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

HEALTH AND ENVIRONMENTAL SCIENCES API PUBLICATION NUMBER 4592 JANUARY 1994

> American Petroleum Institute 1220 L Street, Northwest Washington, D.C. 20005

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

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4592

PREPARED UNDER CONTRACT BY: TRC ENVIRONMENTAL CORPORATION 5 WATERSIDE CROSSING WINDSOR, CONNECTICUT

DECEMBER 1993

American Petroleum Institute



FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFAC-TURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANU-FACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COV-ERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABIL-ITY FOR INFRINGEMENT OF LETTERS PATENT.

Copyright © 1994 American Petroleum Institute

ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACT

Robert Barter Ph.D., Health and Environmental Sciences Department

AD HOC WORKGROUP OF THE TOXICOLOGY TASK FORCE

Charles R. Clark Ph.D., Unocal Corporation

Wayne Daughtrey Ph.D., Exxon Biomedical Sciences

Mark D. Saperstein ARCO

TABLE OF CONTENTS

<u>SECT</u>	ION	<u>PAGE</u>
	EXECUTIVE SUMMARY	ES-1
1.	INTRODUCTION	1-1
2.	EXPERIMENTAL PROCEDURES	2-1
	TASTE EVALUATION PROCEDURES	2-1
	ODOR EVALUATION PROCEDURES Threshold Determinations in Air Samples Threshold Determinations in Aqueous Samples	2-2 2-2 2-8
	CALCULATION OF ODOR AND TASTE THRESHOLD VALUES	2-8
	PANEL	2-12
3.	RESULTS AND CONCLUSIONS	3-1
	TASTE EVALUATION RESULTS	3-1
	ODOR EVALUATION RESULTS Results From the Evaluation of MTBE Results From the Evaluation of Gasoline Results From the Evaluation of the Gasoline and Oxygenate Mixtures	3-1 3-1 3-3 3-5
	CONCLUSIONS	3-9
REFE	RENCES	R-1
	ENDIX A E Data Sheets	

APPENDIX B Gasoline Headspace Vapor Data Sheets

APPENDIX C Gasoline-Oxygenate Headspace Vapor Data Sheets

LIST OF TABLES

<u>TABLE</u>	ï	
2-1	TRC SOLVENT BAG STANDARD PREPARATION DATA FORM	2-3
2-2	ED ₅₀ EVALUATION FORM FOR THE DYNAMIC TRIANGLE OLFACTOMETER	2-9
2-3	TABLE FOR CONVERSION OF RANK DATA TO X-AXIS PLOT VALUES	2-10
3-1	TASTE THRESHOLD VALUES FOR MTBE IN WATER	3-1
3-2	ODOR DETECTION AND RECOGNITION THRESHOLD VALUES FOR MTBE IN AIR AND WATER	3-1
3-3	ODOR INTENSITY VALUES FOR MTBE IN AIR AND WATER	3-2
3-4	ODOR DETECTION AND RECOGNITION THRESHOLD VALUES FOR GASOLINE HEADSPACE VAPOR SAMPLES	3-3
3-5	ODOR INTENSITY VALUES FOR GASOLINE HEADSPACE VAPOR SAMPLES	3-4
3-6	ODOR DETECTION AND RECOGNITION THRESHOLD VALUES GASOLINE-OXYGENATE HEADSPACE VAPOR SAMPLES	3-5
3-7	ODOR INTENSITY VALUES FOR GASOLINE-OXYGENATE HEADSPACE VAPOR SAMPLES	3-7

LIST OF FIGURES

FIGURE

2-1	DYNAMIC DILUTION FORCED-CHOICE TRIANGLE OLFACTOMETER	2-6
2-2	BUTANOL OLFACTOMETER	2-7

EXECUTIVE SUMMARY

The Clean Air Act Amendments of 1990 require that gasoline sold in areas of nonattainment for carbon monoxide or ozone contain specified amounts of fuel oxygenates. Fuel oxygenates include, methyl-tertiary-butyl ether (MTBE), ethyltertiary-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 serve 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

ES-1

API PUBL*4592 94 🎟 0732290 0517420 214 📟

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.

Section 1 INTRODUCTION

The Clean Air Act Amendments of 1990 require that gasoline sold in areas of nonattainment for carbon monoxide or ozone contain specified amounts of fuel oxygenates. Fuel oxygenates include, methyl-tertiary-butyl ether (MTBE), ethyltertiary-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".

1-1

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 $(0.6 \ \mu$ l) 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

2-2

Table 2-1. TRC Solvent Bag Standard Preparation Data Form

TRC Project				Date						
				Technician						
Solvent	Species		2	folecu	lar Wei:	gh C		Density		
Dilution Gas	n 			Ambien Temper:	c aCure			Barometric Pressure		
	Meter Calibr									
	C ppm (V/V) - [v _s (µL)	D(g/L) <u>HW(g)</u>	24.04(L) mole 28.32(L	293	Pm (mm)	(g)	
lag No.	Volume of Injected Solvent (UL)	Im (°F	Ta (°)	1		Pm	Vol Dilu	ume of	Con	Centrati
·										
<u> </u>	<u> </u>	<u>. </u>					·			
								· · · · · · · · · · · · · · · · · · ·		
			<u></u>							
							<u> </u>	<u> </u>		
NOTE: P	m = pressure	Deas	ured a	t the	dry gas	meter (1	PDGH) + 1	berometri	c pr	essure.

NOTE: P_m = pressure measured at the dry gas meter (PDGM) + barometric pressure. Standard conditions are 68°F, 29.92 inches Hg.

2-3

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 ED_{50} 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

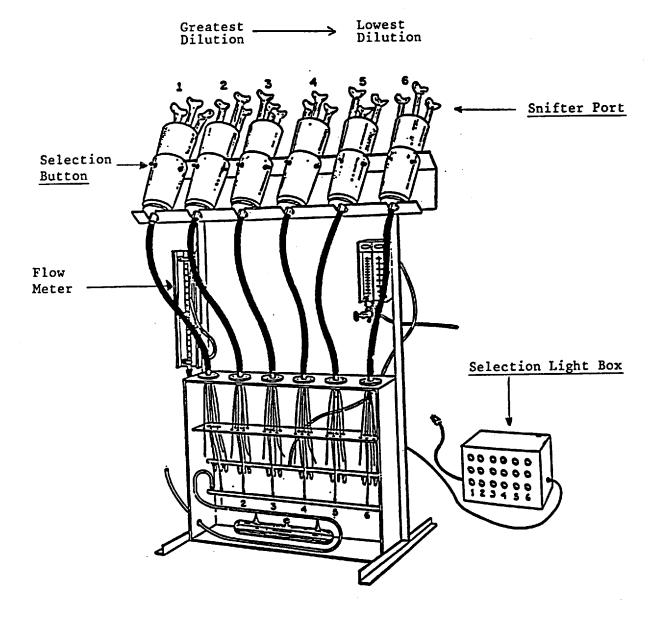
2-4

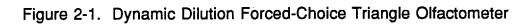
the requirements of ASTM Standard Practice E 679 (ASTM, 1993a). A schematic illustration of the olfactometer is depicted in Figure 2-1. The D/T value was calculated by log dilution level versus probability plots. The probability of correct response at 50 percent was plotted against odorant concentration 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.

2-5





2-6

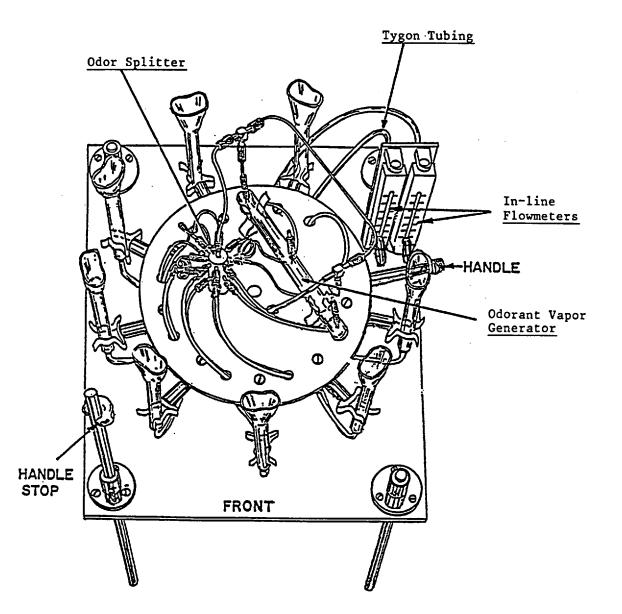


Figure 2-2. Butanol Olfactometer

Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

Threshold Determinations in Aqueous Samples

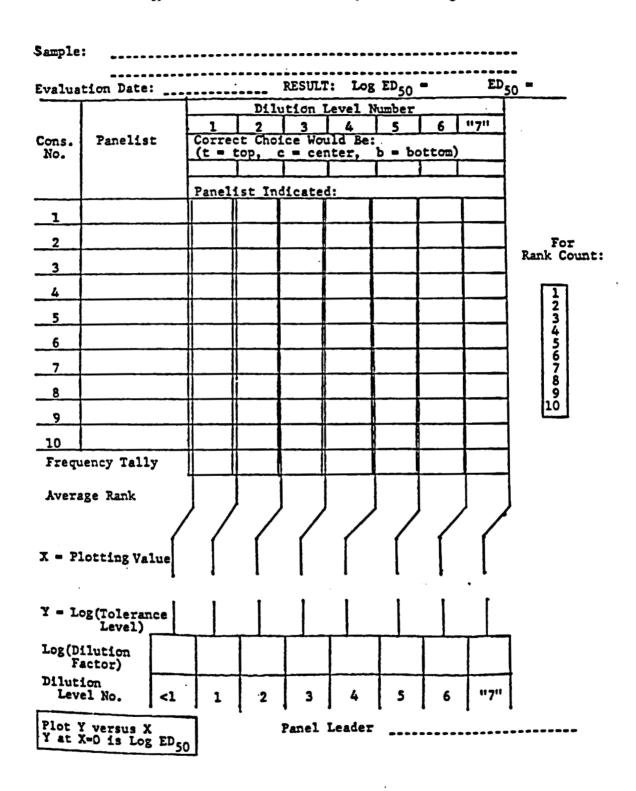
TRC determined the odor thresholds of MTBE in its aqueous phase, following the Standard Method 2150 for the Examination of Water and Wastewater (APHA et al., 1992). A known concentration of MTBE was diluted with distilled water in a fixed ratio and evaluated organoleptically. Following Method 2150, aqueous 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 ED_{50} 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

2-8

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



2-9

Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

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

	Number of Panelists				
Average Rank	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	-D.57	-0.67	-0.77	-0.84	-0.91
2.5	-D.37	-0.49	-0.59	-0.67	-0.7
3.0	-0.18	-0.32	-0.43	-0.52	-0.6
3,5	0	-0.16	-0.28	-0.39	-0.4
4.0	+0.18	O	-0.14	-0.25	-0.3
4.5	+0.37	+0.16	0	-0.13	-0.2
5.0	+0.57	+0.32	+0.14	0	-0.1
5.5	+0.79	+0.49	+0.28	+0.13	O
6.0	+1.07	+D.67	+0.43	+0.25	+0.1
6.5	{	+0.89	+0.59	+0.39	+0.2
7.0	· ·	+1.15	+D.77	+0.52	+0.3
7.5			+0.97	+0.67	+0.4
8.0			+1.22	+0.84	+0.5
8.5	1			+1.04	+0.7
9.0	1		1	+1.28	+0.9
9.5	1				+1.1
10.0	ł				+1.3

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

$$Log D/T = \overline{Y} - \{ \overline{X} \bullet [\{(XY) - N \overline{Y} \overline{X}\}/\{(X^2) - N (\overline{X})^2\}] \}$$
(Equation 2-1)

where:

- \overline{Y} = mean value of all log (tolerance level) values actually used.
- \overline{X} = mean value of plotting values.
- (XY) = sum of products of each X with corresponding Y.
- (X²) = 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 ED_{50} 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 Air ¹	and Water (in ppm)
------------	----------------	-------------------------------------	--------------------

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

¹ Mean <u>+</u> Standard Error

² Combined odor characteristics from each sample within the group.

