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DEVELOPMENT OF NEW GAS ODORANTS

report to

GAS RESEARCH INSTITUTE

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Arthur D. Little, Inc.

DEVELOPMENT OF NEW GAS ODORANTS

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Report to

GAS RESEARCH INSTITUTE

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Arthur D. Little, Inc.

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EXECUTIVE SUMMARY

A. BACKGROUND

The research program discussed in this report was performed under a Gas Research Institute contract (No. 5010-352-0047, dated May 22, 1978) as a continuation of the American Gas Association Project ID2-1 which was initiated in April 1975. The main objective of the program was the development of new odorants for natural gas which would be more resistant to adsorption by soils and to pipeline fading. It was understood that any new odorant developed should exhibit warning characteristics similar to or better than those currently used.

In our previous work,* we examined approximately 150 odorant candidates for odor characteristics, including 34 which we synthesized in our own laboratory. Seven of these showed appropriate intensity and quality at low concentrations and were selected for soil adsorption tests. We developed a simulated soil adsorption method, using highly adsorptive clay as the soil, and then compared our most promising candidates with commercial gas odorants. Several of our compounds compared favorably with, or were superior to, commercial odorants. One of the compounds, 3-methyl-3-pentanethiol, appears worthy of field testing.

We next determined the role of moisture as it affects odorant/soil interaction and we also investigated the effects of soil temperature and odorant concentration on adsorption. We found the moisture in soil to be the major parameter affecting adsorption of odorants. Soils with moisture contents above 5% showed no appreciable adsorption until they became dried by the gas.

While last year's work was concerned primarily with adsorption, this year's effort was directed toward the oxidation and pipeline fading of odorants. Our approach to this study included the development of a test which simulated pipeline fading and allowed us to measure the relative stability of existing and candidate odorants.

B. SUMMARY OF ACTIVITIES

1. Analysis and Selection of Substrate

Initially we examined and identified a group of iron oxide deposits from pipelines located in various parts of the United States. Analysis of the various pipeline deposits showed mainly three forms of iron oxide: Fe_3O_4, α-FeO(OH), and γ-FeO(OH).

In conjunction with the analyses of the pipeline deposits, we examined 11 pure iron oxide samples to determine their effectiveness in destroying the odor of tertiary butyl mercaptan (TBM).

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*Development of New Gas Odorants, AGA Project ID2-1, July 1978 and December 1977.

Of these 11 oxides, the form we found to be most effective in destroying odor was a yellow oxide* which had a structure corresponding to that of α-FeO(OH) or geothite. This oxide form was found in all of the pipeline deposits analyzed. Therefore, we selected a commercially available form of this iron oxide as the reference substrate for the odor stability and pipeline fading studies.

2. Development of Simulated Pipeline Fading Test

We also conducted tests to determine the best method of preparing columns packed with the yellow iron oxide to obtain reproducible and meaningful results. We tested two approaches: (a) columns packed with pure iron oxide, and (b) columns packed with iron oxide "coated" or mixed with an inert carrier. The latter approach was selected.

Based on the results of a series of exploratory studies, we prepared a column packing of α-FeO(OH) coated on Kel-F® beads which allowed us to simulate the loss of t-butyl mercaptan (TBM) in a reproducible fashion within an acceptable experimental time. Typically, we found that 80% of the initial concentration of TBM is reached in 6 hours, while tetrahydrothiophene (THT) reached that breakthrough level in one-half hour, and dimethyl sulfide (DMS) in one-quarter hour.

We evaluated several of the experimental odorants with this procedure in one or more trials, and these results indicated the possible effects of chain branching and steric hindrance. As necessary compounds, both odorants and reactants have been synthesized in adequate quantities to permit investigation under the test conditions. Having established an experimental protocol for comparing the behavior of odorants, we began to evaluate candidate compounds and also initiated odor and fading studies on odorant blends

3. Pipeline Fading Studies

We evaluated seven odorants (six of which were tertiary mercaptans) for stability, using our simulated pipeline fading test. We also examined dimethyl sulfide, tetrahydrothiophene, and the butyl mercaptan isomers. These compounds are listed below in order of decreasing pipeline stability:

Best	dimethyl sulfide	
	tetrahydrothiophene	
	3-methyl-3-pentanethiol	
	2,3-dimethyl-2-butanethiol	
	2,2-dimethyl-3-butanethiol	approximately the same
	2-methyl-2-pentanethiol	
	2-methyl-2-butanethiol	
	tertiary butyl mercaptan	
	1-methylcyclopentanethiol	
	1-methycyclobutanethiol	
	isobutyl mercaptan	
	2-butyl mercaptan	
Worst	n-butyl mercaptan	

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*Yellow iron oxide #4100, Cities Service Co., Columbian Division, Akron, Ohio.

The results observed with a TBM/ethyl mercaptan (EM) mixture showed that the iron oxide catalyst reacted preferentially with the EM rather than the TBM. Contrary to reports in the literature, we observed no evidence of TBM conversion caused by the lower molecular weight ethyl mercaptan.

4. Odorant Blends

We also examined several odorant blends in our odor test chamber to determine their dose response curves. Results of the odor tests of the blends showed that synergism occurs with certain mixtures of DMS and 3-methyl-3-pentanethiol. To our knowledge, TBM and DMS are the only commercially used combinations which exhibit this desirable effect.

We also tested odorant blends for stability, according to our simulated pipeline fading test, to determine whether or not blends might behave differently from a single compound. In the pipeline stability tests, the odorant blends evaluated behaved similarly to the individual compounds in the blend.

I. INTRODUCTION

A. BACKGROUND

Two major problem areas associated with present gas warning odorants are: (1) losses of odorant from natural gas by soil adsorption when underground leaks occur, and (2) odorant losses resulting from fading in both new and old pipelines. Since the initiation of this project we have been working on the development of a gas odorant which would be less strongly adsorbed by soils and less subject to fading in pipelines. As a result of earlier work, we developed methods to facilitate qualitative and quantitative odor-response measurements and we evaluated approximately 150 odorants. We also developed a simulated soil adsorption method using montmorillonite, a highly adsorptive clay that is widely found in soils throughout the United States. With this method, we made relative comparisons between commercial and new odorant candidates.

We synthesized 34 odorants in our laboratory, some of which, to the best of our knowledge, have never been prepared previously. Several appeared to have warning and soil-adsorptive properties comparable or superior to commercial odorants currently in use.

B. OBJECTIVES AND APPROACH

During 1978, we addressed our efforts primarily to determining the pipeline stability of our most promising candidate odorants as well as commercial odorants. Our goals were to:

(1) Develop a laboratory test to simulate pipeline fading;

(2) Determine the relative stability of our new odorant candidates for comparison with existing commercial odorants;

(3) Synthesize odorants and their breakdown products; and

(4) Investigate odorant blends for odor synergism and pipeline stability.

A primary reason for odorant loss in both new and old pipelines is the chemical change which occurs as a result of the catalytic action of active iron oxides. By analyzing pipeline deposits, we identified a highly active iron oxide, α-FeO(OH), which is present in both new and old gas transmission systems throughout the United States. Using this iron oxide, we developed a reliable simulated pipeline fading test to measure the relative stability of gas odorants. Synthesis work involved the preparation of disulfide analytical standards corresponding to those of the new mercaptan odorants and additional quantities of promising odorant candidates. Following development of the pipeline fading test, we compared the new odorants with commercial odorants for relative stability.

C. METHODOLOGY

As in the past work, the feed gas used during the 1978 study effort was high-purity 99.9% methane. The methodology consisted of metering the appropriate odorant into the gas stream after which the mixture passed through a column containing the iron oxide housed in a temperature-regulated chamber, and then to a Tracor 550 flame photometric detector. Moisture was measured in the gas stream before it entered the column and monitored continuously in the exit flow.

II. TECHNICAL DISCUSSION

A. ANALYSIS OF PIPELINE DEPOSITS

1. Approach

To determine the type and general composition of iron oxides present in pipelines, we obtained samples of rust and scale from gas mains located in different parts of the United States. These samples represented deposits from mains in the District of Columbia, Maryland, Virginia, New Jersey, Pennsylvania and Michigan, and included pipe interior rust from new wrapped steel. Although the deposits may not be representative of all pipeline deposits, we believe that they contained certain iron oxides which are common to most. We characterized these samples, along with rust and scale from new pipe, by X-ray diffraction and compared them with several high-purity iron oxides.

We first prepared a composite pipeline deposit sample by blending 30 individual deposits obtained from Washington Gas Light, Philadelphia Electric, and Consumer's Power. The blend was Soxhlet extracted with trichloroethylene to remove the hydrocarbons and odorous components. We then dried it at 65°C to volatilize the solvent. We examined this composite by X-ray diffraction and also studied its visible characteristics in an optical microscope.

The X-ray diffraction study of the composite clearly indicated the presence of an iron oxide-hydroxide, α-FeO(OH); its pattern was similar to, but less distinct than, a commercial yellow iron oxide reference sample. The X-ray diffraction pattern for the composite sample also showed that the crystal structure was not so well formed as that of the reference. For the composite material, the diffraction lines were broader, indicating possibly a smaller crystallite size and slight variations in hydration. There was also a large amount of amorphous or non-crystalline background.

Examination with the optical microscope showed that the composite consisted of a large mass of fairly large, totally opaque black particles, ranging from 25 to 100 microns (μ). A high percentage of these particles were attracted to a magnet. Although these larger magnetic particles constituted a substantial percentage of the sample, there was also an appreciable amount of smaller magnetic particles (below 5 μ). Some of these were red-brown in color and non-magnetic. The composite otherwise appeared to be relatively clean with no significant amount of contaminating material such as fiber, sand, or organic material.

Examination with the x-ray spectrometer showed the composite to be free of other elements. No other heavy element, except iron, was detected. Similarly, there was no evidence of sulfur or chlorine in the light element region.

Results of our x-ray diffraction studies of the composite and various pipeline deposits are summarized in Table 1. Also included in this table are analyses of a group of commercial samples serving as reference standards. Both yellow iron oxide standards yielded patterns corresponding to geothite ($\frac{1}{2}\,Fe_2O_3 \cdot H_2O$) which is often referred to as α-FeO(OH). The other hydroxide type found in the pipe deposits, γ-FeO(OH), or lepidocrocite, showed a darker red color.

TABLE 1

X-RAY DIFFRACTION STUDIES OF PIPELINE DEPOSITS AND IRON OXIDE REFERENCE STANDARDS

Deposit or Reference Standard	Source	Type of Iron Oxide	
Composite of 30 Pipeline Deposits	Washington Gas Light	α-FeO(OH)	75%
	Philadelphia Electric	γ-FeO(OH)	25%
	Consumer's Power		
Rust Deposit #1	Washington Gas Light	α-FeO(OH)	20%
(new wrapped steel)		γ-FeO(OH)	10%
		Fe_3O_4	70%
Rust Deposit #2	Washington Gas Light	α-FeO(OH)	30%
(new wrapped steel)		γ-FeO(OH)	30%
		Fe_3O_4	40%
Pipeline Deposit	Philadelphia Electric	α-FeO(OH)	100%
West Conshohocken			
Pipeline Deposit	Philadelphia Electric	Fe_3O_4	35%
Atglen, N.J.		α-FeO(OH)	30%
		γ-FeO(OH)	10%
		SiO_2	20%
Pipeline Deposit	Consumer's Power	α-FeO(OH)	20%
Charlotte, Michigan		γ-FeO(OH)	10%
		Fe_3O_4	60%
Yellow Iron Oxide	Whittaker, Clark & Daniels	α-FeO(OH)	
Cosmetic Grade #7055	Plainfield, N.J.		
Yellow Iron Oxide #4100	Cities Service	α-FeO(OH)	
	Akron, Ohio		
Crimson Iron Oxide #108	Cities Service	α-Fe_2O_3	
Red Iron Oxide #617	Cities Service	α-Fe_2O_3	
Brown Iron Oxide #422	Cities Service	γ-Fe_2O_3	
Black Iron Oxide #7053	Cities Service	Fe_3O_4	

2. Selection of Substrate

We next contacted manufacturers of iron oxides and procured different types of pure compounds. To determine the form of iron oxide which was most effective in destroying gas odorant, we devised the following static system as a rapid screening technique:

> Three grams of the iron oxide were placed in a 4-oz French square bottle. One-half ml of a 2-ppm* tertiary butyl mercaptan (TBM) in alcohol solution was then added and the bottle capped and shaken. Odor examinations were performed by an odor panel at hourly intervals for 7 hours, and finally after 24 hours. All samples were shaken uniformly at interim periods prior to and following the odor evaluations. A control containing TBM only was examined along with the test samples.

