASTM, 1993a). A schematic illustration of the olfactometer is depicted in Figure 2-1. The D/T value was calculated by log dilution level versus probability plots. The probability of correct response at 50 percent was plotted against odorant concentration for a best fit (least squares) straight line function. This D/T determination method is recommended for use with the IITRI Olfactometer System, and is also recommended by ASTM Standard Practice E 679 (ASTM, 1993a).

Composite scores were used to determine two types of thresholds, detection and recognition. The detection threshold value differs from the recognition threshold value in that, the detection threshold is the dilution at which a panelist is capable of determining that there is a difference between the sample and filtered air. The recognition threshold value is the dilution at which a panelist is capable of rating the intensity of the odor on the butanol scale. Both the odor thresholds of detection and recognition are expressed in parts-per-million. The thresholds were calculated by dividing the concentration (ppm) in the sample bag by the D/T ratio (dimensionless) as determined by odor panel evaluation. In addition, once panelists were able to rate the intensity of the odor on the butanol scale, they were asked to describe the odor associated with the sample.

The perceived odor intensity was measured with a dynamic dilution binary scale olfactometer arranged in a "lazy Susan" configuration (Figure 2-2). Supra-threshold levels of 1-butyl alcohol (Standard Reference ASTM E 544) were presented in two-fold concentration steps (the butanol scale) (ASTM, 1993b). Panelists compared the ports of the triangle olfactometer with the butanol and indicated the comparable level. The panelists were asked to rate the intensity of the odor on all subsequent dilutions after the odor was detected. The intensity of the odor was rated on a scale of 1 to 8 (as compared to port number 1 through 8). Ratings of 1 through 3 are considered weak odors, ratings of 4, 5 and 6 are considered moderate odors and ratings of 7 and 8 are strong odors.