3-1

average detection and recognition threshold values for MTBE were 0.053 and 0.125 ppm, respectively. In addition, each panelist was asked to describe the odor associated with the sample. These odor descriptions included chemical, alcohol, ether and butane. The average odor detection and recognition threshold values for MTBE in water were 0.045 ppm and 0.055 ppm, respectively. In general, compounds that exhibit odor threshold values below 1 ppm, such as MTBE, are in general considered highly odorous. The average odor intensity ratings for MTBE in air and water are presented in Table 3-3. The average odor intensity rating for MTBE in air was 5.17 which indicates that this oxygenate has a moderate odor level at the concentration tested, while the odor intensity for MTBE in water was 2.86.

Oxygenate	Average Conc.(ppm) ¹	Average Odor Intensity ²	Odor Intensity at 0 Dilution ³	Slope of Odor Intensity
97% MTBE (air)	11.17	5.17	6.82	-0.42
97% MTBE (water)	0.74	2.86	3.94	-0.82

Table 3-3. Odor Intensity Values for MTBE in Air and Water

¹ Average of the nominal starting concentrations of the samples.

² Average odor intensity of the last dilution cup (8-fold dilution step).

³ Average odor intensity at 0 dilution, extrapolated value using linear regression (odor intensity vs. log dilution level).

The intensity values for each sample were extrapolated to a zero (0) dilution and the slope values of the odor intensity vs. concentration line were also calculated. Since odorant intensity increases as a function of concentration, these data indicate that the odor of MTBE in water is more intense compared with MTBE in air. The slope of the increase in the intensity of the odor of MTBE in water is also larger than the slope of MTBE in air, indicating a faster increase in intensity as the concentration is increased.

The D/T evaluation forms for the dynamic triangle olfactometer, which include the

Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

perceived odor characteristics of MTBE, as well as the aqueous MTBE odor and taste data sheets, are provided in Appendix A and present the responses of each panelist. The detection and recognition threshold values for each sample are calculated using this data as described in Section 2.

Results From the Evaluation of Gasoline

The threshold values and odor intensity ratings for the individual headspace samples of the three gasolines are presented in Tables 3-4 and 3-5, respectively. The average detection and recognition threshold values for the summer blend of gasoline were 0.576 and 0.802 ppm, respectively. The odor of the summer gasoline was associated primarily with gasoline and a chemical odor by the panelists. The average odor intensity rating of 2.26 for the summer

Table 3-4. Odor Detection and Recognition Thresholds ¹ For Gasoline H	eadspace
Vapor (in ppm)	

Gasoline	Odor Detection	Odor Recognition	Odor Characteristics ²
Summer Blend	0.444 0.571 0.714	0.741 0.833 0.833	gasoline, chemical, rubber, smokey, lemony, garbage
avg	0.576 <u>+</u> 0.08	0.802 <u>+</u> 0.03	
Winter Blend	0.530 0.430 0.476	1.330 1.080 0.952	gasoline, kerosene, chemical
avg	0.479 <u>+</u> 0.03	1.121 <u>+</u> 0.11	
Composite Sample	0.457 0.400 0.566	0.761 0.794 0.741	gasoline, organic solvent, rancid, alcohol, smokey
avg	0.474 <u>+</u> 0.05	0.765 <u>+</u> 0.02	

¹ Mean <u>+</u> Standard Error

² Combined odor characteristics from each sample within the group.

Gasoline	Average Conc.(ppm) ¹	Average Odor Intensity ²	Odor Intensity at 0 Dilution ³	Slope of Odor Intensity
Summer Blend	20	2.26	3.98	-0.50
Winter Blend	26	2.03	3.04	-0.75
Composite	47	3.33	5.67	-0.39

Table 3-5. Odor Intensity Values for Gasoline Headspace Vapor Samples

¹ Average of the nominal starting concentrations of the samples.

² Average odor intensity of the last dilution cup (8-fold dilution step).

³ Average odor intensity at 0 dilution, extrapolated value using linear regression (odor intensity vs. log dilution level).

blend of gasoline, at the highest concentration evaluated (2.27 ppm), indicates that this gasoline has a relatively weak odor. The average detection and recognition threshold values for the winter blend of gasoline were 0.479 and 1.12 ppm, respectively. The odor of the winter gasoline was associated with gasoline and kerosene by the panelists. The average odor intensity rating for this blend of gasoline. at the highest concentration evaluated (2.95 ppm) was rated at 2.03 which indicates that this blend of gasoline also has a weak odor. The average detection and recognition threshold values for the "composite" blend of gasoline are 0.474 and 0.765 ppm, respectively. The odor of the "composite" gasoline was primarily associated with gasoline and organic solvents by the panelists. The average odor intensity rating for this blend of gasoline was rated at 3.33 which indicates that this blend of gasoline has a weak odor at the highest concentration evaluated (5.43 ppm). The intensity values for each sample were also extrapolated to a zero (0) dilution and the slope values of the odor intensity vs. concentration line were also calculated. Since odorant intensity increases as a function of concentration, these data indicate that the odor intensities of the summer and winter blends of gasoline are similar, while the odor intensity of the composite sample is actually less intense than the two blends. The composite sample of gasoline also has a low slope value, indicating that the increase in intensity is smaller as concentration increases, compared with the summer and winter blends of

gasoline.

The D/T evaluation forms for the dynamic triangle olfactometer, which include the perceived odor characteristics of the summer, winter and "composite" blends, are provided in Appendix B and present the responses of each panelist. The detection and recognition threshold values for each sample are calculated using this data as described in Section 2.

Results From the Evaluation of the Gasoline and Oxygenate Mixtures

The threshold values and odor intensity ratings for the headspace samples of the gasoline-oxygenate mixtures are presented in Tables 3-6 and 3-7, respectively. The summer blend of gasoline was evaluated in combination with the 99% pure MTBE (15% volume) and the 97% pure MTBE (3%, 11% and 15% volume). In general, the odor detection threshold decreased with increases in MTBE concentration. However, there was no difference between the summer blend of gasoline mixed with 11% MTBE (97% purity) or 15% MTBE (97% purity). The average detection and recognition threshold values for the summer blend of gasoline combined with 15% MTBE (99% purity) were 0.113 ppm and 0.358 ppm, respectively. The odors described by the panelists for this mixture included organic volatile, gasoline, ether and car exhaust. The average odor intensity score for this mixture is 4.59 (moderate odor) at the highest concentration tested (2.95 ppm). In comparison, the average detection and recognition threshold values for the summer blend of gasoline combined with MTBE were 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.

3-5

Table 3-6.	Odor Detection	and Recognition	Thresholds ¹	For Gasoline-Oxygenate
Headspace	Vapor Samples	; (in ppm)		

(,	
Gasoline	Odor Detection	Odor Recognition	Odor Characteristics²
Summer Blend + 15% MTBE (99%)	0.118 0.085 0.137	0.410 0.215 0.448	organic volatile, gasoline, ether, car exhaust, solvent, fragrance, adhesive
avg	0.113 <u>+</u> 0.015	0.358 <u>+</u> 0.070	
Summer Blend + 3% MTBE (97%)	0.531 0.400 0.568	0.800 0.537 0.750	gasoline, sweet, cleaning fluid, gasoline + ether
avg	0.500 <u>+</u> 0.05	0.696 <u>+</u> 0.080	
Summer Blend + 11% MTBE (97%)	0.341 0.248 0.237	0.938 0.619 0.574	gasoline, sweet, benzene, gasoline + ether
avg	0.275 <u>+</u> 0.03	0.710 <u>+</u> 0.110	
Summer Blend + 15% MTBE (97%)	0.305 0.279 0.207	0.865 0.596 0.596	gasoline, sweet, gasoline + ether, oily
avg	0.264 <u>+</u> 0.030	0.686 <u>+</u> 0.090	
Summer Blend + 15% ETBE (99%)	0.075 0.082 0.036	0.171 0.154 0.091	ether, gasoline, chemical with gasoline, natural gas, cleaner, alcohol
avg	0.064 <u>+</u> 0.010	0.139 <u>+</u> 0.020	
Summer Blend + 15% TAME (94%)	0.110 0.091 0.141	0.160 0.198 0.262	natural gas, gasoline, chemical, cleaning fluid, alcohol
avg	0.114 <u>+</u> 0.020	0.207 <u>+</u> 0.030	
Winter Blend + 15% MTBE (97%)	0.228 0.230 0.198	0.321 0.519 0.354	gasoline, chemical, ether, solvent, burning, plastic
avg	0.219 <u>+</u> 0.010	0.398 <u>+</u> 0.060	
Composite Sample + 15% MTBE (97%)	0.105 0.071 0.079	0.220 0.150 0.184	sweet gasoline, gasoline with ether, alcohol, permanent marker
avg	0.085 <u>+</u> 0.010	0.185 <u>+</u> 0.020	

¹ Mean \pm Standard Error ² Combined odor characteristics from each sample within the group.

3-6

Gasoline	Average Conc.(ppm) ¹	Average Odor Intensity ²	Odor Intensity at 0 Dilution ³	Slope of Odor Intensity
Summer Blend + 15% MTBE (99%)	26	4.59	6.28	-0.46
Summer Blend + 3% MTBE (97%)	21	3.05	5.45	-0.37
Summer Blend + 11% MTBE (97%)	28	2.95	5.02	-0.42
Summer Blend + 15% MTBE (97%)	31	3.07	5.15	-0.41
Summer Blend + 15% ETBE (99%)	30	3.92	5.23	-0.59
Summer Blend + 15% TAME (94%)	26	3.50	5.14	-0.51
Winter Blend + 15% MTBE (97%)	27	4.05	5.43	-0.47
Composite Sample + 15% MTBE (97%)	57	4.60	6.33	-0.49

Table 3-7.	Odor Intensity	Values for	Gasoline-Oxygenate	Headspace	Vapor Samples

¹ Average of the nominal starting concentrations of the samples.

² Average odor intensity of the last dilution cup (8-fold dilution step).

³ Average odor intensity at 0 dilution, extrapolated value using linear regression (odor intensity vs. log dilution level).

The odors that were described for these mixtures included organic volatile, gasoline, ether, car exhaust, sweet gasoline and gasoline with ether. The average odor intensity ratings for these mixtures ranged from 2.9 to 4.6 (weak to moderate odors) at concentrations ranging from 2.4 ppm to 3.5 ppm. The intensity ratings were proportional to the recognition thresholds, the higher the recognition threshold concentration (and therefore the weaker the odor), the lower the intensity rating, the lower the recognition threshold concentration (and therefore the stronger the odor), the higher the intensity rating (see Table 3-5 for individual descriptions and intensities).

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 odor intensity ratings for these mixtures were 3.92 (ETBE mixture) at 3.4 ppm and 3.5 (TAME mixture) at 2.95 ppm. The intensity values for each sample were also extrapolated to a zero (0) dilution and the slope values of the odor intensity vs. concentration line were also calculated. Since odorant intensity increases as a function of concentration, the data indicates that the summer blend + 15% MTBE (99%) has the most intense odor. The odor of the summer blend of gasoline combined with MTBE, ETBE or TAME was more intense than the odor of the summer blend of gasoline alone.