We screened 11 different iron oxides for effectiveness in reducing TBM odor. Their particle sizes ranged from 0.4-1.1 μ and their shapes were acicular, spheroidal, and cubical. The pH's of the iron oxides ranged from 6.0-9.0. These compounds are listed in Table 2.

TABLE 2

IRON OXIDES EXAMINED FOR ODOR REDUCTION

Compound	General Formula	Source
Black iron oxide (cosmetic grade)	Fe_3O_4	Whittaker, Clark & Daniels, Plainfield, N.J.
Brown iron oxide (cosmetic grade)	–	Whittaker, Clark & Daniels, Plainfield, N.J.
Yellow iron oxide (cosmetic grade)	α-FeO(OH)	Whittaker, Clark & Daniels, Plainfield, N.J.
Transparent iron oxide red #444	–	BASF Wyandotte Corp., Parsippany, N.J.
Brown iron oxide #422	$(FeO)_x(Fe_2O_3)_y$	Cities Service Co., Columbian Div., Akron, Ohio
Crimson iron oxide #108	Fe_2O_3	Cities Service Co., Columbian Div., Akron, Ohio
Red iron oxide #617	α-Fe_2O_3	Cities Service Co., Columbian Div., Akron, Ohio
Red iron oxide #516	Fe_2O_3	Cities Service Co., Columbian Div., Akron, Ohio
Black iron oxide (magnetite) #7053	$FeO \cdot Fe_2O_3$	Cities Service Co., Columbian Div., Akron, Ohio
Yellow iron oxide #4100	α-FeO(OH)	Cities Service Co., Columbian Div., Akron, Ohio
Magnetic pigment #81066	–	Wright Industries, Inc., Brooklyn, N.Y.

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*Original screening with 4-ppm TBM resulted in odor intensities too high for the panel.

Although all of the oxides showed some activity, the following three compounds – all pure synthetic iron oxides – were found to be the most effective in destroying TBM odor:

	General Formula	Particle Size (μ)	Shape	pH
Yellow iron oxide #4100	α-FeO(OH)	1.00	Acicular	6.0
Black iron oxide #7053	$FeO \cdot Fe_2O_3$	0.50	Cubical	9.0
Crimson iron oxide #108	Fe_2O_3	1.10	Acicular	5.0

The yellow iron oxide #4100 showed the greatest amount of activity, with no odor evident after 24 hours. It should also be noted that a substantial quantity of an iron oxide similar to this yellow oxide was found in each of the pipeline deposits analyzed, including the two samples of interior rust from new wrapped steel.

Transparent red #444, and magnetic pigment #81066 reduced TBM odor, but at a slower rate. Red #617, red #516, cosmetic brown, and brown #2 were not very effective in reducing TBM odor.

Results of our odor-screening tests of the three most effective iron oxides are shown in Figure 1. We also screened a sample of the montmorillonite used in last year's adsorption experiments for comparative purposes to demonstrate the effect of odorant adsorption versus catalytic decomposition. Figure 1 shows that the yellow 4100 FeO(OH) is the most active iron oxide. The rate of odor decrease from the first six hours approaches that of montmorillonite, and odor reduction is complete within 24 hours.

As our x-ray diffraction studies of the composite pipeline deposit showed the presence of an appreciable amount of amorphous material in addition to the crystalline form of iron oxide, we decided to investigate the catalytic activity of amorphous oxides. Since we could find no commercial source, we prepared some amorphous product by reacting ferric chloride with aqueous ammonia. The gelatinous precipitate was washed, dried, and screened by the static bottle technique for effectiveness in destroying TBM odor. Results of the screening test showed that this "amorphous" iron oxide had little, if any, catalytic effect. Therefore, we made no attempt to determine its composition, and, in fact, discontinued further work on an amorphous iron oxide substrate.

B. ODOR FADING IN PIPELINES

Quantitative measurements of odorant fading can be carried out by using the test system and instrument set-up used in our previous studies on odorant adsorption by soil.*

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*Development of New Gas Odorants, AGA Project Number ID2-1, report to Gas Research Institute, December 1977.

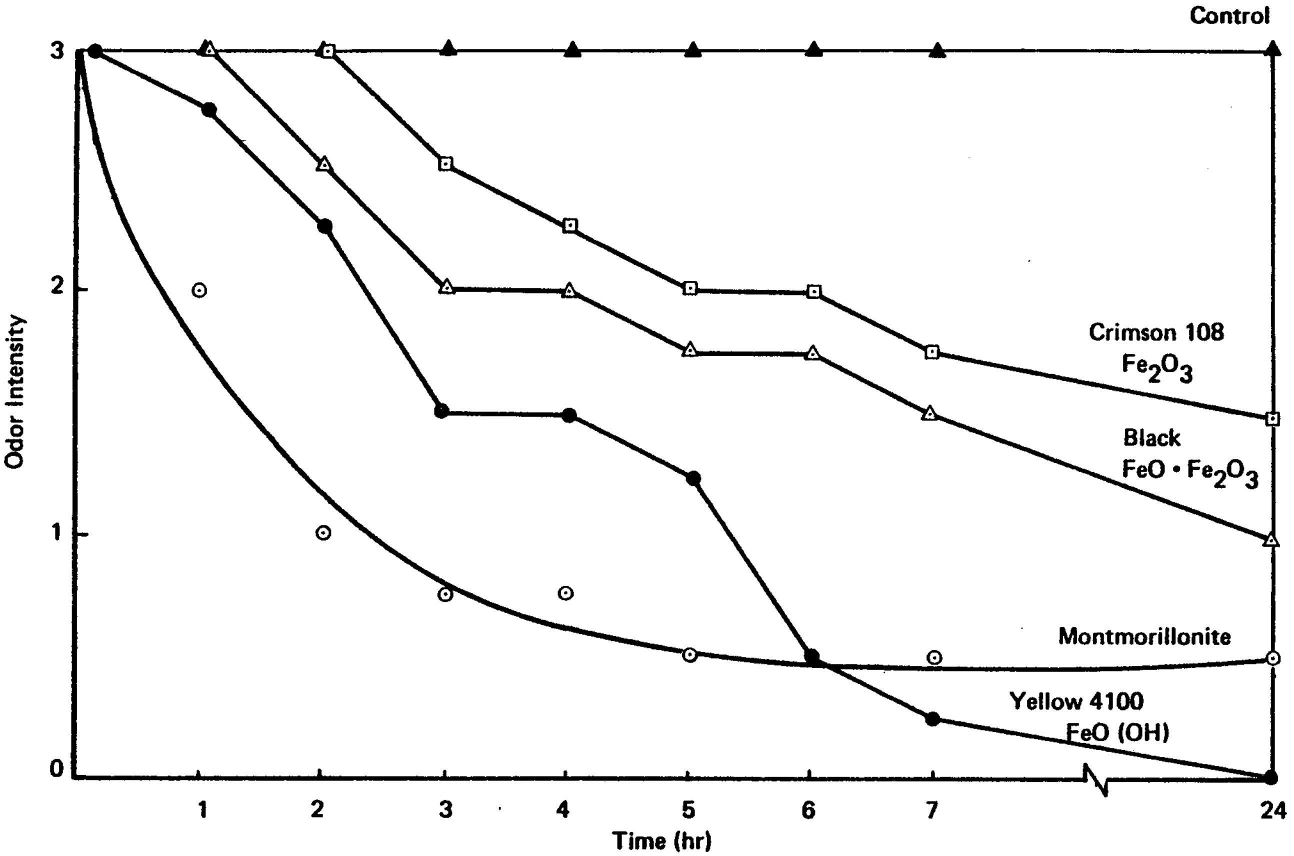


FIGURE 1 SCREENING OF IRON OXIDES FOR ODOR REDUCTION
(3 Grams of Iron Oxide—TBM 2ppm)

In lieu of the montmorillonite columns used for those studies, we used columns containing the iron oxide specie of interest for these fading tests. We examined different methods of preparing the column packing material to obtain reproducible results and information that would allow meaningful comparative evaluation of the various odorants to be tested. The fading tests were designed so they could be completed within an 8-hour working day.

For reasons described earlier, we used yellow iron oxide (#4100, 0.5 to 1.1 μ)* for these studies. We used two methods to prepare the substrate for evaluation in a column bed.

In the first approach, we agglomerated the fine powder by preparing large pellets on a Carver press (15,000 psi on the ram), and then crushed and screened the pellets to the desired mesh size. We then packed the screened particles directly into a column.

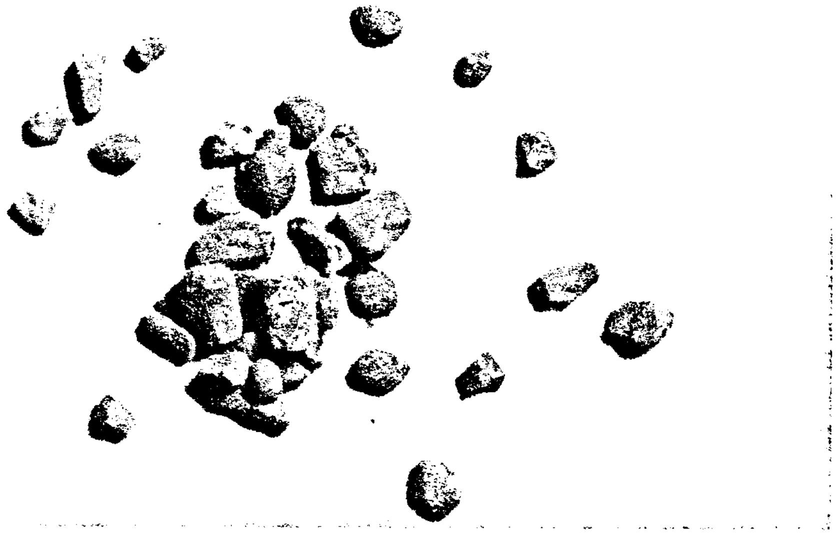
In the other method, we mixed the iron oxide powder with an inert carrier, such as glass or Kel-F® plastic beads.** This approach offered greater flexibility since the amount of oxide could be varied without changing the column dimensions. We therefore used the following procedure to prepare and coat the beads:

> *Glass beads, 20/30 mesh, and Kel-F® 300LD beads, 30/40 mesh, were precleaned by extraction with methanol in a Soxhlet extractor for 4 hours. The beads were heated overnight at 100°C to remove any residual solvent and were then placed in a desiccator prior to coating with the iron oxide.*
>
> *The uncoated glass and Kel-F® beads were separately screened for inertness by packing a piece of Teflon tube, 11.5 cm long x 0.48 cm ID, with either 2.5 g of glass beads or 1.0 g of Kel-F® beads. These columns exhibited a pressure drop across the tubes of 5 and 6 cm of water, respectively, at a gas flow rate of 150 ml per minute. When an odorized methane stream containing 5 ppm of tertiary butyl mercaptan (TBM) was passed through either one of these tubes, all of the TBM passed through the packing unaltered.*

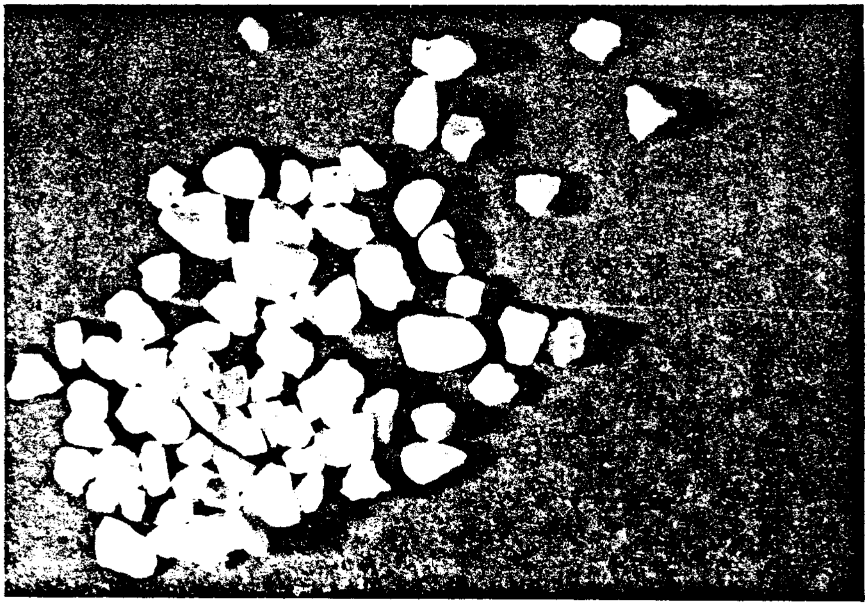
In subsequent experiments, we added known and controlled amounts of iron oxide to weighed batches of glass and Kel-F® beads. These initial tests showed that the iron oxide adheres to the Kel-F® beads better than it does to glass and also produces a more uniform coating. To determine the uniformity of the iron oxide coating on the Kel-F® substrate, photomicrographs (Figure 2) were prepared at 5X magnification. Examination of the coated substrate showed good adhesion and coverage. Thus, we used the Kel-F® beads as the inert carrier for all subsequent work.