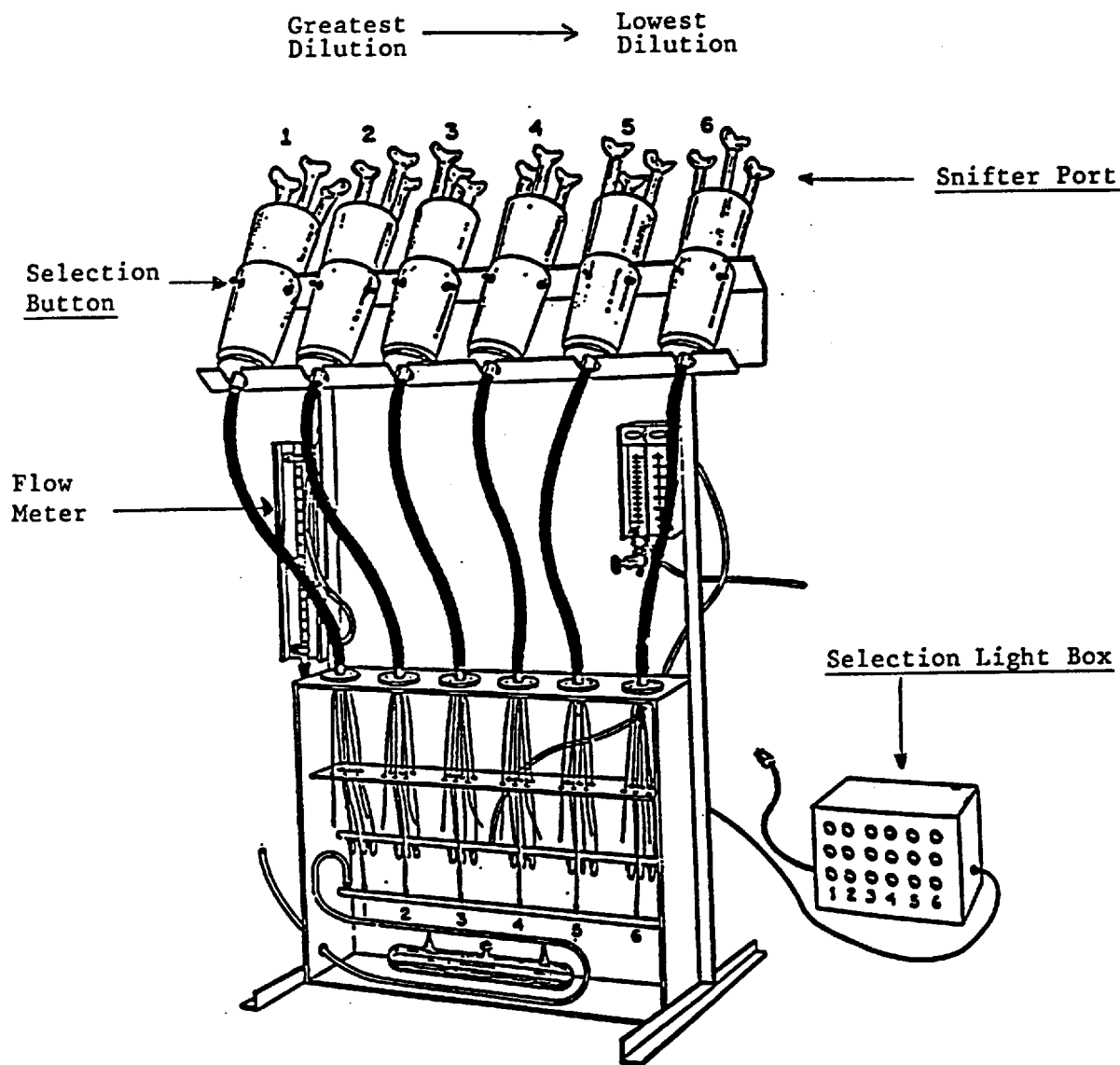


Figure 2-1. Dynamic Dilution Forced-Choice Triangle Olfactometer

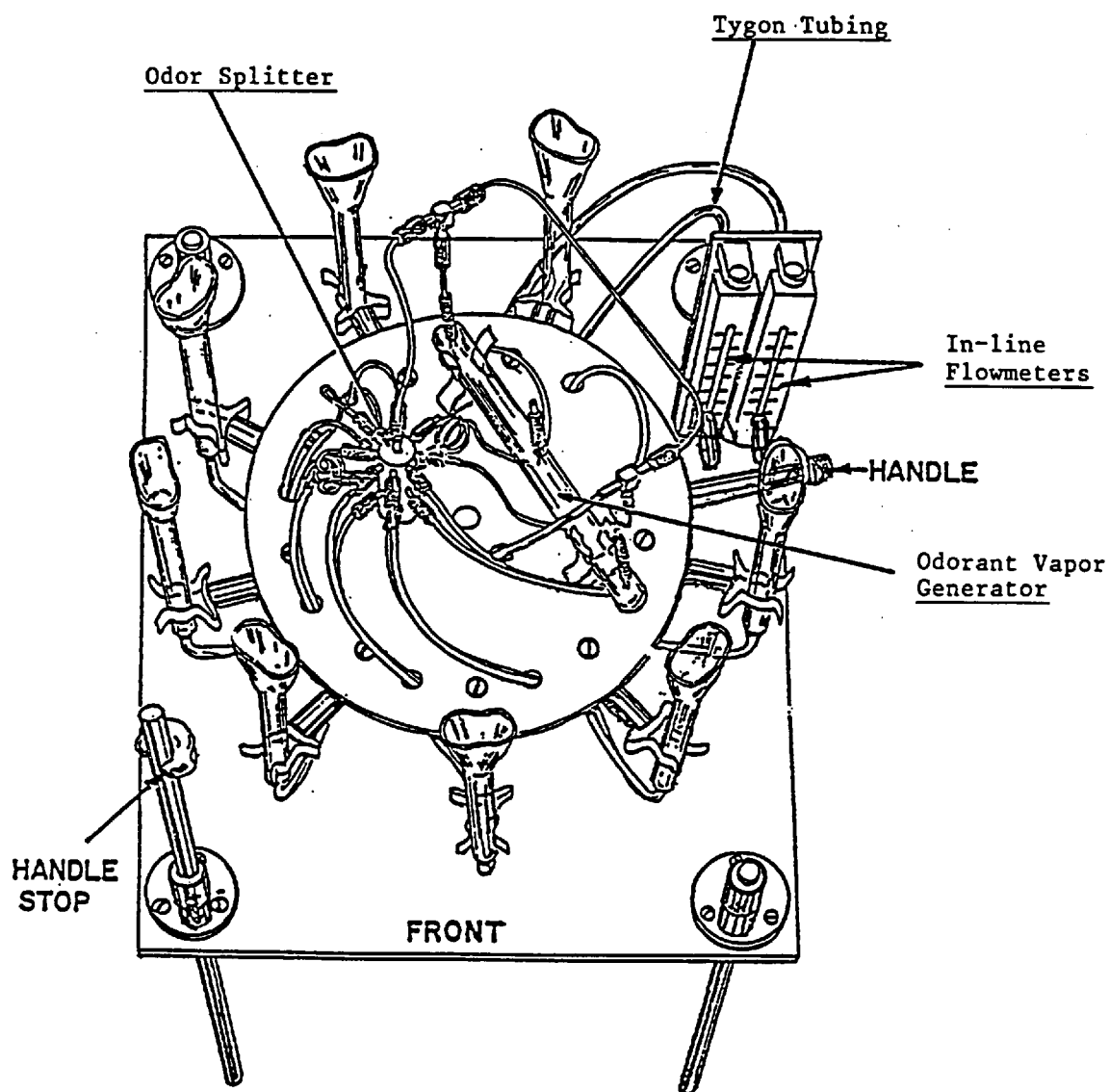


Figure 2-2. Butanol Olfactometer

Threshold Determinations in Aqueous Samples

TRC determined the odor thresholds of MTBE in its aqueous phase, following the Standard Method 2150 for the Examination of Water and Wastewater (APHA et al., 1992). A known concentration of MTBE was diluted with distilled water in a fixed ratio and evaluated organoleptically. Following Method 2150, aqueous samples (contained in flasks) with known concentrations of MTBE were presented to each panelist in ascending order from the weakest to the highest concentration. Based on the results of preliminary tests, a set of dilutions of MTBE was prepared. The nominal concentrations of the samples used in the aqueous odor testing were calculated to be 0.023 ppm, 0.046 ppm, 0.093 ppm, 0.185 ppm, 0.370 and 0.740 ppm MTBE. Each sample was presented to the panelist accompanied by two flasks that contained distilled water. The panelist sniffed the headspace of each flask and indicated which flask was different from the other two. The odor threshold is the dilution ratio at which the odor was just detected.

CALCULATION OF ODOR AND TASTE THRESHOLD VALUES

The odor and taste threshold values were calculated using a statistical-linear regression method. Tables 2-2 and 2-3 are used to calculate the threshold values. Table 2-2 is the ED₅₀ Evaluation Form for the Dynamic Triangle Olfactometer. The Y-values of the linear regression are derived from the calibration data of the olfactometer. These Y-values are the log of the tolerance level concentration