The winter and composite gasolines were each mixed with 15% MTBE (97% purity) and the average detection and recognition threshold values for these mixtures are 0.219 and 0.398 ppm (winter blend + MTBE) and 0.085 and 0.185 ppm (composite blend + MTBE). The odor of the winter gasoline - MTBE mixture was associated with gasoline, chemical and ether by the panelists. The average odor intensity rating for this mixture was rated at 4.05 which indicates that this blend of gasoline also has a moderate odor. The odor of the "composite" gasoline - MTBE mixture was associated with gasoline, gasoline with ether, and permanent marker by the panelists. The average odor intensity rating for this mixture was rated at 4.60 which indicates that this blend of gasoline has a moderate odor. The odor of the summer blend of gasoline has a moderate odor. The odor intensity rating for this mixture was rated at 4.60 which indicates that this blend of gasoline has a moderate odor. The odor intensity rating for the summer blend of gasoline with MTBE was similar to the intensities of the summer blend combined with MTBE, ETBE or TAME. Consistent with the composite gasoline alone, the composite gasoline with 15% MTBE added exhibited the lowest odor intensity when the starting concentration was taken into consideration.

The D/T evaluation forms for the dynamic triangle olfactometer, which include the perceived odor characteristics of the summer, winter and "composite" blends, are provided in Appendix C and present the responses of each panelist. The detection and recognition threshold values for each sample are calculated using this data as described in Section 2.

CONCLUSIONS

MTBE, ETBE and TAME are powerful odorants that are capable of significantly reducing the odor thresholds of gasoline. The commercial grade of MTBE has an odor detection threshold of 0.053 ppm in air and 0.045 ppm when in water. The reduction in the odor threshold of gasoline after the addition of MTBE is dependant on the amount of MTBE added. There was no reduction in the odor threshold of the summer blend of gasoline after the addition of 3% (by volume) of commercial grade of MTBE when compared to the gasoline alone. However, the addition of 11% and 15% commercial grade MTBE to summer gasoline, resulted in an average 53% reduction (52% and 54%, respectively) in the odor threshold of the summer gasoline blend alone. There was an 80% decrease in the detection threshold of the summer blend when 15% MTBE (99% purity) was added.

The odor thresholds of the three gasolines were similar, ranging from 0.474 ppm to 0.576 ppm. The addition of commercial grade MTBE (15%) to the three gasoline blends resulted in reductions in the odor detection thresholds ranging from 54% to 82%. The most significant reduction was seen with the addition of MTBE to the composite gasoline sample. The reason for this large reduction is unknown.

Finally, a comparison of the summer blend of gasoline combined with MTBE, ETBE or TAME yielded results consistent with the odor detection thresholds of the oxygenates themselves. Previous investigations have shown ETBE to be the most odorous oxygenate (TRC, 1993a), followed by TAME (TRC, 1993b) then MTBE. The addition of ETBE or TAME to the summer blend produced an 89% and 80% decrease,

3-9

respectively, in the odor threshold of the summer blend alone. The order of the odor detection thresholds (from lowest to highest) is: summer blend + ETBE (0.064 ppm) < summer blend + TAME (0.114 ppm) < summer blend + commercial grade MTBE (0.264 ppm).

It is evident from the data therefore, that the addition of 11% to 15% (by volume) MTBE, as well as 15% (by volume) TAME or ETBE to gasoline results in a significant reduction in the odor detection and recognition thresholds of gasoline. This decrease in the odor threshold was also associated with an increase in the odor intensity of the oxygenated gasoline.

REFERENCES

TRC Environmental Consultants, Inc. 1985. *Review of Published Odor and Taste Threshold Values of Soluble Gasoline Components*. API Publication No. 4419. American Petroleum Institute, Washington, D.C.

Clayton Environmental Consultants. 1993. *Gasoline Vapor Exposure Assessment at Service Stations*. API Publication No. 4553. American Petroleum Institute, Washington, D.C.

ASTM (American Society for Testing and Materials), 1993a. ASTM E 679, Standard Practice for Determination of Odor and Taste Thresholds By a Forced-Choice Ascending Concentration Series Method of Limits. *ASTM Book of Standards*. v. 15.07, Philadelphia, PA.

ASTM (American Society for Testing and Materials), 1993b. ASTM E 544, Standard Practices for Referencing Suprathreshold Odor Intensity. *ASTM Book of Standards.* v. 15.07, Philadelphia, PA.

APHA, AWW, WEF, 1992. In A.E. Greenberg, L.S. Clesceri and A.D. Eaton, eds. *Standard Methods for the Examination of Water and Wastewater, 18th ed.* American Public Health Association (APHA), Washington, D.C.

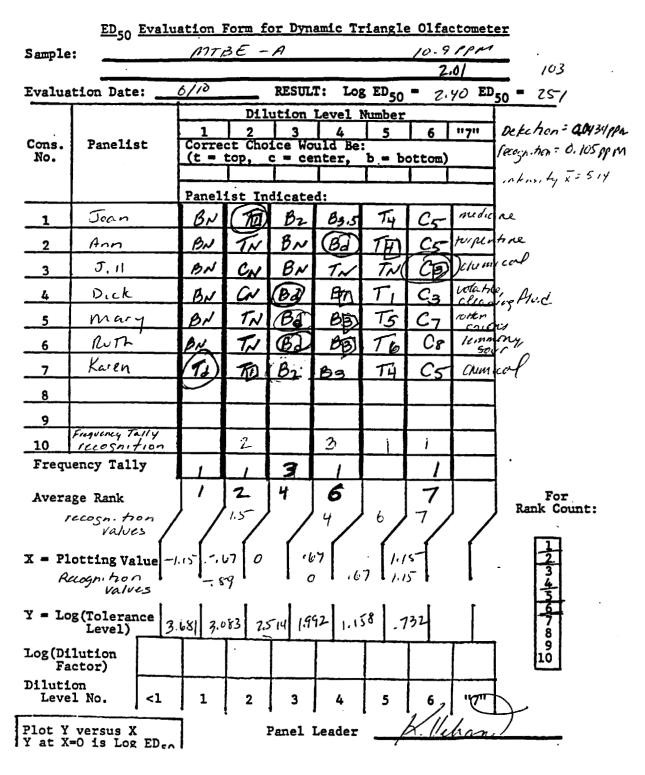
TRC Environmental Corporation, 1993a. *Final Report to ARCO Chemical Company on the Odor and Taste Threshold Studies Performed with Methyl Tertiary-Butyl Ether (MTBE) and Ethyl Tertiary-Butyl Ether (ETBE).* TRC Project No. 13442-M31, ARCO Chemical Co., Newtown Square, PA.

TRC Environmental Corporation, 1993b. *Odor and Taste Threshold Studies Performed With Tertiary-Amyl Methyl Ether (TAME)*. API Project No. 08200-0300-SA13, American Petroleum Institute, Washington, D.C. API PUBL*4592 94 📰 0732290 0517446 520 📰

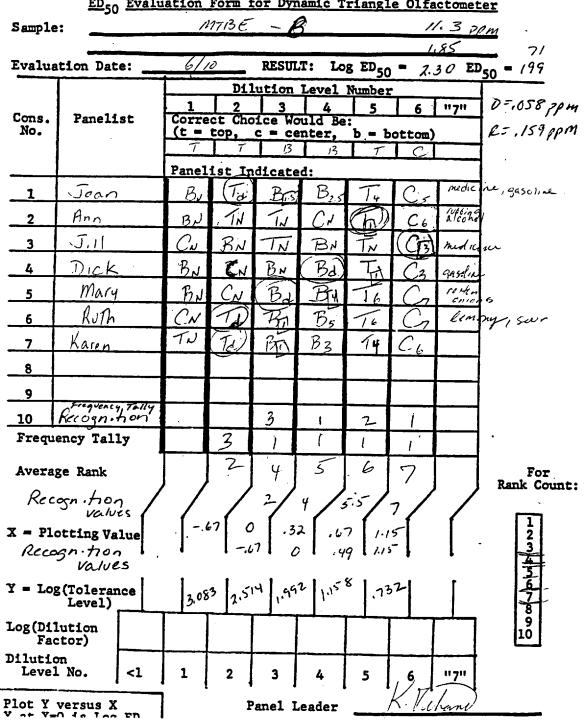
APPENDIX A

MTBE DATA SHEETS

. . .







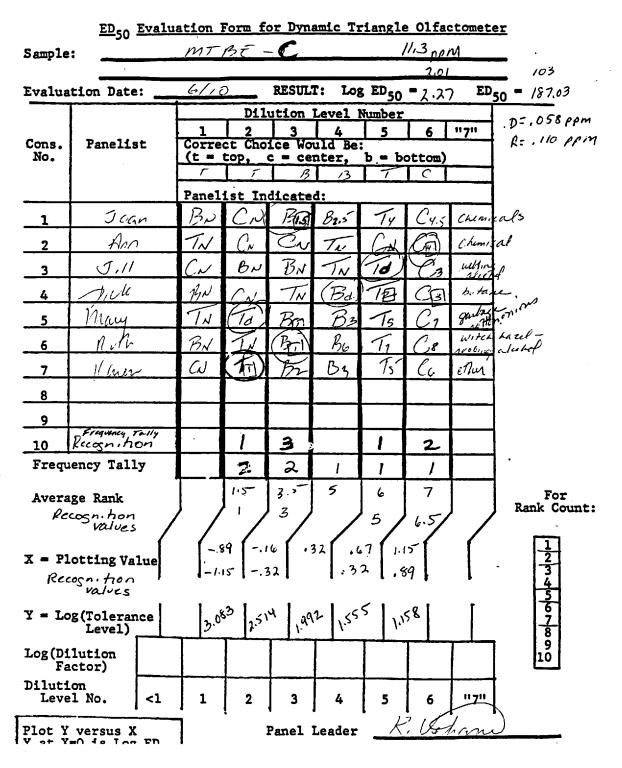
ED₅₀ Evaluation Form for Dynamic Triangle Olfactometer

• :

A-2

.

• •



A-3

AQUEOUS MTBE ODOR THRESHOLD STUDY DATA SHEET

		Star	Rou ting concentra	nd 1 ation = 0.740 j	naa		
	A	B	C	C	A	В	Odor
Panelist	(0.023 ppm)	(0.046 ppm)	(0.093 ppm)	(0.185 ppm)	(0.370 ppm)	(0.740 ppm)	Characteristics
Nolya C.	С	8	C .	С	A	В	medicine, alcohol
Alma D.	B	A	4 C	5 C	5 A	5 B	alcohol
Terry A.	C d	A N	C n	C n	A di	В	ether, sweet
Don P.	A	A	C 2	C 3	A	B	hospital, medicine
Mary S.	C d	B	C 2	C 2	A 3	B 3	rubbing alcohol
Florence T.	An	Bn	C d	С 1	A2	B 3	medicine
Irene C.	C n	Bn	Cn	Cd	A 1	B 2	rubbing alcohol
Frequency Taily (detection)		2	2	1	1	1	······································
Frequency Tally (recognition)		2	1	1	1	2	

Results²:

D/T detection = 15.35 (0.048 ppm) D/T recognition = 11.38 (0.065 ppm)

		Star	ting concentra	ation = 0.740	ppm		
	A	B	C	C	A	B	Odor
Panelist	(0.023 ppm)	(0.046 ppm)	(0.093 ppm)	(0.185 ppm)	(0.370 ppm)	(0.740 ppm)	Characteristics
Nolya C.	A	C	C	C	Α	B	medicine, ether
	n	n	2	3	3	4	
Alma D.	A	8	c	С	A	В	hospital
	n		2	3	3.5	2	
Terry A.	В	A	¢	С	A	В	sweet, alcohol
	d	n	đ	11	2	2.5	
Don P.	A	A	C	С	A	В	alcohol
	n		2	2	2	3	
Mary S.	В	С	C	C	A	В	hospital
	d	d		2	2.5	3	
Florence T.	С	A	В	A	A	B	medicine
	d		n	n n	2	3.5	
Irene C.	В	C	A	C	A	В	rubbing alcohol
	<u>n</u>	<u>n</u>	n		1.5	2	
Frequency Tally		1	4	1	1		
(detection)							
Frequency Tally (recognition)		1	3	2	1		