***Source:** Cities Service Co., Columbian Division, Akron, Ohio.

****Source:** Kel-F® Analabs, Inc., No. Haven, Conn. (a subsidiary of New England Nuclear).



Kel-F® Coated with FeO(OH)



Uncoated Kel-F®

FIGURE 2 **KEL-F® SUBSTRATE – UNCOATED AND COATED WITH FeO(OH) (Magnification 5X)**

1. Studies with Coated Kel-F® Beads

In preliminary experiments we passed odorized gas through columns containing beads coated with various percentages of iron oxide. The tests were performed under the following conditions:

Methane flow rate:	155 cc/min
TBM odorant:	1 lb/MMCF = 4.4 ppm (volume basis)
Temperature:	80°F. (26.6°C)

Exploratory columns tested for TBM fading contained Kel-F® beads coated with yellow iron oxide #4100 at levels of 1.0, 6.7, and 13.0%, and packed in Teflon tubing 11.5 cm x 0.48 cm ID. Since this size column holds 1.0 g of the coated packing, the three columns, respectively, contained 10, 67, and 130 mg of iron oxide. Methane odorized with TBM (1 lb/MMCF) was passed through the column at ambient temperature (80°F). TBM and the corresponding oxidation product, tertiary butyl disulfide (TBDS), were observed to elute at longer times as the iron oxide loading was increased.

Figure 3 shows the effect of three different levels of iron oxide on TBM. In addition to percent TBM (output/input x 100), we also plotted information on the rate of appearance of TBDS. Since calibration of the system for the TBDS response had not been performed at the time of these experimental runs, the disulfide data are based on a direct reading of detector output in log peak height units.

The data show that the breakthrough times and amounts of both TBM and TBDS are functions of the amount of iron oxide on the substrate. A 100% breakthrough of TBM occurred within 5 minutes for the 10-mg loading, and with 130 mg of iron oxide a 90% breakthrough was observed after approximately 4 hours.

Similarly, the TBDS was observed early (40 min) when 10 mg of iron oxide were used, and much later at the higher loadings. The observations noted are attributable to the effect of both adsorption and catalysis as catalytic action goes through the cycle of adsorption, reaction, and desorption of the products.

2. Columns Packed with Iron Oxide Pellets

Preliminary experiments using the crystalline yellow iron oxide, α-FeO(OH), as a substrate at ambient temperature indicated that this iron oxide caused complete fading of TBM under conditions approximating those occurring in a gas main. We also found that a column 7.5 cm long by 0.48 cm ID and packed with 0.6 g of iron oxide substrate would remove all of the TBM from a gas steam for a period of at least 5 hours.

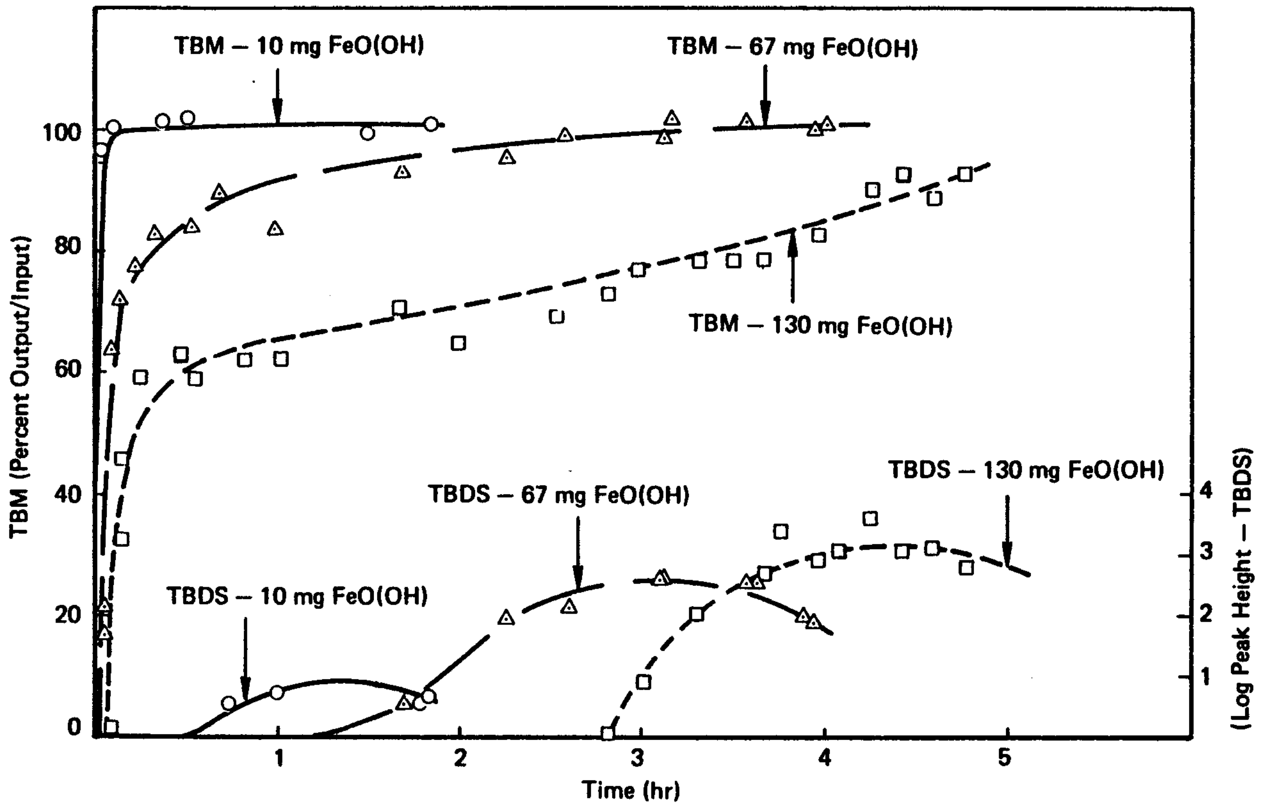


FIGURE 3 DECOMPOSITION OF TBM ON IRON OXIDE COATED KEL-F® BEADS

It was suggested that the iron oxide be examined following a TBM test run to determine whether any changes had taken place. The FeO(OH) was removed from the carrier and examined by x-ray diffraction. The x-ray diffraction of the oxide appeared to be identical to FeO(OH) which had not been exposed to TBM. A small amount of sulfur detected by x-ray fluorescence was estimated at not more than 100 ppm.

C. BREAKTHROUGH EXPERIMENTS

1. Background

As a result of our work in 1976 and 1977, we developed methods for comparing the permeation of commercial gas odorants – DMS, TBM and THT – through adsorptive soils. We also obtained, or synthesized, a number of alternate compounds and evaluated them for odor intensity and quality. Those which showed promise compared to commercial odorants (odor intensity, type, and soil penetration) under standard conditions were selected as candidates to be evaluated for resistance to pipeline fading.

2. Test Protocol

We selected the test conditions for evaluating the pipeline stability of new odorants on the basis of our being able to differentiate between stable and unstable commercial odorants, using the active iron oxide α-FeO(OH). To accomplish this, we optimized and refined our preliminary tests to demonstrate different degrees of stability or odor fading within an 8-hour time frame. A column packing consisting of 200 mg of FeO(OH) coated on 4.0 g of 10/20 mesh Kel-F® beads was found to be most suitable. Packed in a 0.48-cm ID Teflon tube, this quantity of substrate resulted in a column length of 19 cm. With a methane flow rate of 155 cc/min, the pressure drop was 13-14 cm of water. The odorant concentration was held at 16 mg/m^3 (1 lb/MMCF) and temperature was maintained at 75°F (24°C). We did not examine the effects of moisture in these studies, but moisture was monitored continuously and controlled within the 10-20 ppm range. These conditions were used for virtually all of the pipeline fading studies.

3. Statistical Analysis of Breakthrough Experiments

We decided to conduct replicate experiments on four odorants of primary interest to confirm the empirical relationship of breakthrough rate as a function of time. By repeating test conditions, it was possible to establish the precision of estimated breakthrough times and test for significant differences among the four odorants. We conducted a total of 14 tests, 4 each with tetrahydrothiophene (THT) and dimethyl sulfide (DMS) and 3 using tertiary butyl mercaptan (TBM) and 2,3-dimethyl-2-butanethiol (DMBT). Results of these tests are summarized graphically in Figures A-1 through A-4 of the Appendix.

To measure the precision, or reproducibility, of this experiment, we analyzed the data given in Table 3 according to a statistical technique known as the Analysis of Variance (ANOVA). This technique is one of the most effective statistical tools used to analyze experimental data. In this case, each observed breakthrough time is assumed to consist of two measurable components; namely, an effect due to the specific odorant considered, plus an effect due to the inherent variability in the data. This latter term, known as "experimental error," accounts for random variation in observed breakthrough times when identical test conditions are repeated. By comparing the variation among average times for different odorants to the variation within replicates, it is possible to test the hypothesis that there is, in fact, *no difference* in observed breakthrough time among the different odorants tested. Breakthrough times from the curves at four different reference points were analyzed by this method; namely, the time of initial breakthrough (θ_B), and the times at which 20, 50, and 80% concentrations were detected (θ_{20}, θ_{50}, and θ_{80}, respectively).

TABLE 3

RESULTS OF REPLICATE EXPERIMENTS
(minutes to breakthrough)

Replicate	TBM	DMBT	THT	DMS	
1	14	61	19	1	Initial Breakthrough Time (θ_B)
2	16	70	16	1	
3	12	64	8	1	
4			25	1	
1	24	71	21	1	Time at 20% Breakthrough (θ_{20})
2	24	77	19	1	
3	27	78	16	1	
4			29	1	
1	112	91	25	2	Time at 50% Breakthrough (θ_{50})
2	147	90	25	2	
3	160	100	24	2	
4			33	2	
1	356	148	29	12	Time at 80% Breakthrough (θ_{80})
2	354	162	30	10	
3	346	158	35	9	
4			38	4	

We conducted separate analyses for each of the four breakthrough levels. The ANOVA results indicated remarkably consistent estimates of experimental error which, as stated above, measures the inherent variability in the data that cannot be "explained" by a known or controllable source.

For illustrative purposes, the ANOVA result for the set of 10 initial breakthrough times (excluding DMS) given in Table 3 is presented below:

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square
Equality of odorants	2	5116	2558.00
Within odorants (experimental error)	7	200	28.57
Total	9	5316	

We excluded DMS data from these calculations since breakthrough was essentially instantaneous and clearly different from the other three odorants considered. The experimental error variance (S^2) in the above example is estimated to be 28.57, and this value can be used to construct confidence interval estimates. For example, the average initial breakthrough time (θ_B) for the three replicates using TBM was 14 minutes. By calculating the interval:

$$\bar{\theta}_B \pm t \sqrt{\frac{S^2}{n}}$$

where n = 3 and t represents a tabular value based on distribution theory, we can make a probability statement about the "true" average initial breakthrough time for TBM as follows:

$$14 \pm 2.365 \sqrt{\frac{28.57}{3}} = 14 \pm 7.3 \text{ minutes.}$$

Therefore, this experiment indicates that the interval (6.7 to 21.3 minutes) includes the true (but unknown) average time at which initial breakthrough of TBM will occur, with a probability of 0.95. Similar 95% confidence interval estimates are given in Table 4.

TABLE 4

95% CONFIDENCE INTERVAL ESTIMATES OF MEAN BREAKTHROUGH TIMES (minutes)

	θ_B	θ_{20}	θ_{50}	θ_{80}
TBM	6-22	19-31	78-202	345-359
DMBT	57-73	69-81	86-101	149-163
THT	10-24	16-27	20-33	27-39
DMS	–	–	–	3-15

In addition to demonstrating experimental reproducibility, these results support the following conclusions:

- DMS and THT do not show significant pipeline fading.
- DMS breakthrough is significantly faster than all other odorants at each percentile level considered.
- THT and TBM are equivalent up to θ_{20}; THT then exibits a much faster rate at θ_{50} and θ_{80}.
- DMBT exhibits a slower rate than TBM initially, but requires significantly less time to achieve 80% breakthrough.

D. CHEMICAL STRUCTURE AND DISULFIDE BEHAVIOR

1. Chemical Structure

Tests, mostly in triplicate, were run on each of the following odorants:

dimethyl sulfide (DMS),
tetrahydrothiophene (THT),
n-butyl mercaptan (NBM),
isobutyl mercaptan (IBM),
sec-butyl mercaptan (2BM)
2,3-dimethyl-2-butanethiol (DMBT),
tertiary butyl mercaptan (TBM).