which is calculated by averaging adjacent dilution levels. Once each panelist has evaluated the sample, a frequency tally is taken which indicates the number of times the sample is first detected per concentration. An average rank for all panelists is then determined using the rank count number scale. The X-plotting value is determined using a conversion table (Table 2-3). The pairs of X and Y values are then used to

Table 2-2. ED₅₀ Evaluation Form for the Dynamic Triangle Olfactometer

Sample:

Evaluation Date: RESULT: Log ED₅₀ = ... ED₅₀ = ...

Cons. No.	Panelist	Dilution Level Number							
		1	2	3	4	5	6	"7"	
		Correct Choice Would Be: (t = top, c = center, b = bottom)							
		Panelist Indicated:							
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
Frequency Tally									
Average Rank									
X - Plotting Value									
Y - Log(Tolerance Level)									
Log(Dilution Factor)									
Dilution Level No.		<1	1	2	3	4	5	6	"7"

For Rank Count:

1
2
3
4
5
6
7
8
9
10

Plot Y versus X
Y at X=0 is Log ED₅₀

Panel Leader

Table 2-3. Table for Rank Conversion of Rank Data to X-Axis Plot Values

Average Rank	Number of Panelists				
	6	7	8	9	10
.1.0	-1.07	-1.15	-1.22	-1.28	-1.33
1.5	-0.79	-0.89	-0.97	-1.04	-1.10
2.0	-0.57	-0.67	-0.77	-0.84	-0.91
2.5	-0.37	-0.49	-0.59	-0.67	-0.75
3.0	-0.18	-0.32	-0.43	-0.52	-0.60
3.5	0	-0.16	-0.28	-0.39	-0.47
4.0	+0.18	0	-0.14	-0.25	-0.35
4.5	+0.37	+0.16	0	-0.13	-0.23
5.0	+0.57	+0.32	+0.14	0	-0.11
5.5	+0.79	+0.49	+0.28	+0.13	0
6.0	+1.07	+0.67	+0.43	+0.25	+0.11
6.5		+0.89	+0.59	+0.39	+0.23
7.0		+1.15	+0.77	+0.52	+0.35
7.5			+0.97	+0.67	+0.47
8.0			+1.22	+0.84	+0.60
8.5				+1.04	+0.75
9.0				+1.28	+0.91
9.5					+1.10
10.0					+1.33