Round 2

Results²: D/T detection = 17.95 (0.041 ppm) D/T recognition = 16.82 (0.044 ppm)

¹Panelists had the option of choosing 1 of 3 flasks per dilution group. The letter of the correct flask (A, B, or C) for each dilution heads the column. Each panelist then rated the chosen flask, where:

n = nothing

d = different from other two flasks, but cannot rank on butanol scale

1-5 = butanol scale ranking (8 highest possible ranking)

²The detection threshold was determined by a linear regression method

= detection

= recognition

A-4

API PUBL*4592 94 🖿 0732290 0517451 998 📰

MTBE-TASTE THRESHOLD STUDY DATA SHEET

Rοι	Ind	1
1100	AI 10	

·····	1	2	3	ng concentrat	5			1 0	Taste
Panelist	(0.023 ppm)	(0.046 ppm)	(Blank)	(0.093 ppm)	(0.185 ppm)	(0.370 ppm)	(Blank)	(0.740 ppm)	Characteristics
Nolya C.	-	+	•	+	+	+	-	+	bitter, nasty
Alma D.	-	+	-	+	+	+	-	+	·····
Terry A.	-	-	-	-	-	+	-	+	nauseating
Don P.	-	-	-	-	•	•	-	+	
Mary S.	-	•	•	+	+	+	•	+	rubbing alcoho
Florence T.	-	-	-		-	+	-	+	
Irene C.	-	+	-	+	+	+	-	+	
requency Tally detection)		4				3		1	

Result²: D/T detection = 19 (0.039 ppm)

			Starti	Roune ng concentrat		pm					
Panelist	1 (0.023 ppm)	2 (0.046 ppm)	3 (Blank)	4	5	6 (0.370 ppm)	7 (Blank)	8 (0.740 ppm)	Taste Characteristics		
Nolya C.	+	+	-	+	+	+	-	+	nasty		
Alma D.	-	+	-	+	+	+	•	+			
Terry A.	-	-	-	-	-	+	-	+	rubbing alcohol		
Don P.	-	-	•	-	-	+	-	+			
Mary S.	-	+	-	+	+	+	•	+	bitter		
Florence T.	-	-	-		-	+	-	+			
Irene C.	-	+	-	+	+	+	-	+	bitter		
Frequency Tally (detection)	1	3				3					

Result²: D/T detection = 19 (0.039 ppm)

¹Panelists compared each test sample with a water reference and rated them either "-" (not different from water) or "+" (different from water).

²The detection threshold was calculated using a linear regression method

= detection

API PUBL*4592 94 🔳 0732290 0517452 824 📟

4

APPENDIX B

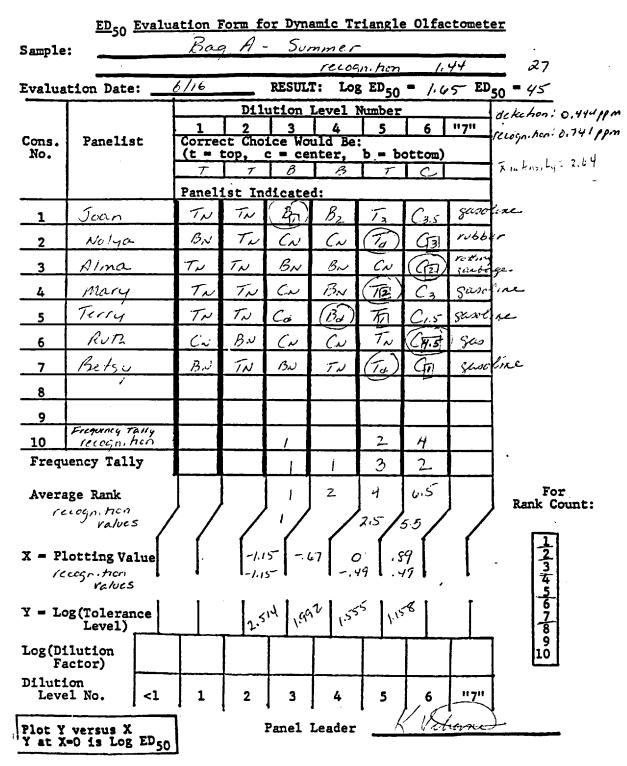
GASOLINE HEADSPACE VAPOR DATA SHEETS

Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

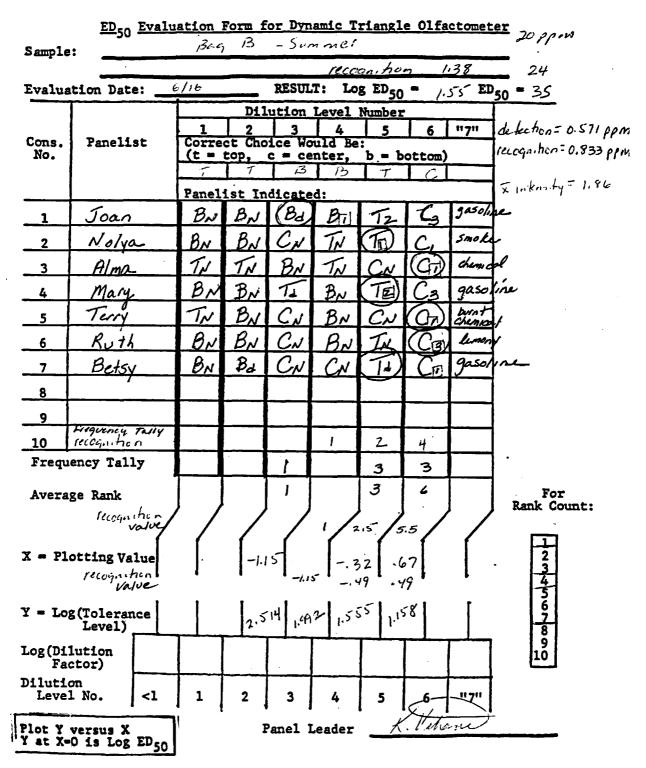
API PUBL*4592 94 🔳 0732290 0517453 760 🔳

:

20 ppm



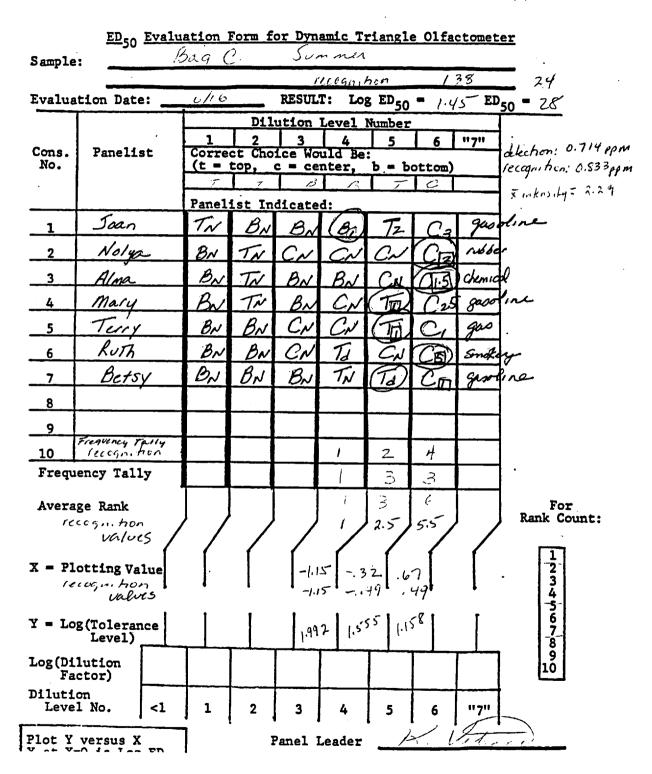






:

20 ppm

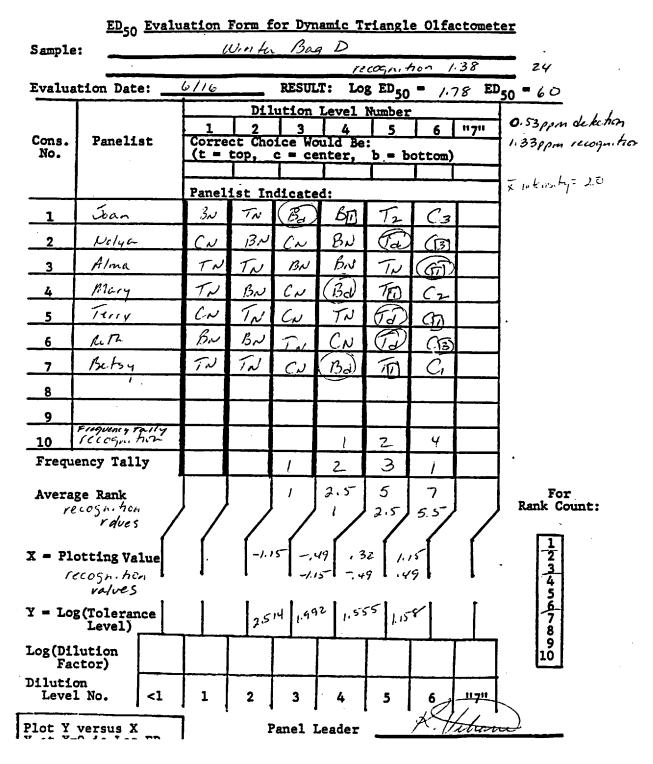




. .

• •

32 ppm

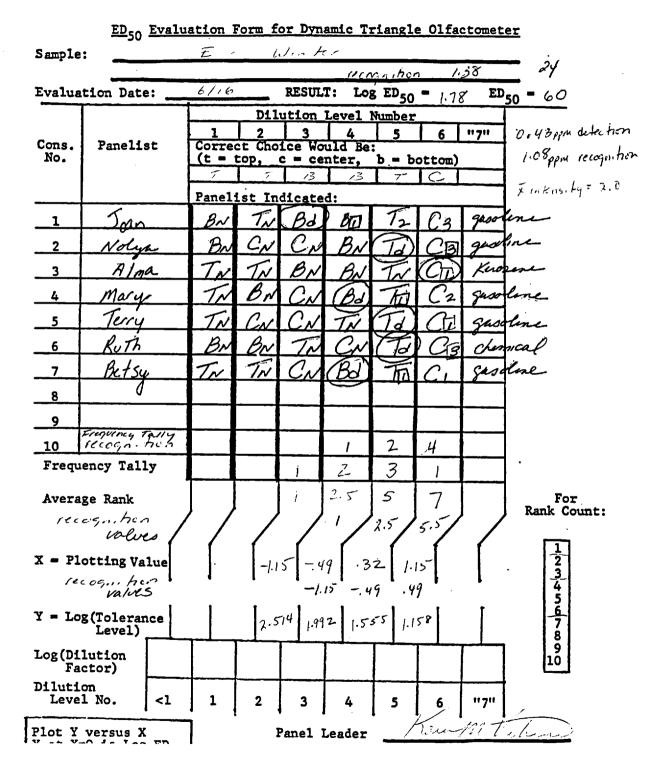


B-4

Not for Resale

• :