Table 5 summarizes the chemical structures of these odorants, while Table 6 indicates potential oxidation products that can be formed as well as the boiling point for the parent and oxidation compound (disulfide).

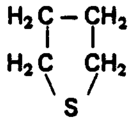
TABLE 5

CHEMICAL STRUCTURE OF ODORANTS EVALUATED

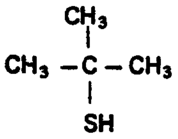
dimethyl sulfide (DMS)

$CH_3 - S - CH_3$

tetrahydrothiophene (THT)



t-butyl mercaptan (TBM)

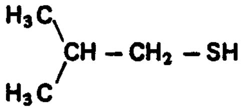


$$CH_3 - \underset{\displaystyle SH}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - CH_3$$

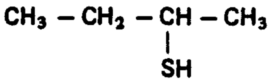
n-butyl mercaptan (NBM)

$CH_3 - CH_2 - CH_2 - CH_2 - SH$

isobutyl mercaptan (IBM)

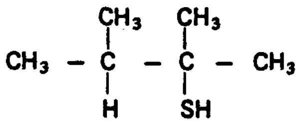


sec-butyl mercaptan (2BM)



$$CH_3 - CH_2 - \underset{\displaystyle SH}{\underset{|}{CH}} - CH_3$$

2,3-dimethyl-2-butanethiol (DMBT)

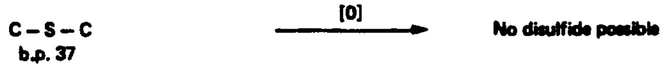


$$CH_3 - \underset{\displaystyle H}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - \underset{\displaystyle SH}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - CH_3$$

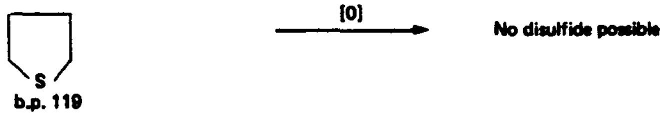
TABLE 6

POTENTIAL OXIDATION PRODUCTS

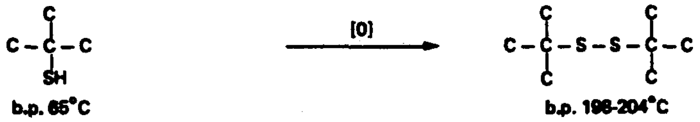
DMS



THT

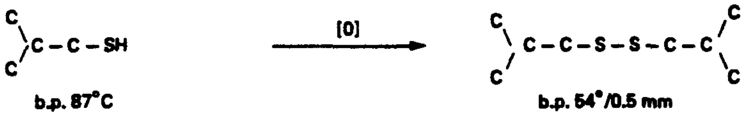


TBM

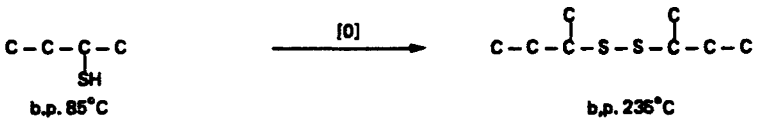


NBM

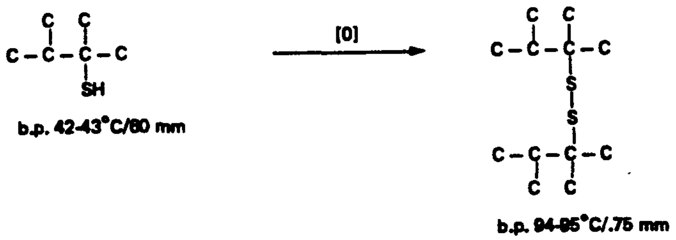
IBM



2BM



DMBT



TBM was the only butyl mercaptan isomer which, when passed through the iron oxide column, showed both the mercaptan and disulfide forms (See Figure A-1). For the n-butyl, isobutyl, and sec-butyl mercaptans, only the disulfide form was observed (see Figure 4). This indicates the greater stability of TBM to oxidation by iron oxide as compared to its isomers whose thiol group is sterically less hindered.

Disulfide formations from the butyl mercaptan isomers are shown in Figure 4. The t-butyl disulfide exhibited a somewhat erratic breakthrough and more than 100% was reported. This was undoubtedly due to elution of residual disulfide from the column.

Tertiary butyl disulfide, a small molecule which is presumably less strongly adsorbed, appeared in the effluent before the other disulfides. This may be due to the lower boiling point and consequently higher vapor pressure than the other disulfides. It is also possible that the methyl groups shielding the sulfur can minimize the attractive forces on the sulfur which would help explain the early penetration.

Isobutyl disulfide and 2-butyl disulfide showed similar breakthrough times and patterns, while n-butyl disulfide, which is the least branched, was held up or adsorbed on the column for a longer period of time.

Figure 5 shows representative curves of odorant penetration through iron oxide by THT, DMS, TBM, and 2,3-dimethyl-2-butanethiol (DMBT). Additional raw data for these compounds may be found in the Appendix (Figures A-1 through A-4). DMS and THT, as expected, show greater stability than the mercaptans. The initial breakthrough time for DMS was instantaneous, while that for THT was approximately 10 minutes. Both penetrated the iron oxide rapidly with 100% breakthrough occurring approximately 40 minutes into the run. It appears that only small amounts of THT and DMS adsorbed or reacted relative to the mercaptans.

It is interesting to note that the DMBT which was synthesized at Arthur D. Little penetrated the iron oxide at a much more rapid rate than TBM, although the initial breakthrough was approximately 40 minutes later. It has been suggested that DMBT may have a greater inductive effect and therefore be more resistant to oxidation than TBM, but this has not been proved. Another possible explanation is that there is greater shielding of the thiol group in DMBT by the methyl groups; this should prevent contact with the active FeO(OH) sites. We did not observe any breakdown product (disulfide) from DMBT. There is a possibility that some was formed, but was held up on the iron oxide column due to its high boiling point.

2. Disulfide Synthesis

Five disulfides were synthesized for use as analytical standards in our simulated pipeline fading studies. These compounds, which are listed below, were prepared by treating the sodium salt of the parent thiol with iodine in tetrahydrofuran:

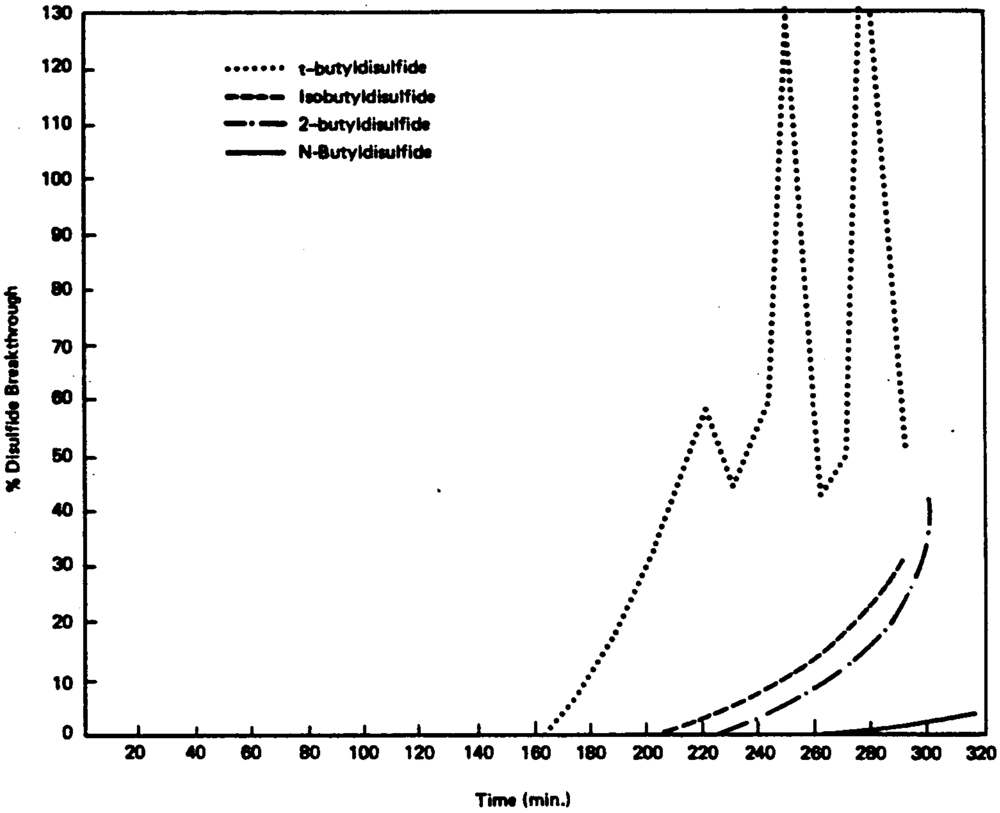


FIGURE 4 DISULFIDES FROM BUTYL MERCAPTAN ISOMERS

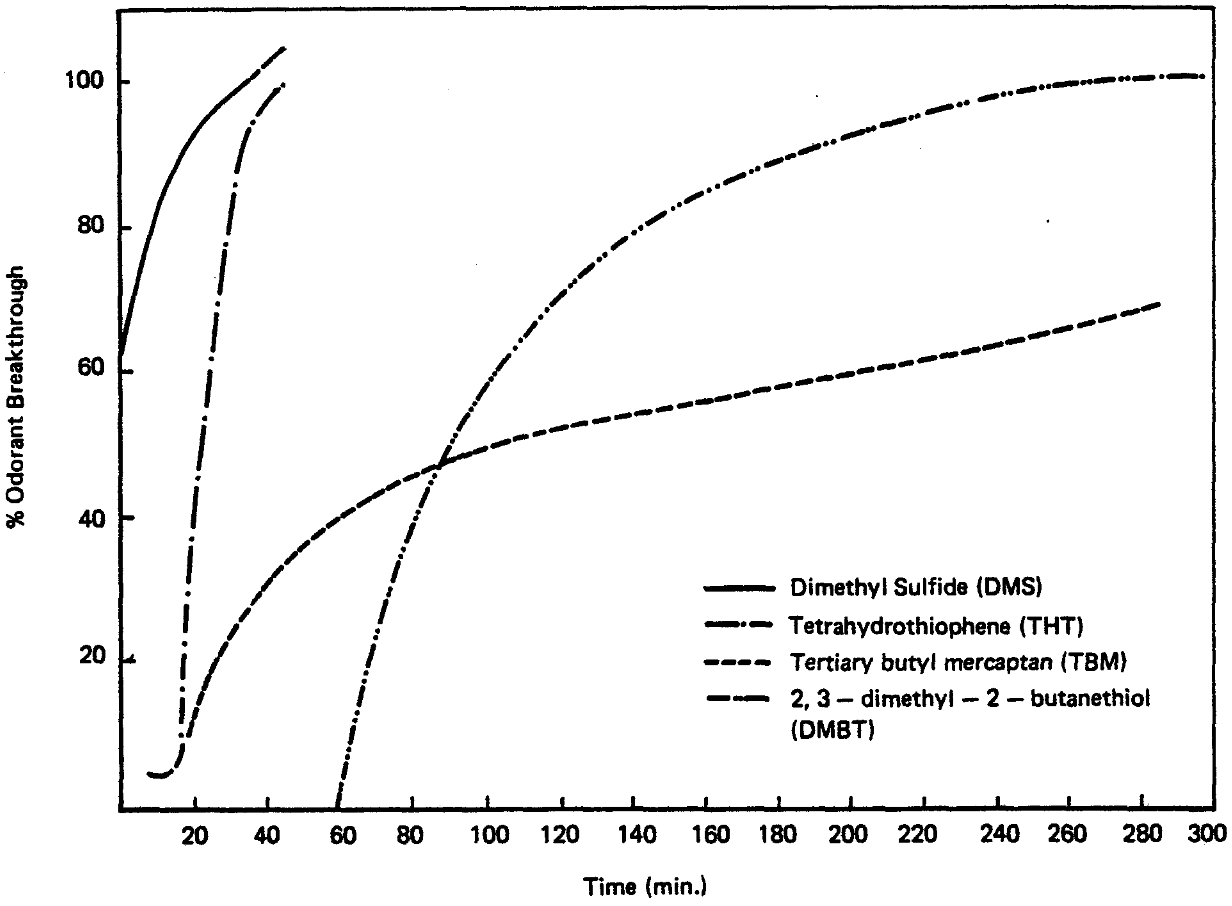


FIGURE 5 ODORANT PENETRATION THROUGH IRON OXIDE

isobutyl disulfide
secondary butyl disulfide
3-methyl-3-pentyl disulfide
2,2-dimethyl-3-butyl disulfide
2,3-dimethyl-2-butyl disulfide

E. SIMULATED PIPELINE FADING OF SINGLE ODORANTS AND BLENDS

1. Single Odorants

The following odorants, all but one of which were synthesized at Arthur D. Little, Inc., were also evaluated:

1-methylcyclobutanethiol
1-methylcyclopentanethiol
2-methyl-2-pentanethiol
2,2-dimethyl-3-butanethiol
3-methyl-3-pentanethiol.