calculate the dilution-to-threshold (D/T) by a least squares method. The equation that is used is:

$$\text{Log D/T} = \bar{Y} - \{ \bar{X} \cdot [(XY) - N \bar{Y} \bar{X}] / [(X^2) - N (\bar{X})^2] \} \quad (\text{Equation 2-1})$$

where:

- $\bar{Y}$ = mean value of all log (tolerance level) values actually used.
- $\bar{X}$ = mean value of plotting values.
- (XY) = sum of products of each X with corresponding Y.
- (X^2) = sum of squares of X values.
- N = number of plotting values.

This equation automatically calculates the best-fit straight line for the data and provides the log of the D/T. For example, Appendix A provides the olfactometer ED₅₀ evaluation forms for the vaporized MTBE samples, in which the D/T values were calculated as just described. As seen in the first sheet (Sample A) the Y values (log tolerance level) to plot the detection threshold are 3.681, 3.083, 2.514, 1.992 and 0.732. A frequency tally of the initial odorant detection is made (circled samples on ED₅₀ sheet). The frequency tallies (with respective average rank values in parentheses) are 1 (1), 1 (2), 3 (4), 1 (6) and 1 (7). The average rank values were then converted to the X values of -1.15, -0.67, 0, 0.67 and 1.15 respectively. Therefore the X,Y plotting values are -1.15, 3.681; -0.67, 3.083; 0, 2.514; 0.67, 1.992, and 1.15, 0.732. Using the least squares method, the D/T value is calculated to be 251. The concentration of MTBE in the bag (ppm) is divided by the D/T value to obtain the odor threshold value in ppm (0.043 ppm). The recognition threshold is calculated the same way except that the frequency tally is of the initial odorant recognition (first intensity ranking, designated on ED₅₀ sheet by a number value in a square). The odor and taste threshold values in water are also determined in a similar manner.

PANEL

TRC Environmental Corporation maintains a pool of well-trained and experienced panelists from the Hartford, Connecticut area for olfactory evaluation at TRC's Olfactory Laboratory located in Windsor, Connecticut. For these odor and taste evaluation studies, the panel consisted of at least six individuals chosen to represent a normal distribution of olfactory sensitivity such as found in the general population. Prior to sample evaluation for odor thresholds, the panel was calibrated with a butanol intensity series.

Section 3

RESULTS AND CONCLUSIONS

TASTE EVALUATION RESULTS

MTBE (97%) was evaluated for its taste threshold in water (Table 3-1). The average taste detection threshold value for this oxygenate, in these studies, was 0.039 ppm. The panelists found the taste of MTBE (even at the lowest concentrations) to be highly objectionable.

Table 3-1. Taste Threshold Values for MTBE in Water (in ppm)

Oxygenate	Taste Threshold	Taste Characteristics ¹
97% MTBE	0.039 0.039	"nasty", bitter, rubbing alcohol, nauseating
avg	0.039	

¹ Combined odor characteristics from each sample within the group.

ODOR EVALUATION RESULTS

Results From the Evaluation of MTBE

The odor threshold values for MTBE in air and water are presented in Table 3-2. The

Table 3-2. Odor Threshold Values for MTBE in Air¹ and Water (in ppm)

Oxygenate	Odor Detection	Odor Recognition	Odor Character ²
97% MTBE (air)	0.043 0.058 0.058	0.105 0.159 0.110	chemical, ether, sour, butane, alcohol, medicine, cleaning fluid
avg	0.053±0.005	0.125±0.017	
97% MTBE (water)	0.048 0.041	0.065 0.044	alcohol
avg	0.045	0.055	

¹ Mean ± Standard Error

² Combined odor characteristics from each sample within the group.