26 ppm

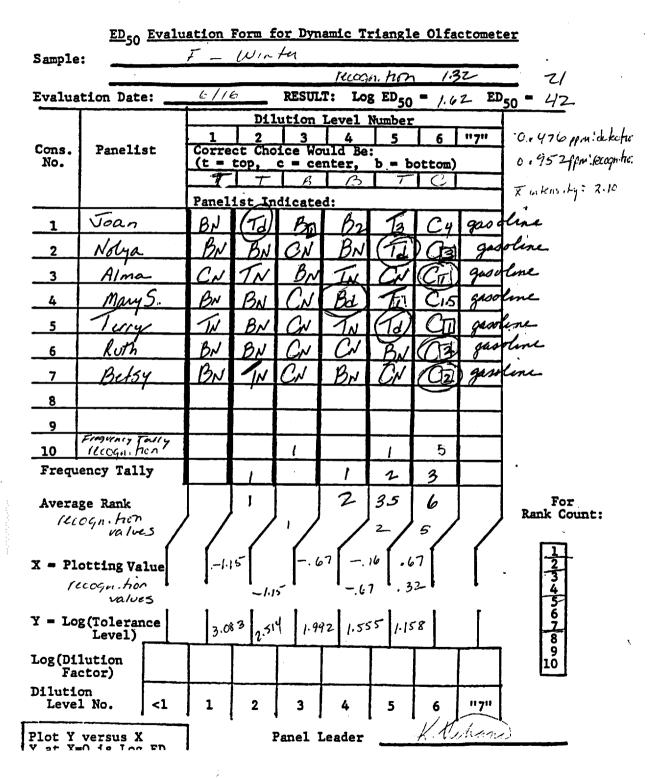




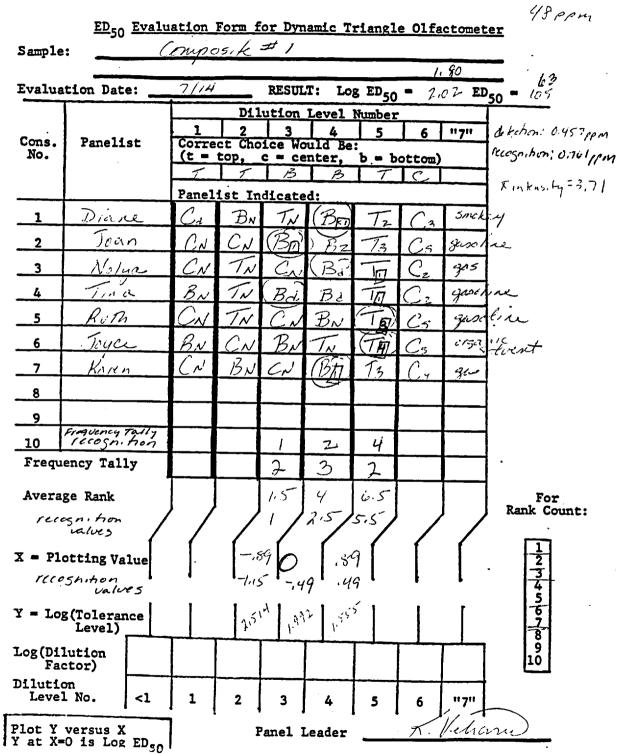
Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

• .

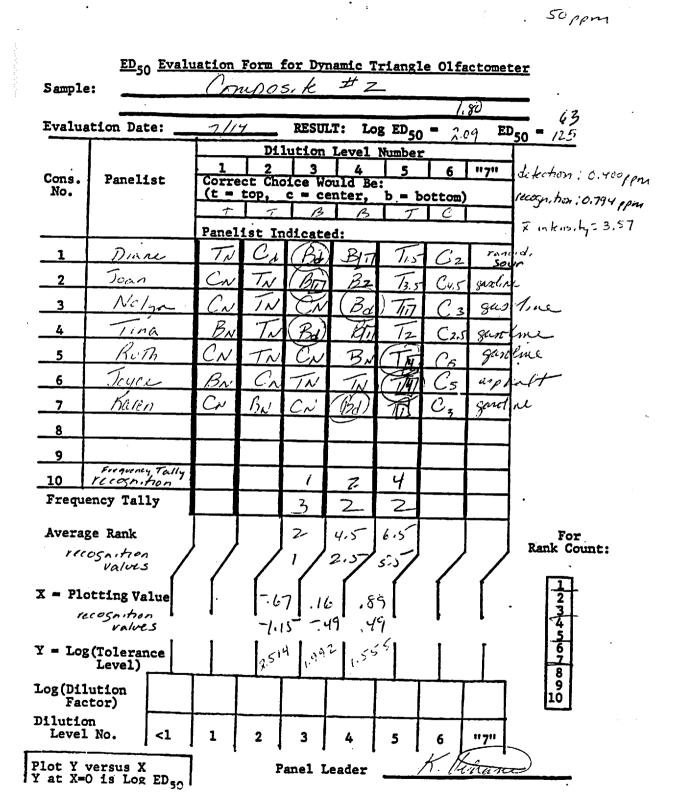
20 ppm



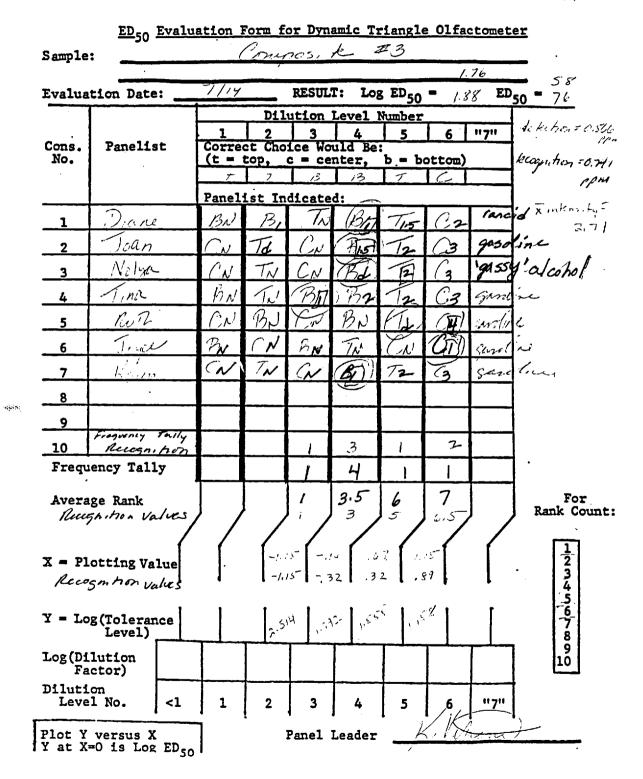




B-7



43 ppm





API PUBL*4592 94 🛲 0732290 0517462 773 페

.

:

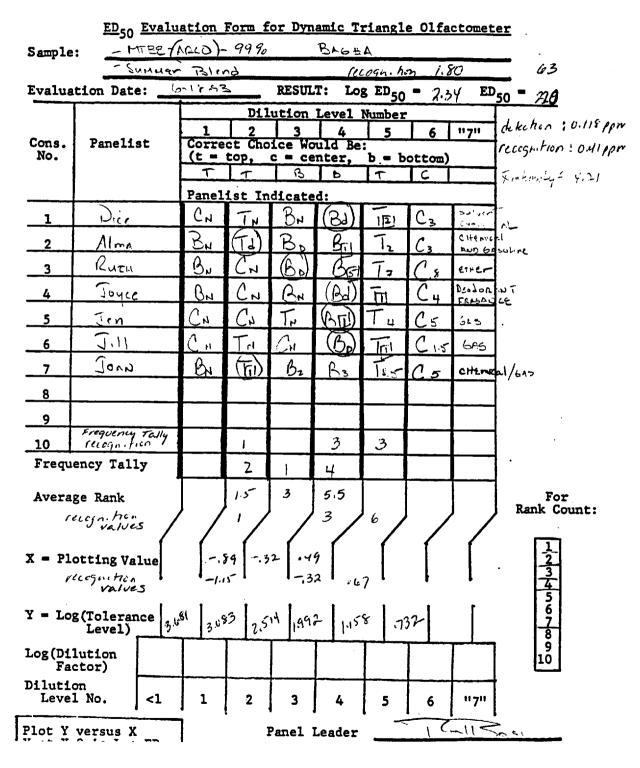
APPENDIX C

GASOLINE-OXYGENATE HEADSPACE VAPOR DATA SHEETS

Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

٠.