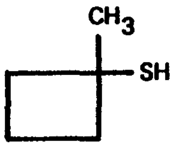
These compounds were synthesized last year and found to be most promising from the standpoint of odor intensity and soil penetration. Structural formulas are shown in Figure 6.

As in the preceding tests, all of the compounds were examined at a concentration of 1.0 lb/MMCF. The column was packed with 200 mg of FeO(OH) mixed with 4.0 g of Kel-F®. Results of these tests are shown in Figures 7 and 8. For comparative purposes, we have included TBM and 2,3-dimethyl-2-butanethiol tests.

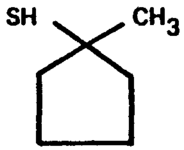
Pipeline stability of odorants is shown to be structurally related and appears to be dependent upon steric hindrance. The 3-methyl-3-pentanethiol which shows the greatest stability has two ethyl groups which could hinder or inhibit the approach of the odorant's thiol group to the catalyst surface. The 3-methyl-3-pentanethiol, 2,3-dimethyl-2-butanethiol, 2,2-dimethyl-3-butanethiol and 2-methyl-2-butanethiol are isomers with the same molecular weights and empirical formulas, but are structurally different.

It is interesting to note that the 2,2-dimethyl-3-butanethiol and 2-methyl-2-pentanethiol have approximately the same stability. The former is a highly hindered secondary mercaptan, and with its t-butyl and methyl groups represents the highest degree of hindrance of any of the secondary mercaptans evaluated. The latter compound is a tertiary mercaptan. The least stable odorant, 1-methylcyclobutanethiol, is the least hindered.

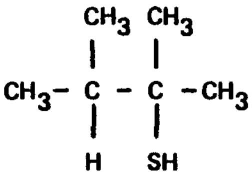
1—methylcyclobutanethiol



1—methylcyclopentanethiol

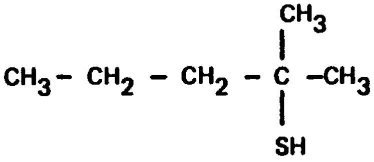


2,3—dimethyl-2-butanethiol



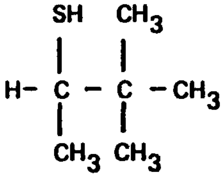
$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{SH}{\overset{CH_3}{C}}-CH_3$

2—methyl-2-pentanethiol



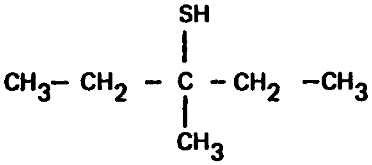
$CH_3-CH_2-CH_2-\underset{SH}{\overset{CH_3}{C}}-CH_3$

2,2—dimethyl-3-butanethiol



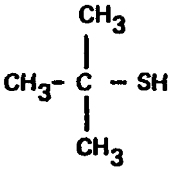
$H-\underset{CH_3}{\overset{SH}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

3—methyl-3-pentanethiol



$CH_3-CH_2-\underset{CH_3}{\overset{SH}{C}}-CH_2-CH_3$

tertiary butyl mercaptan*



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-SH$

*Commercial odorant.

FIGURE 6 STRUCTURAL FORMULAS OF ODORANTS

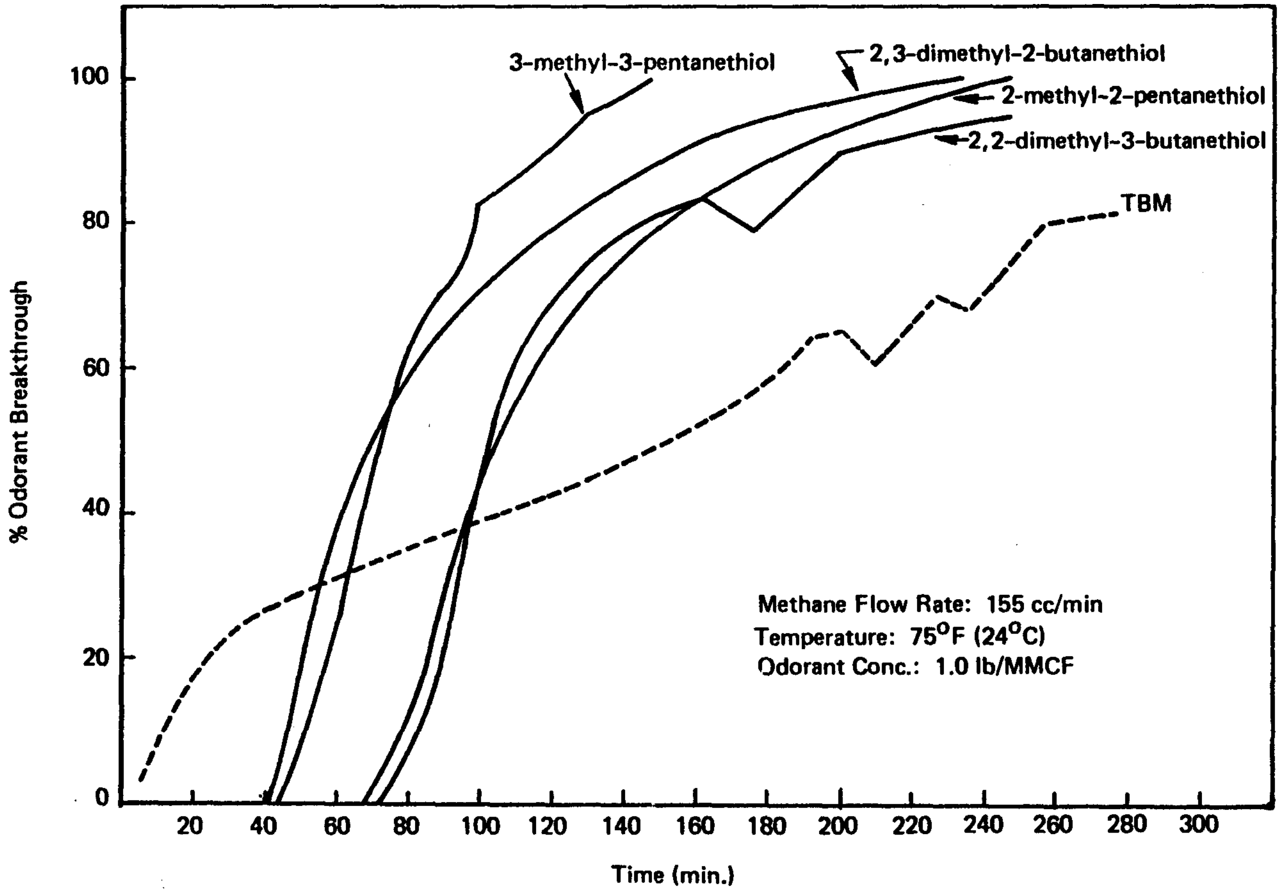


FIGURE 7 **SIMULATED PIPELINE FADING TESTS**

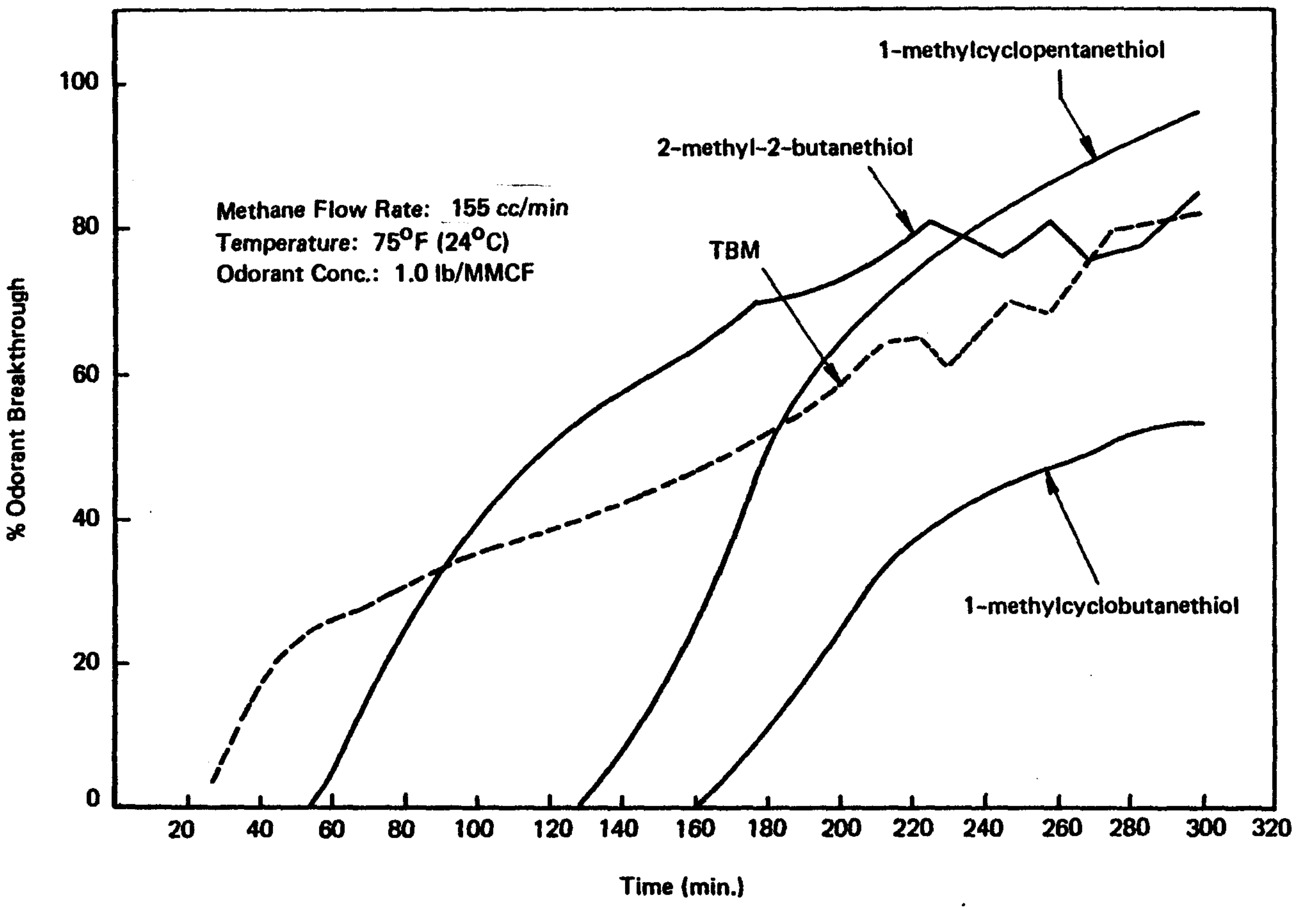


FIGURE 8 SIMULATED PIPELINE FADING TESTS

Our tests showed that these odorants fall in the following order of decreasing pipeline stability:

Best
dimethyl sulfide
tetrahydrothiophene
3-methyl-3-pentanethiol
2,3-dimethyl-2-butanethiol
2,2-dimethyl-3-butanethiol } approximately the same
2-methyl-2-pentanethiol }
2-methyl-2-butanethiol
tertiary butyl mercaptan
1-methylcyclopentanethiol
1-methylcyclobutanethiol
isobutyl mercaptan
2-butyl mercaptan
n-butyl mercaptan
Worst

2. Stability Evaluation of Odorant Blends

3-methyl-3-pentanethiol, 2,3-dimethyl-2-butanethiol, and tertiary butyl mercaptan were each blended 50:50 with DMS and examined for stability to determine whether blends might behave differently from a single compound. One-half lb/MMCF of each odorant was used, resulting in a total concentration of 1.0 lb/MMCF in the methane. Results of the odorant blend tests are shown in Figures 9, 10, and 11. Figure 12 is a composite of these tests. The blends behaved similarly to the individual odorants. As would be expected, the breakthrough and build-up times were greater than those shown in Figures 7 and 8 because the individual odorant concentrations were less.

At the suggestion of one of the project monitors, ethyl mercaptan and a tertiary butyl mercaptan/ethyl mercaptan blend were examined for stability using the simulated pipeline fading test. The ethyl mercaptan alone was run for 5 hours under the standard test conditions [odorant conc. 1 lb/MMCF; flow rate 155 ml/min, temp. 75°F (24°C)] and there was no evidence of any ethyl mercaptan breakthrough. However, ethyl disulfide was observed after 90 minutes and increased steadily during the remainder of the run. The ethyl mercaptan was completely converted to the disulfide.

A tertiary butyl mercaptan/ethyl mercaptan blend (5:1) was also run under similar test conditions with the same concentration of TBM (1.0 lb/MMCF), but a total concentration of 1.2 lb/MMCF. After 20 minutes, TBM was observed and it increased more rapidly than normal until 90% breakthrough was observed (3 hours into the run). This indicates that the catalyst reacted preferentially with the ethyl mercaptan rather than the TBM.

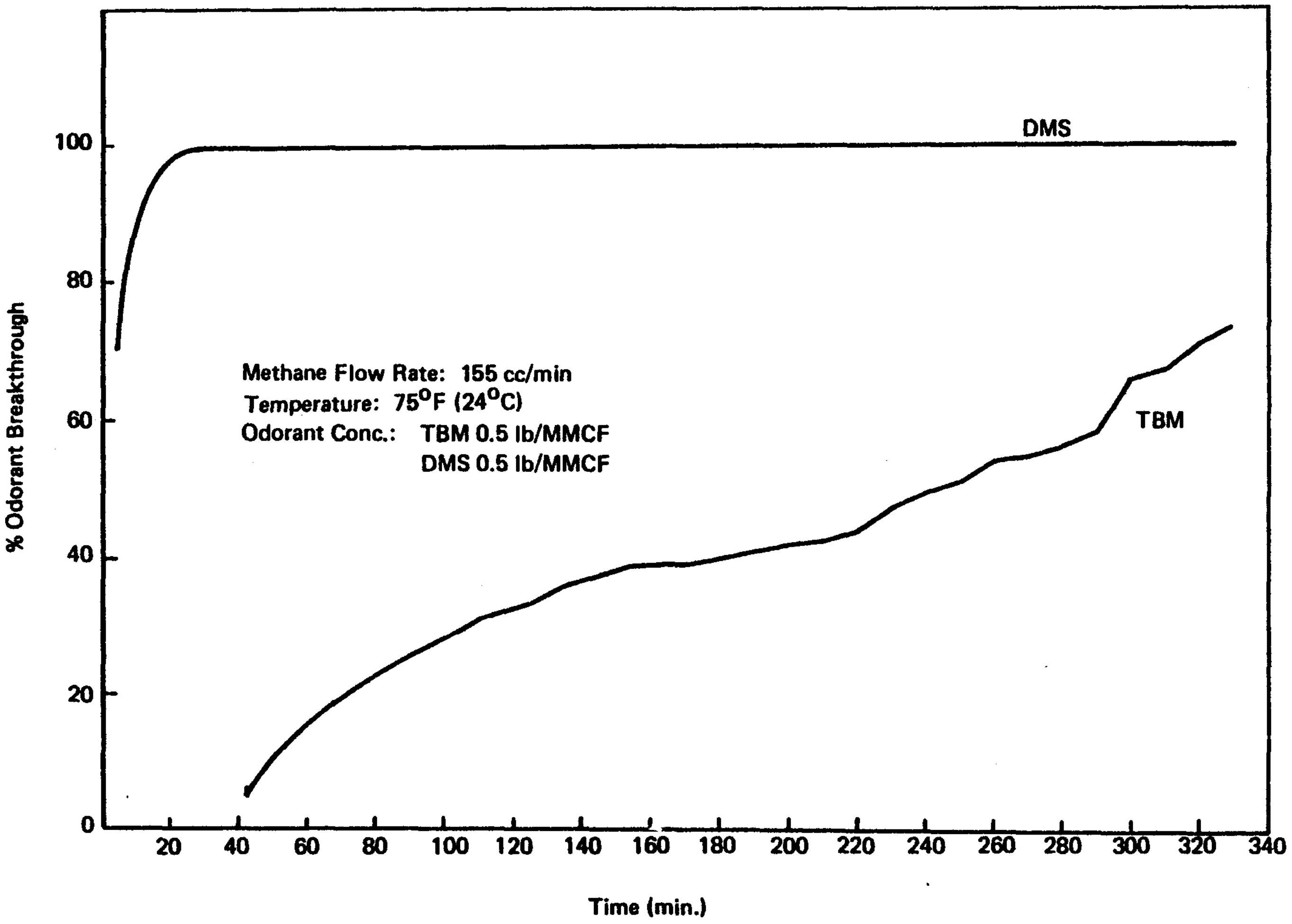


FIGURE 9 **TBM/DMS BLEND**

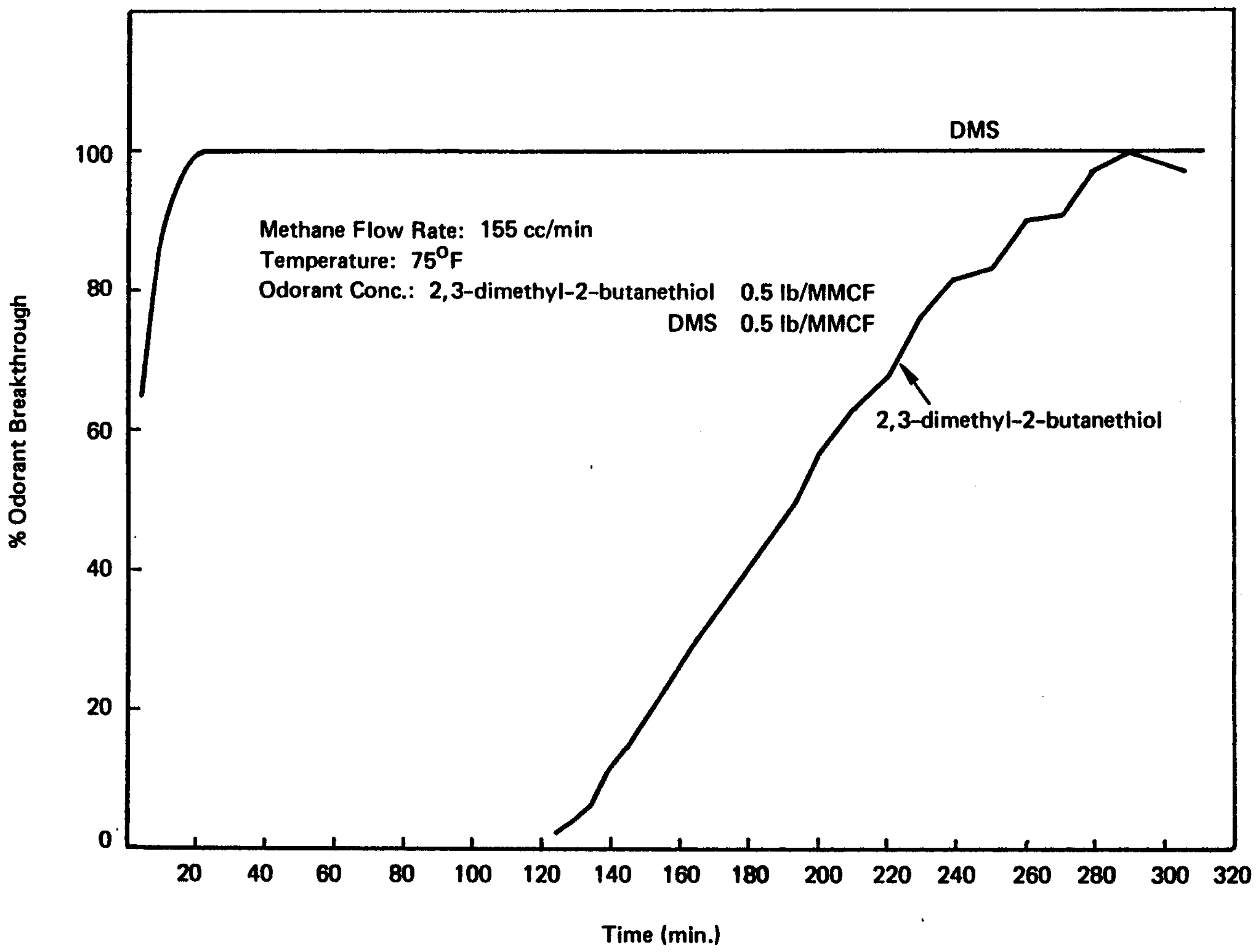


FIGURE 10 2,3-DIMETHYL-2-BUTANETHIOL/DMS BLEND

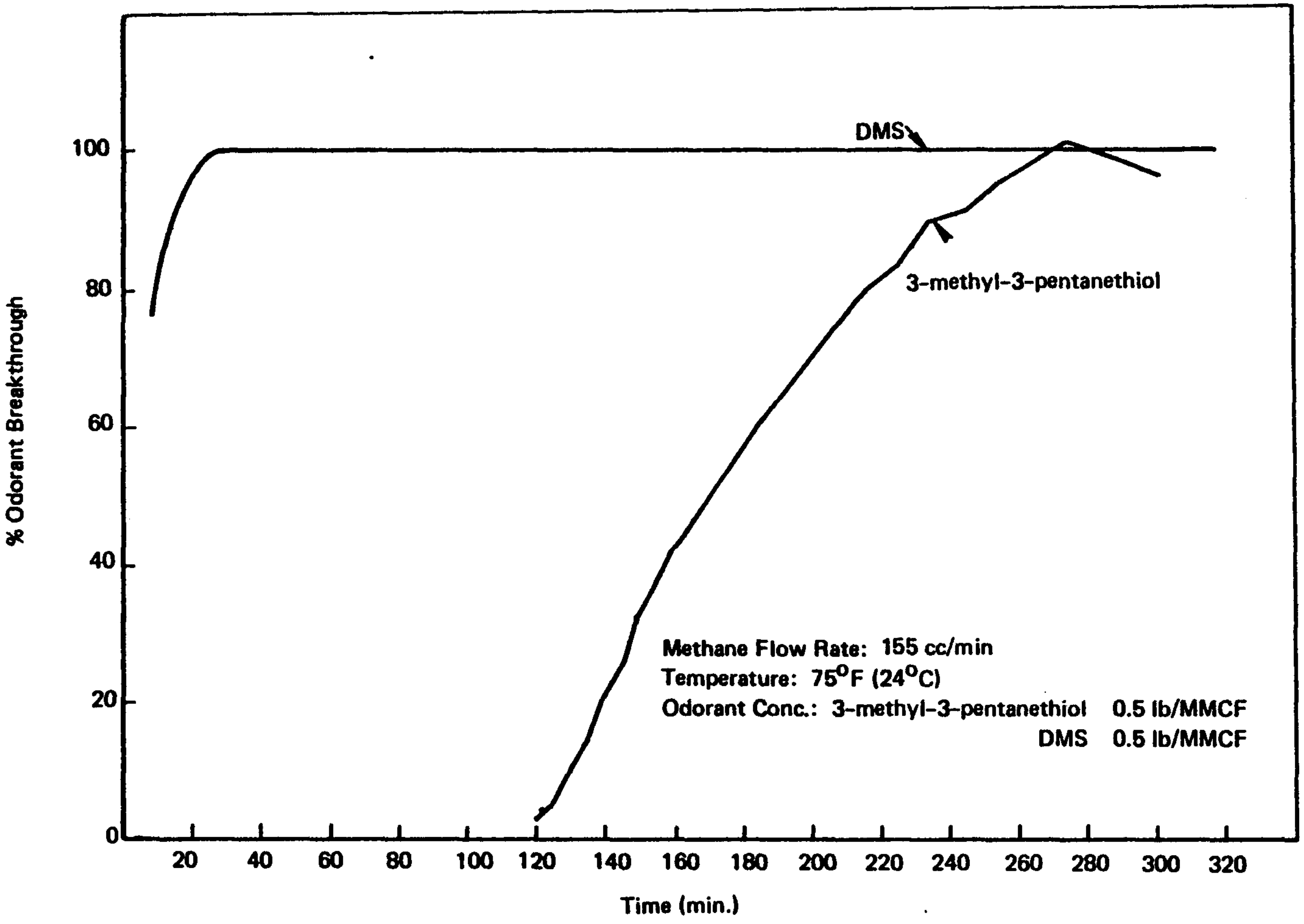


FIGURE 11 3–METHYL–3–PENTANETHIOL/DMS BLEND

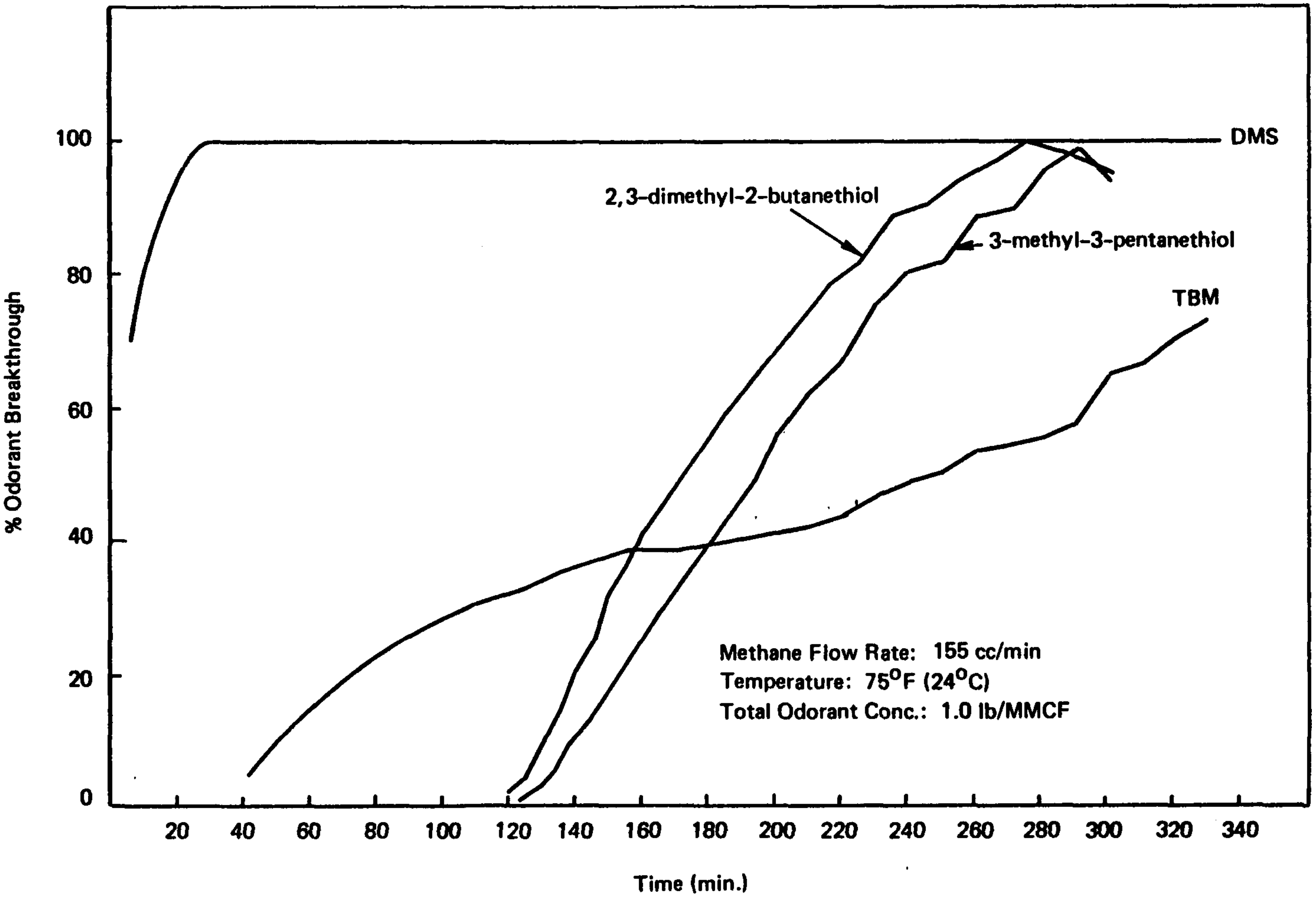


FIGURE 12 COMPOSITE OF ODORANT BLENDS

During this run a small amount of ethyl disulfide was observed, along with an unidentified compound believed to be ethyl tertiary butyl disulfide. Ethyl mercaptan was not observed until the TBM breakthrough reached 100%.

The addition of a compound, such as ethyl mercaptan, may be an approach to improving the performance of mercaptans, such as TBM, in respect to pipeline fading. The results we have observed with mixtures of mercaptans seem to contradict the earlier findings reported by Johnson.[1] Johnson's work indicated that lower molecular weight mercaptans promote the conversion of the higher molecular weight mercaptans.

3. Extended TBM Simulated Fading Experiment

One longer run using TBM was performed to reach a steady state and thus to determine if the catalyst activity remained constant. The run was continued for more than 9 hours the first day. Within approximately 400 minutes, a steady state was reached with the disulfide being about zero, and the TBM outlet concentration was approximately the same as the inlet concentration (Figure 13). The run was continued the next day for another 145 minutes and immediate 100% breakthrough of TBM was noted with only minimal detection of the disulfide. This may indicate that the iron oxide sites were saturated, but in any case the catalyst was completely inactivated. During the first 400 minutes of the run, our calculations indicated that approximately 0.5 mg of TBM was reacted and/or adsorbed on the iron oxide.

Without knowing more about the kinetics of the reaction involved in forming the tertiary butyl disulfide, it is not possible to scale the tests to full-scale pipeline flows. Simple scaling of the results, however, indicate that 1.0 mg of TBM deactivates about 0.4 g FeO(OH), or every cubic meter of flow (16 mg TBM/m^3) deactivates about 6.0 g FeO(OH).

4. TBM Fading Tests: Mass Balance of Input/Output

These experiments were run to support the breakthrough data and to aid in understanding the phenomenon occurring when gas odorants are exposed to an iron oxide catalyst. The experimental design was based on testing the following mass balance:

$$\text{Input} = \text{Amount Retained in Tube} + \text{Measured Output.}$$

The objective of the experiment was to measure the amount of odorant retained in the tube and to compare this measured value with the value calculated based on input and output data. For these test runs, TBM was the odorant and three time intervals were chosen based on the observed breakthrough pattern of TBM as typified in the breakthrough

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[1] Johnson, J.L., "Stability of Odorant Compounds," American Gas Association Production Conference, 1965.

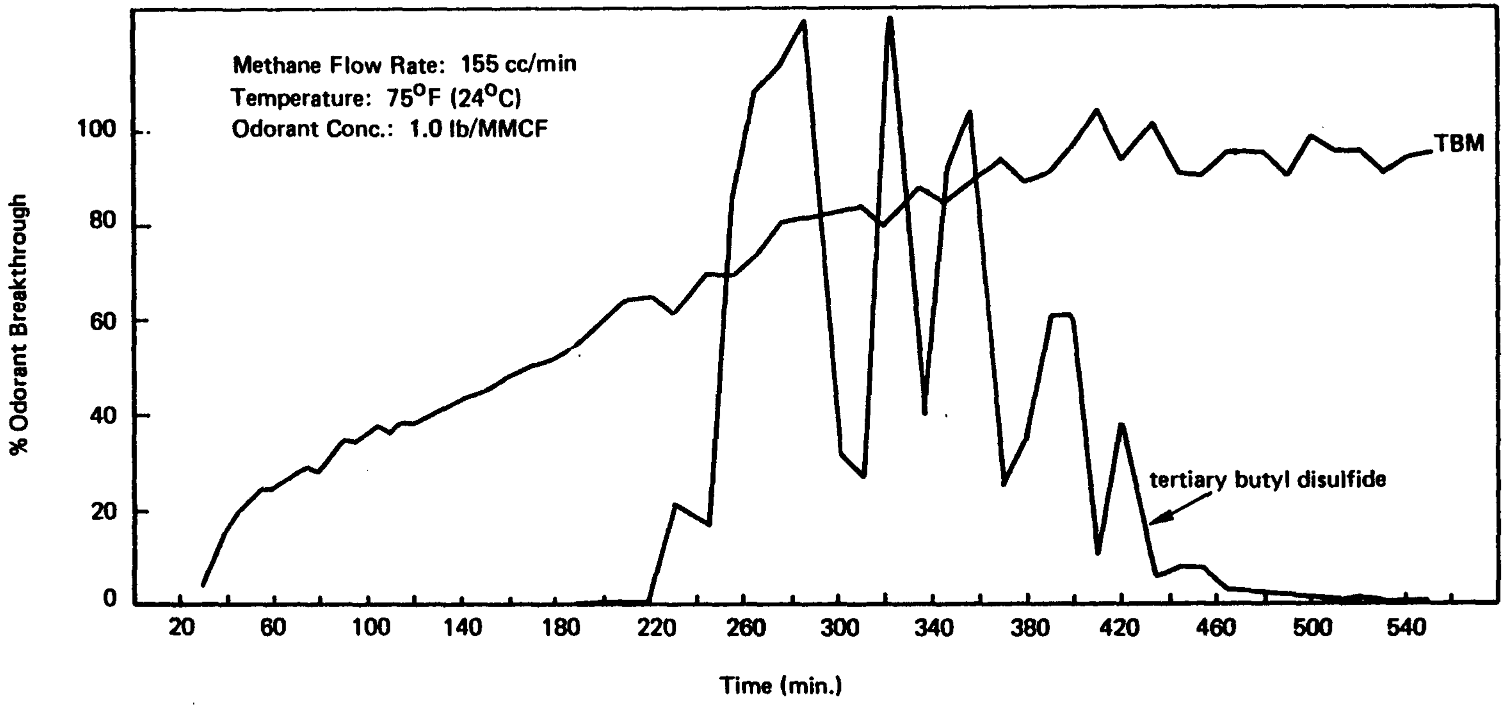


FIGURE 13 EXTENDED TBM RUN

curve shown in Figure 13. These time intervals corresponded to:

(1) the time when TBM breakthrough was first observed (~ 20 minutes);

(2) the time when TBDS breakthrough was first observed (~ 200 minutes); and

(3) the time when 100% TBM breakthrough occured (~420 minutes).