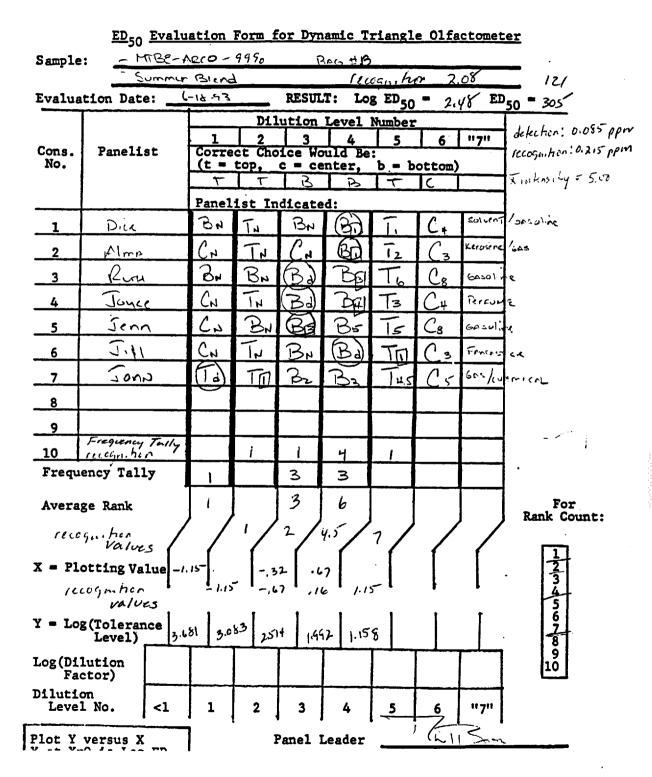


C-1

•

• •

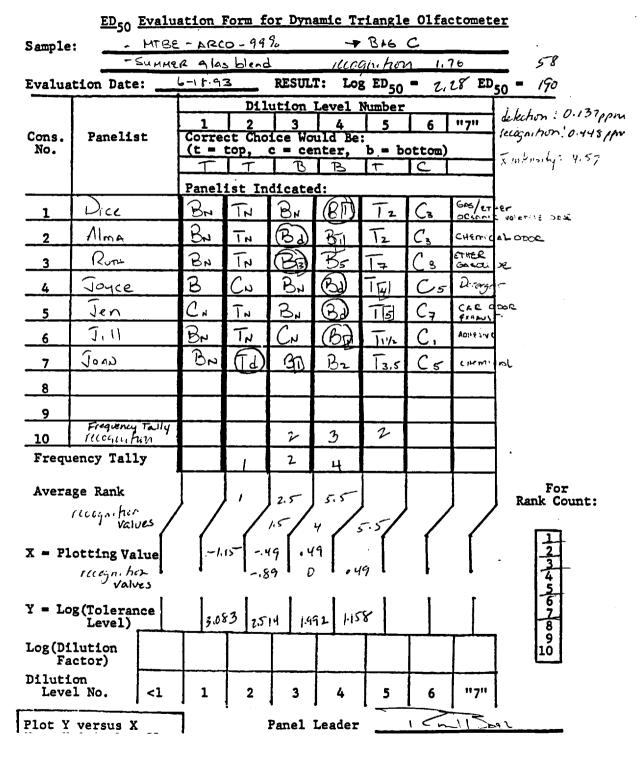
LOppm



C-2

• •

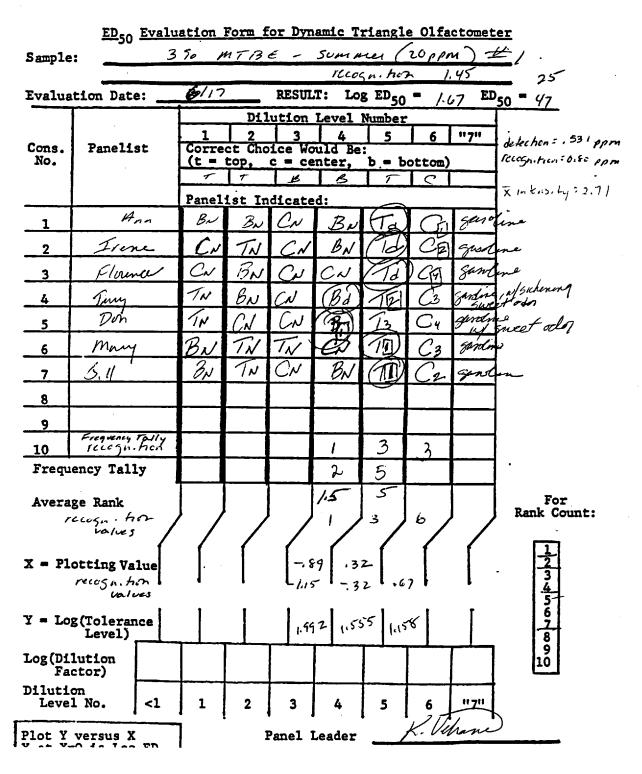
ZOppm



C-3

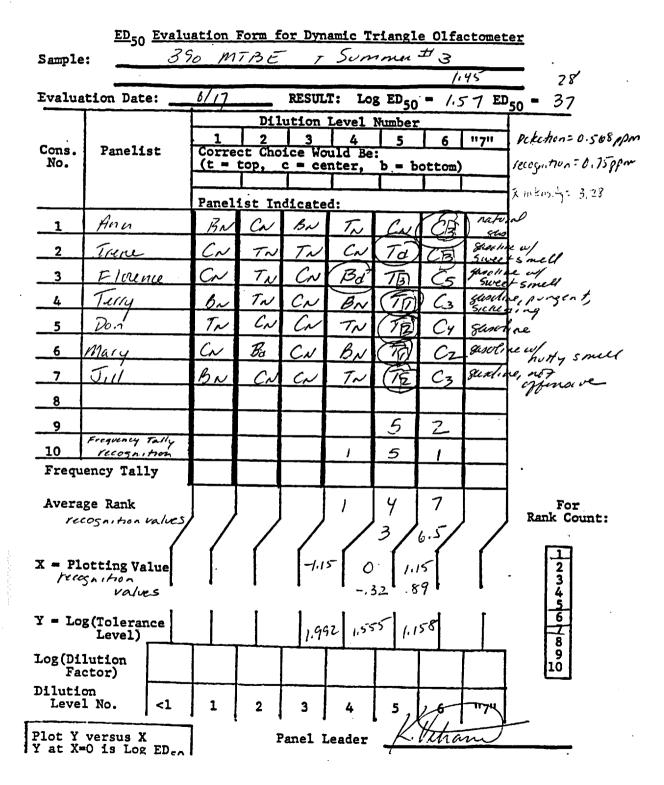
Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

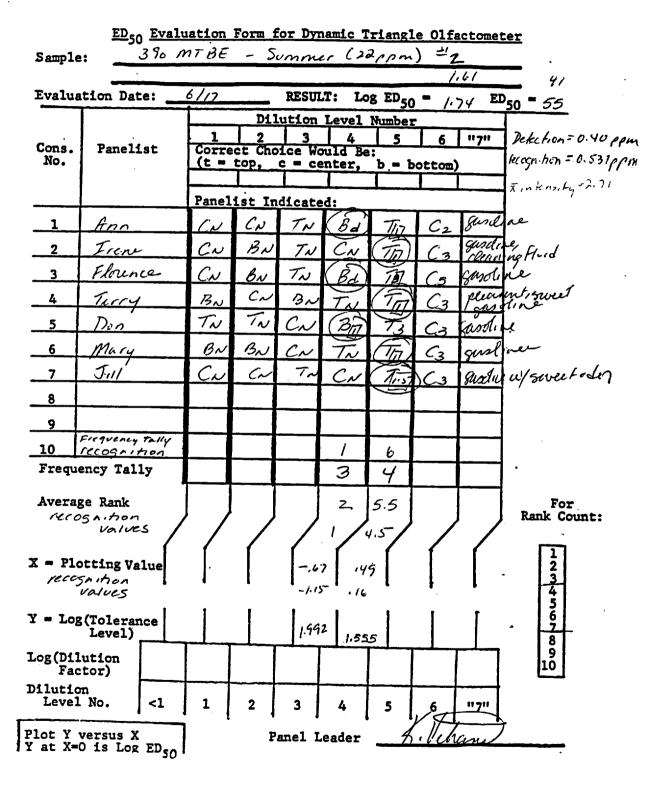
.



C-4

21 ppm

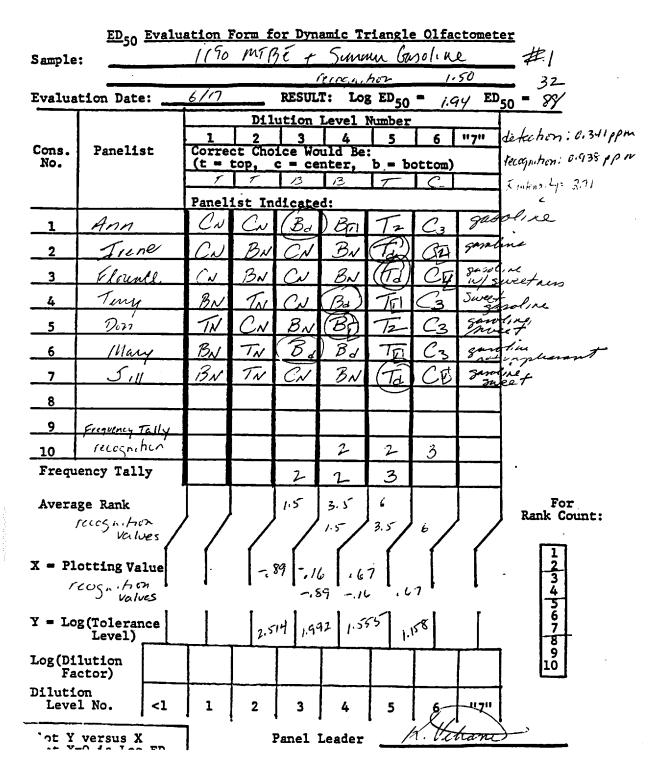




C-6

• :

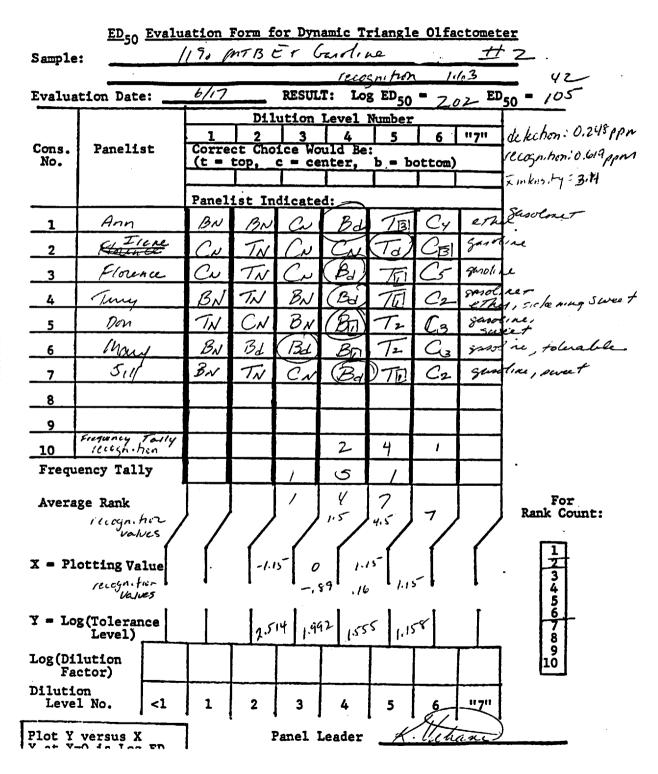




C-7

• •





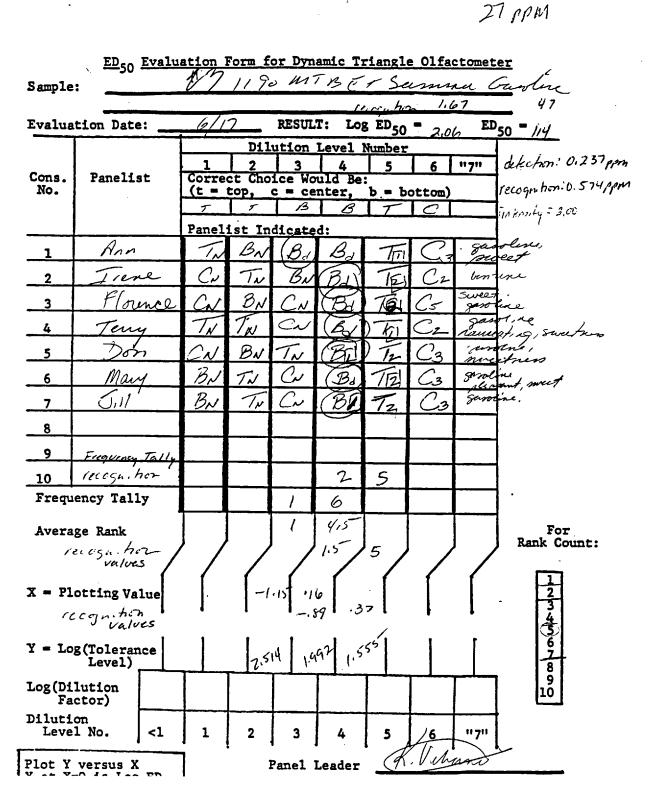
C-8

<u>ج</u>

٠

API PUBL*4592 94 🔳 0732290 0517471 786 📰

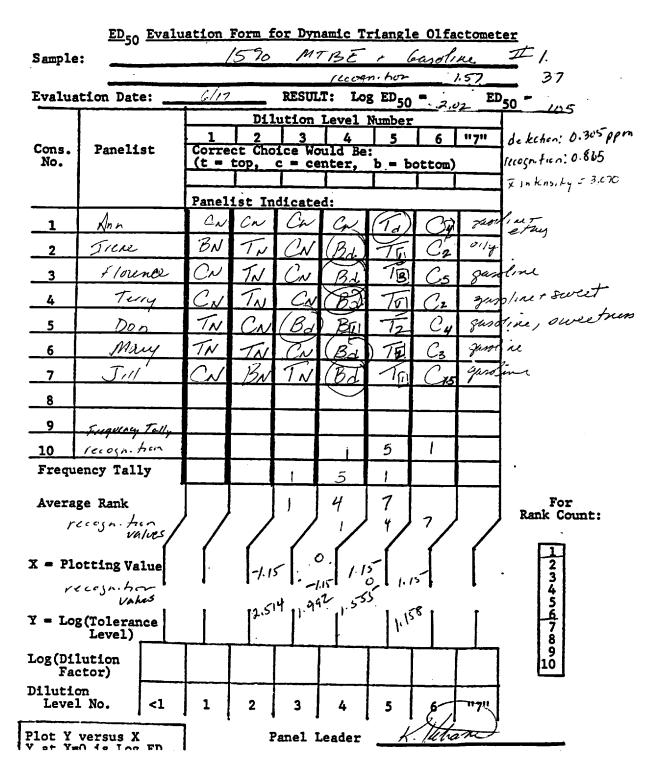
• .