Thus, three standard tubes packed with 200 mg of iron oxide on 4.0 g of Kel-F® were used for three independent test runs where the TBM concentration was 16 mg/m^3 (1.0 lb/MMCF) and the average flow rate was 145 ml/min. The three runs were stopped, respectively, after 21 minutes (run 1), 210 minutes (run 2) and 420 minutes (run 3).

The analytical method* used consisted of desorbing the odorant from the iron oxide/Kel-F® matrix with methylene chloride and analysis by gas chromatography with a flame photometric detector (FPD).

The amount of the TBM + TBDS found by the procedure is also a function of a recovery factor associated with the effective removal of the components from the iron oxide/Kel-F®. Thus, a few experiments were carried out to determine the recovery factor as a function of amount of odorant applied directly to the iron oxide/Kel-F®. Samples were prepared by adding known amounts of TBM (100 and 500 μg), and TBDS (100 and 500 μg), using a microliter syringe, directly to an iron oxide/Kel-F® mixture in glass bottles. These samples were analyzed in the same manner as the breakthrough samples. The analytical data for the four samples shown in Table 7 give an estimate of the recovery factor which should be applied as a correction for the data for the three TBM breakthrough test runs.

The data in Table 7 also indicate that the TBM is converted to TBDS on the iron oxide/Kel-F® matrix and that the 200 mg of iron oxide has a finite capacity for degrading TBM. When 500 μg of TBM were added, 95 μg of TBM were found; when 100 μg of TBM were added, no TBM was detected. Evidence of TBM conversion to TBDS is illustrated by the significantly higher amount of TBDS found relative to what had been added; for example, 620 μg found versus 500 μg added. Thus, in treating these data, we assumed that all the TBM not accounted for had been converted to TBDS, and that the correlation was based on the fact that 2 moles of TBM = 1 mole of TBDS; i.e., 1 μg TBM = 1 μg TBDS. Ideally the TBM and TBDS should have been added to the iron oxide/Kel-F® separately. For our current purpose, however, we estimated that the recovery factor of 70% and 50% corresponded respectively to a total dose of 1000 μg and 200 μg.

---

*The details are as follows: The iron oxide/Kel-F® column packing was transferred to a glass bottle and treated with 10 ml of methylene chloride immediately after each of the three test runs. The samples were manually agitated, centrifuged, and the methylene chloride solution analyzed in a Varian 2400 gas chromatograph equipped with a flame photometric detector (FPD) and operated in a sulfur mode.

TABLE 7

ANALYTICAL DATA ON TBM AND TBDS ADDED* DIRECTLY TO IRON OXIDE/KEL-F®

Sample Code	TBM		TBDS		Total % Recovery
	μg Added	μg Found	μg Added	μg Found	
A	500	95	500	620	72
B	Sample was lost		Sample was lost		
C	100	ND**	100	120	60
D	100	ND	100	100	50

*1- and 5-μℓ aliquots of a solution of TBM and TBDS in methylene chloride were added directly to 4.0 g of Kel-F® and 200 mg of iron oxide in glass bottles.

**ND = not detectable.

The analytical data obtained for runs 1 to 3, shown in Table 8, are of special interest. No TBM was found in any of the three samples, nor was any TBDS found in the 420-minute run. The TBDS pattern indicated in Table 8 is in excellent agreement with the TBDS pattern shown in Figure 13 where the TBDS peak begins to appear at about 200 minutes, reaches some maximum level, and then gradually drops off to zero beginning at the time when the TBM breakthrough reaches 100%. The chart and data in Table 8 both indicate that the TBM is catalytically degraded to TBDS which is, in turn, initially adsorbed on the column packing. Then the gas stream chromatographically elutes the TBDS until it reaches the point where all the TBDS formed is completely eluted at around 420-450 minutes.