C-9

• •

32 ppm

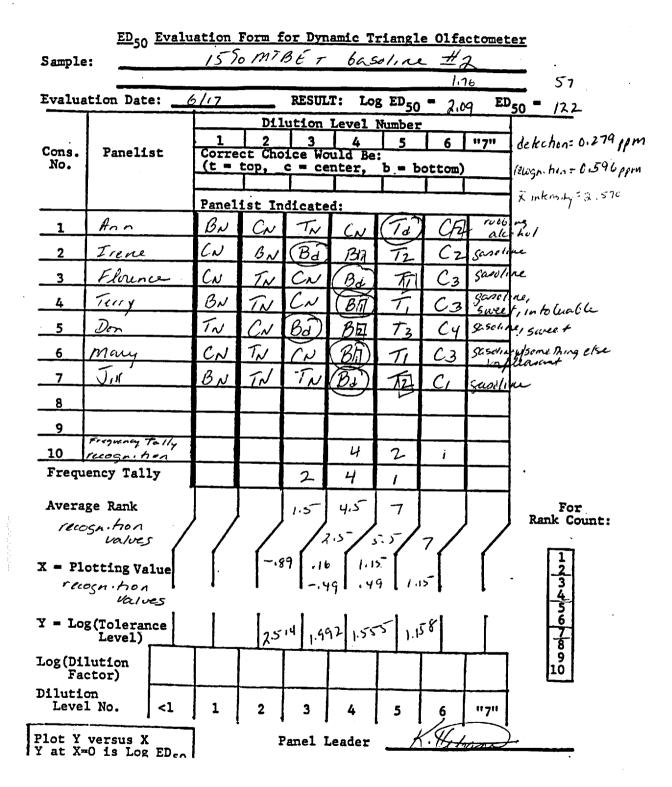


C-10

.

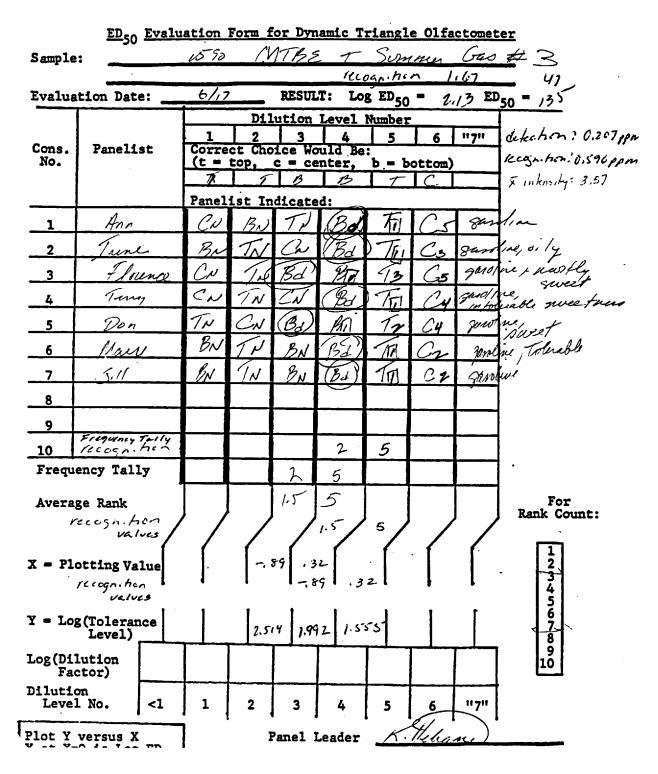
.

34 ppm



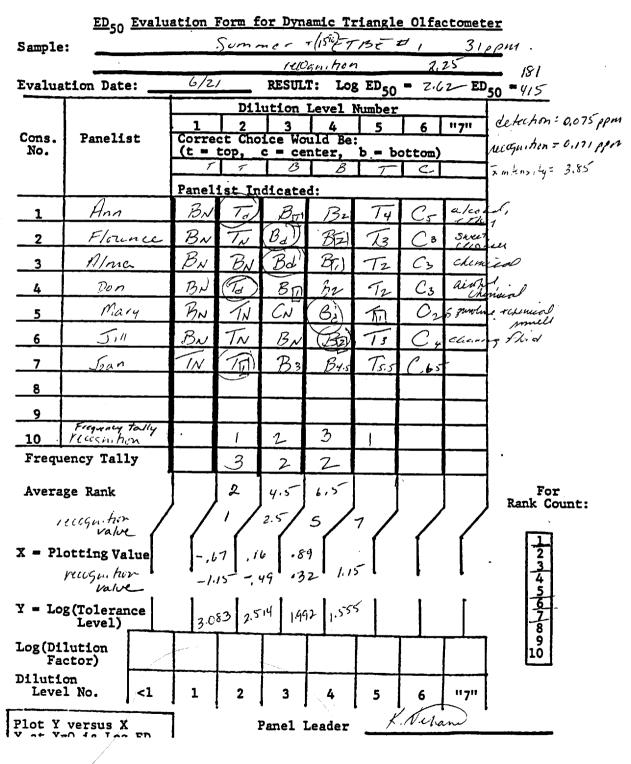






C-12

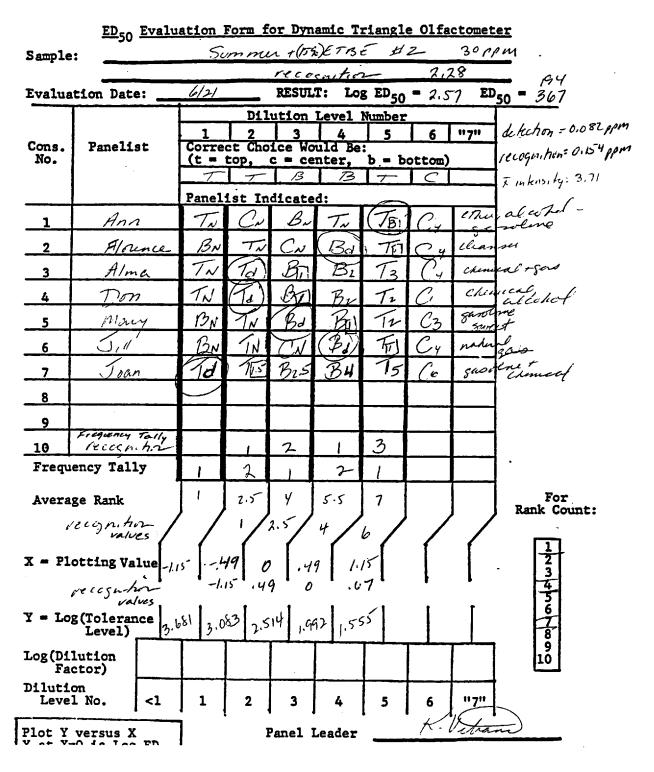
• •





• •

a



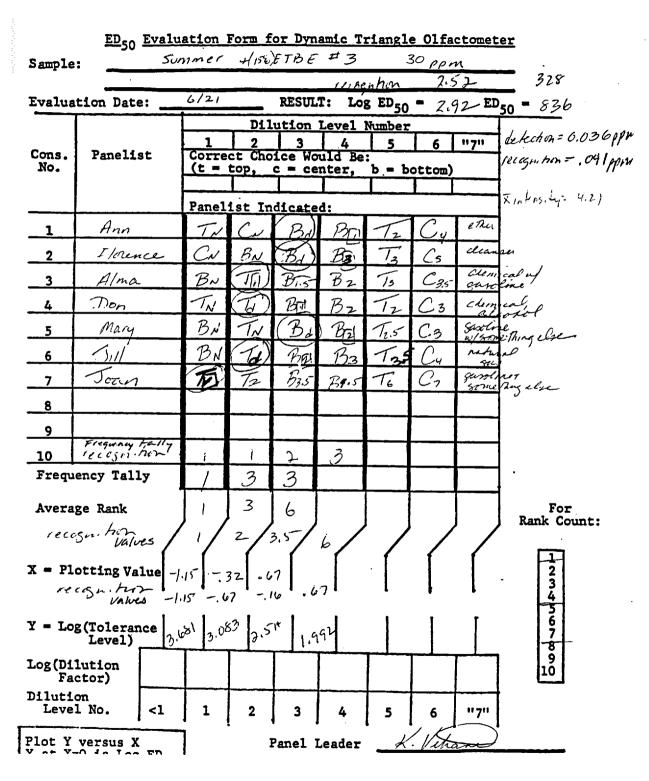
:

C-14

Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

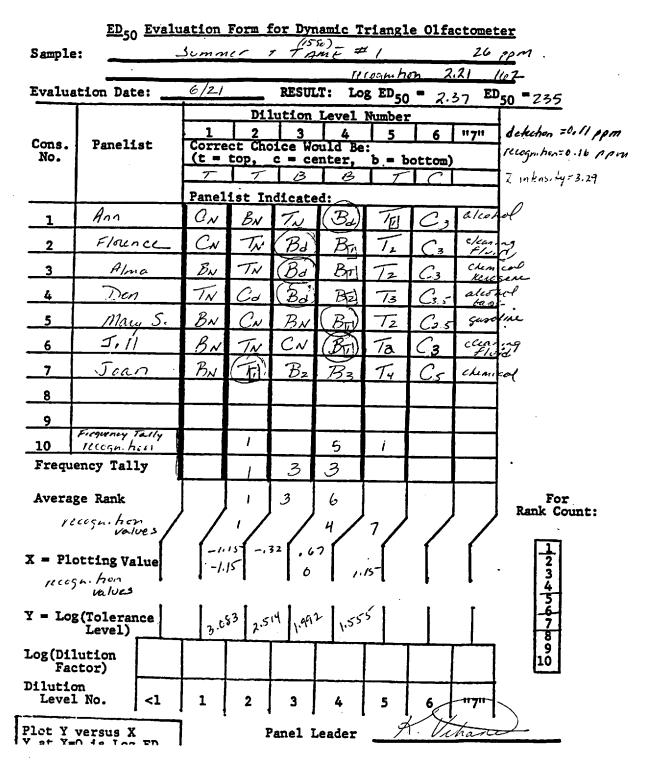
.

• :

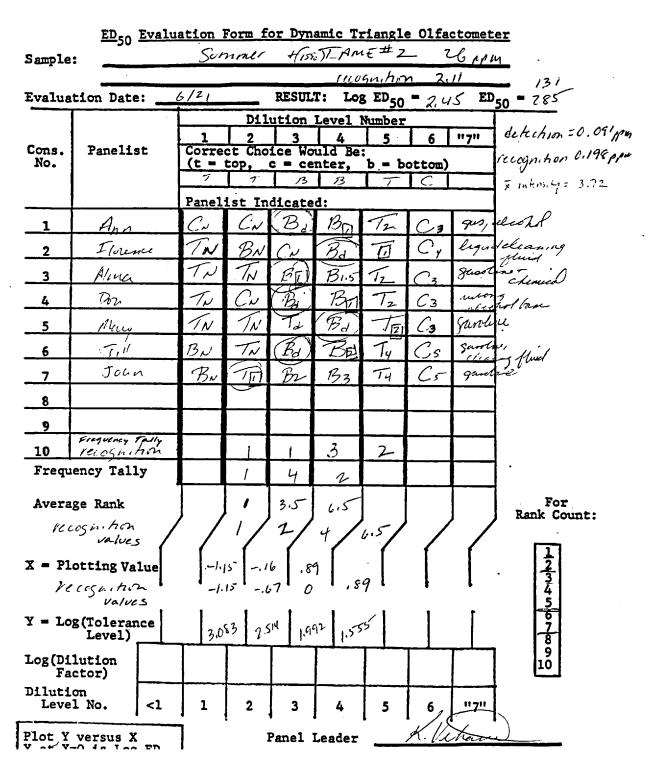


C-15

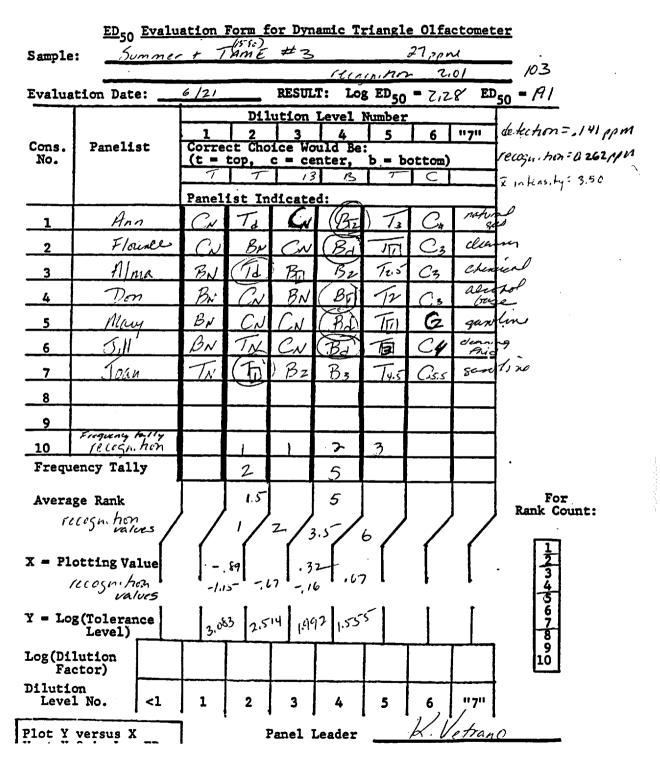
• :



C-16

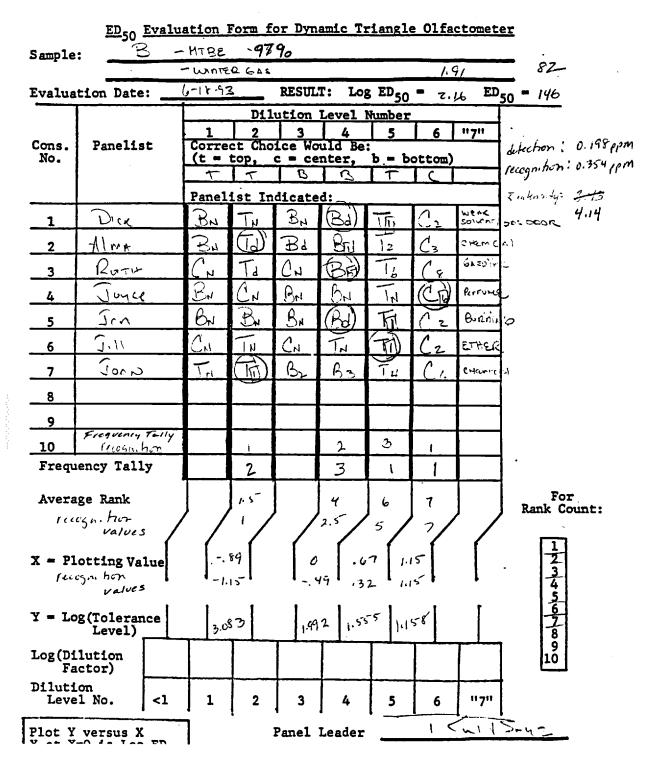






• 1

29ppm

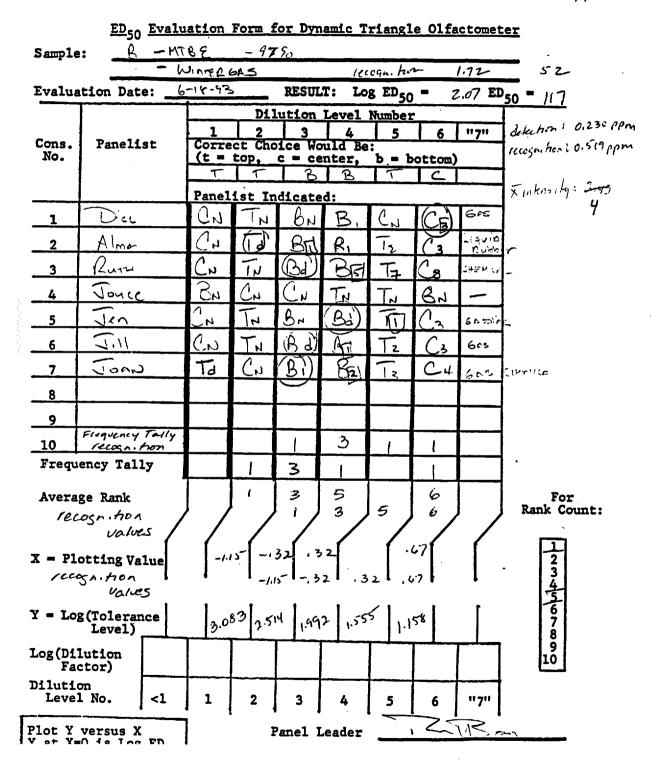


C-19

•

• .

27ppm

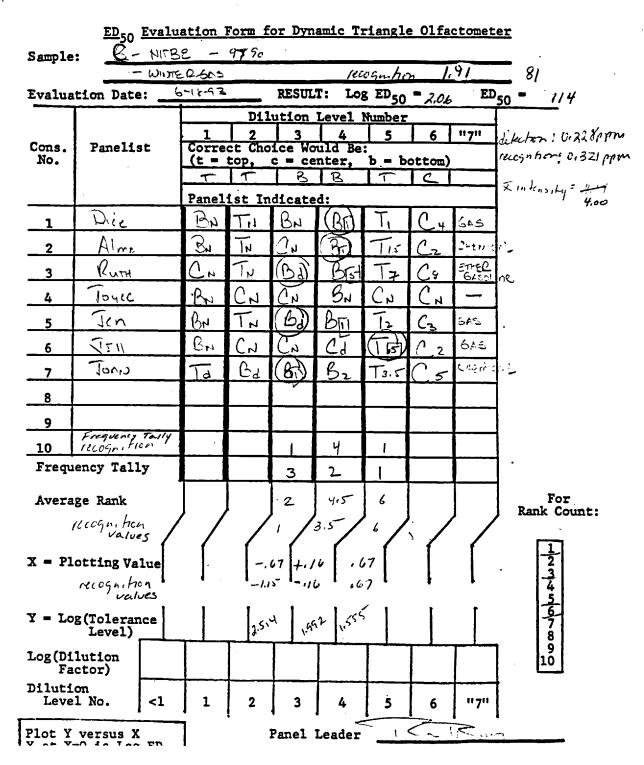


C-20

.

• .

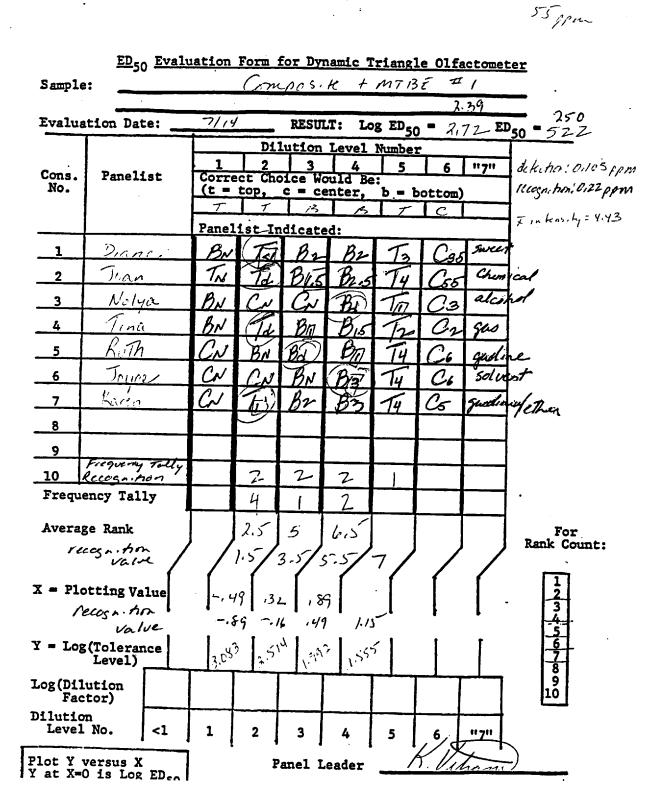
26 ppm





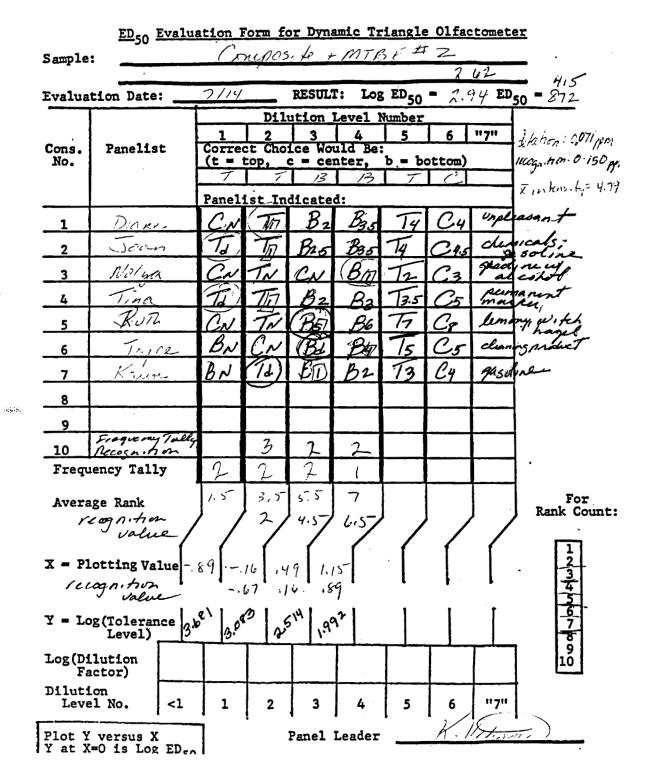
Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS

•



C-22

63 pran



C-23

.

•

. **:**

Sampl		Ĉ'n	n pop	~	r MIT			- 3	· ·
Evalu	ation Date:	71	14	RESU	LT: Lo	g ED ₅₀			238 50 718
	1	<u> </u>	ditection: C.C						
Cons.	Panelist	1	2	3	4 Juld Be	5	6	"7"	Pecage tion; D.1
No.	191161496	(t =							
		T	7	13	nter, 13	T	ottom)		K intensity= (
		Panel	ist In	dicate	ed:				
_1	Viane	10	The	B1.5	B2	72.5	C3	alco.	ko1
2	John	(\mathcal{F}_{1})	Th	B	72.5	13.5		chen	icals up
3	Notna	T.	TN	CN	BR	Tz	C		to 1
4	Tind	CN	T.	BA	\mathbf{S}	1	$\overline{\bigcirc}$	PLANO	
5	Run	CN		Bat	<i>D</i> /	12	<u>(4</u>	<u> </u>	marker
	Trace		TN		B7	18	<u>Cr</u>		line other
6	1	BN	CN C	DN	Bd	181	<u>C,6</u>		OTIK
7	Kener	CN	(1)	Bi	Bz	T3	<u>Cy</u>	900	
8									
9									
_10	Frequency Fully recognition		2	3		i			
Freq	ency Tally	2	2		2				•
Avore	ige Rank	1.5	3.5	5					For
	-		1.5	4	6.5 6	7		J	Rank Cou
	cognition values				· /	· /			
X = P1	otting Value	P9	16 .3	2 .8	, [. [1	ſ	3
	3 n. tron values	- 2	1	1 '		<u>_</u>			3
	- values		•			~ 1		• .	17 34 5
Y = Lo	dg(Tolerance على (Level)	81 3.0	3 25	14 1.9	92 155	5			9 10
Log(Di Fa	lution ctor)								9 10
Diluti Leve	on 1 No. <1	1	2	3	4	5	6	"7"	
Plot Y	versus X	<u>ו</u>		anel 1		Ľ	F	tom)

5 BRALL

.

C-24

www.

•

Not for Resale

Order No. 841-45920

API PUBL*4592 94 🎟 0732290 0517488 T&T 🖿

2

American Petroleum Institute 1220 L. Street, Northwest

Washington, D.C. 20005