To test the mass balance, the TBDS analytically found in the tubes was compared with the calculated TBDS values based on the breakthrough data from Figure 13. These respective values are shown in Table 8. For this mathematical mass balance attempt, only the data for TBM run 2 is functional because the recovery factor for run 1 is unknown. (The data in Table 7 as well as previous experience suggest that the recovery factor is a function of the concentration and therefore the factor for 50 μg should be less than for 200 μg TBDS.) For run 2, the corrected quantity of TBDS is 220 μg versus 320 μg calculated from the known input and measured output. The 70% agreement between the determined and calculated values is very good, considering that these values are influenced by error factors associated with several measurements such as recovery factor, breakthrough data, and test concentration.

Although the tests we performed were limited and based on single data points, the data support the catalytic action of iron oxide and indicate that when the catalyst becomes inactive, no further odorant decomposition takes place. However, the constant formation of oxides in iron pipe in gas transportation systems can result in recurrent odor fading.

TABLE 8

TBM BREAKTHROUGH TESTS: COMPARISON OF ANALYTICALLY DETERMINED VALUES FOR TBM AND TBDS VS CALCULATED VALUES

A. Analytically Determined Values

	μg Found		
Sample Code	TBM[a]	TBDS[b]	Corrected μg TBDS
TBM Run 1, 21 minutes	ND*	~5	Factor Unknown**
TBM Run 2, 210 minutes	ND	110	222[c]
TBM Run 3, 420 minutes	ND	ND	0

B. Calculated Values

Based on 16 μg/m³ TBM test concentration and a flow rate of 145 mℓ/min.

	Calculated μg	
Sample Code	TBM Passed	TBDS Formed
TBM Run 1, 21 minutes	46	46[d]
TBM Run 2, 210 minutes	490	320[e]
TBM Run 3, 420 minutes	970	392[f]

a. Column was 1½ ft x 1/8-inch Teflon tubing packed with Supelpak S; column temperature = 120°C.
b. Column was 6 ft x 1/4 inch glass packed with 3% OV-101; column temperature = 130°C.
c. Based on analytical recovery factor of 50% from Table 7.
d. Based on the assumption that in the first 20 minutes where no TBM breakthrough was observed, complete conversion of TBM to TBDS occurs.
e. Based on the assumption that the average TBM breakthrough over the 210 minutes is 35%; i.e., TBDS = 490 x 0.65 = 320 μg.
f. Based on the assumption as in (e), plus an average TBM breakthrough of 85% over the next 210 minutes; i.e., TBDS = 320 + 480 x 0.15 = 392.

*Not detectable.
**Recovery factor not determined at this concentration level.

An alternative method was also used to determine the mass balance of odorant input and output. Using a planimeter, we determined the areas under the TBM and TBDS curves. These data also indicated that approximately 70% of the odorant input could be accounted for, and this was in good agreement with our previous findings.

Upon reviewing these experiments, it was suggested that a gas mixture containing a reactive component (which does not necessarily have odor), plus a non-reactive but highly odorous species, might be a means of overcoming catalytic breakdown of odorants. A reactive component (i.e., a volatile oxygenated material or metallo-organic compound) would preferentially destroy the catalytic action of the iron oxide and allow the odorant molecules to pass through. The current use of TBM/DMS blends is a partial answer to the fading problem. The TBM can be completely destroyed in a pipeline, but the more stable DMS will survive. Unfortunately, DMS does not have a high odor intensity at the concentrations of interest.

5. Odor Evaluation of Blends

Odorant dose response tests were carried out on two of our best candidates, blended in different ratios with THT and DMS. All tests were conducted in our dynamic odor test chamber, and observations were performed by a panel of profile-trained observers. Different concentrations of each blend were presented in random order. Total odorant concentration in the blend was kept constant at 0.1% gas in air. The following odorant blends were evaluated:

2,3-dimethyl-2-butanethiol/THT	25:75
2,3-dimethyl-2-butanethiol/THT	50:50
2,3-dimethyl-2-butanethiol/THT	75:25
2,3-dimethyl-2-butanethiol/DMS	25:75
2,3-dimethyl-2-butanethiol/DMS	50:50
2,3-dimethyl-2-butanethiol/DMS	75:25
3-methyl-3-pentanethiol/DMS	25:75
3-methyl-3-pentanethiol/DMS	50:50
3-methyl-3-pentanethiol/DMS	75:25

The terms used by the panel members to describe the different odorants and odorant blends are listed in Table 9.

a. Dose Response Curves

The dose response curves, i.e., least squares lines (Figures 14, 15, and 16), and the odor response data in Tables 10-13 show the relationship between perceived intensity and micrograms (μg) of odorant per cubic meter (m^3) of air. The data are plotted as equal concentrations of total odorant. A gas odorization rate of 0.5 lb/MMCF is equivalent to 8 mg of odorant per cubic meter of gas. When this is diluted to 0.1% gas in air, it produces an

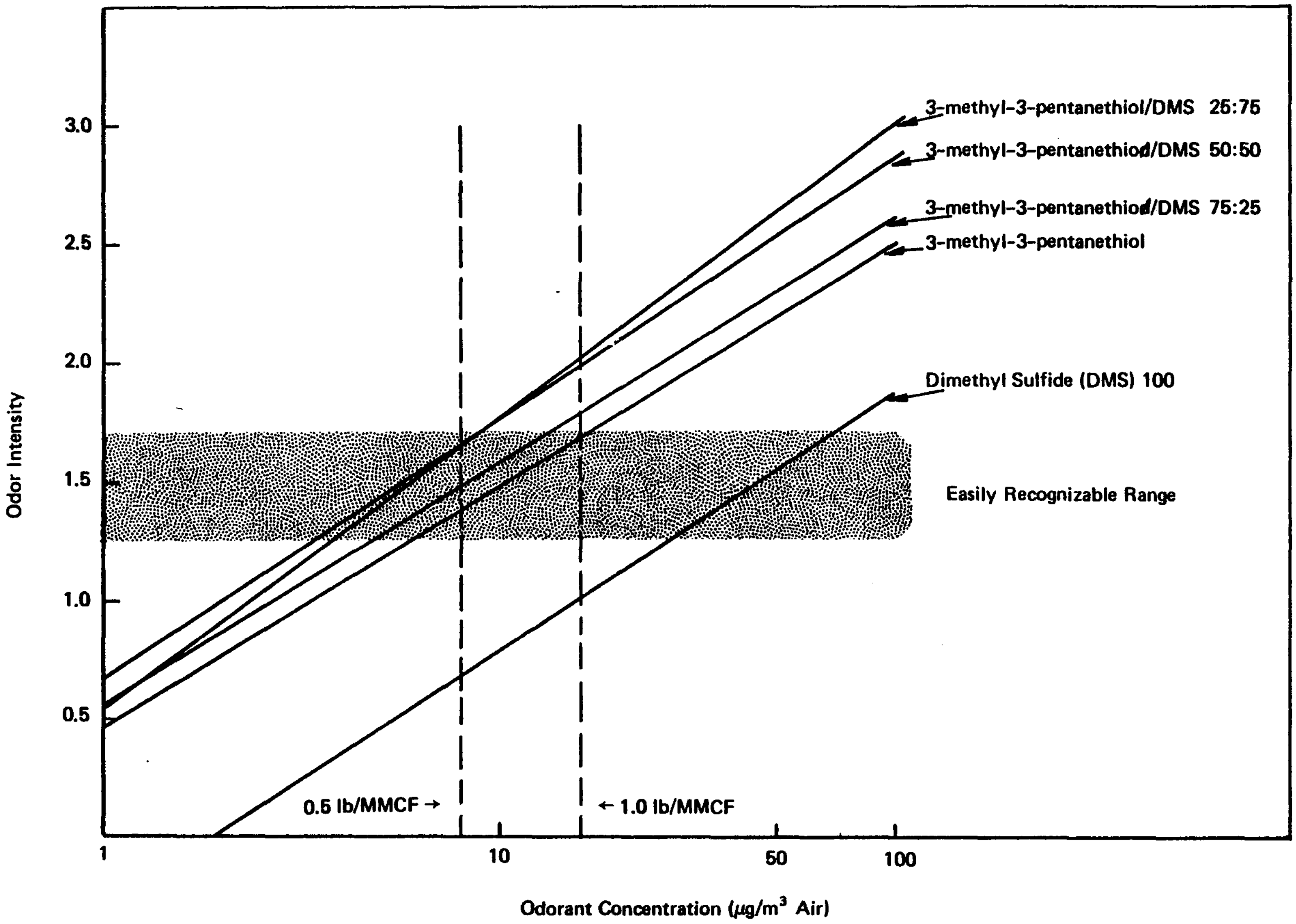


FIGURE 14 DOSE RESPONSE CURVES – ODORANT BLENDS

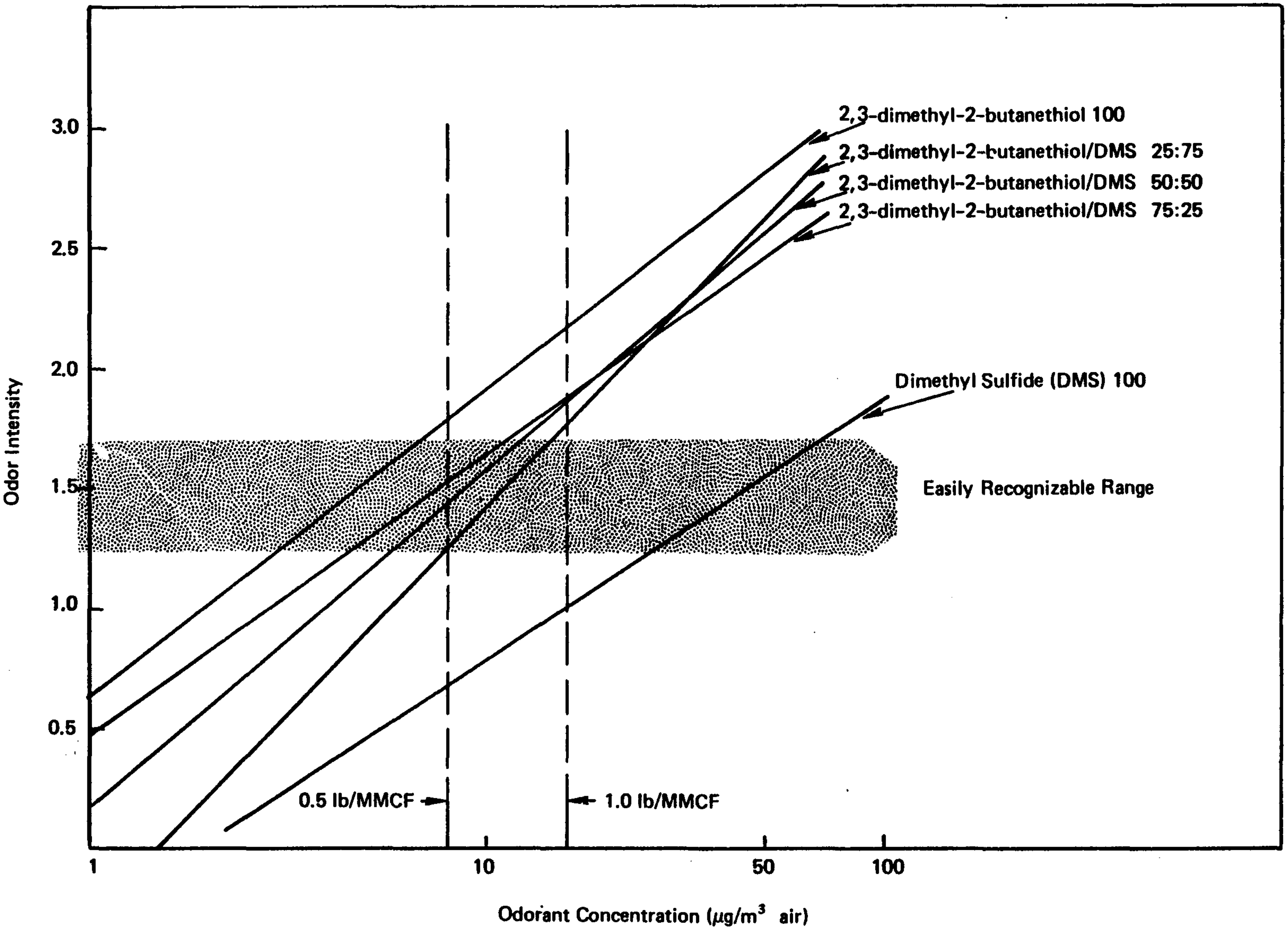


FIGURE 15 DOSE RESPONSE CURVES – ODORANT BLENDS

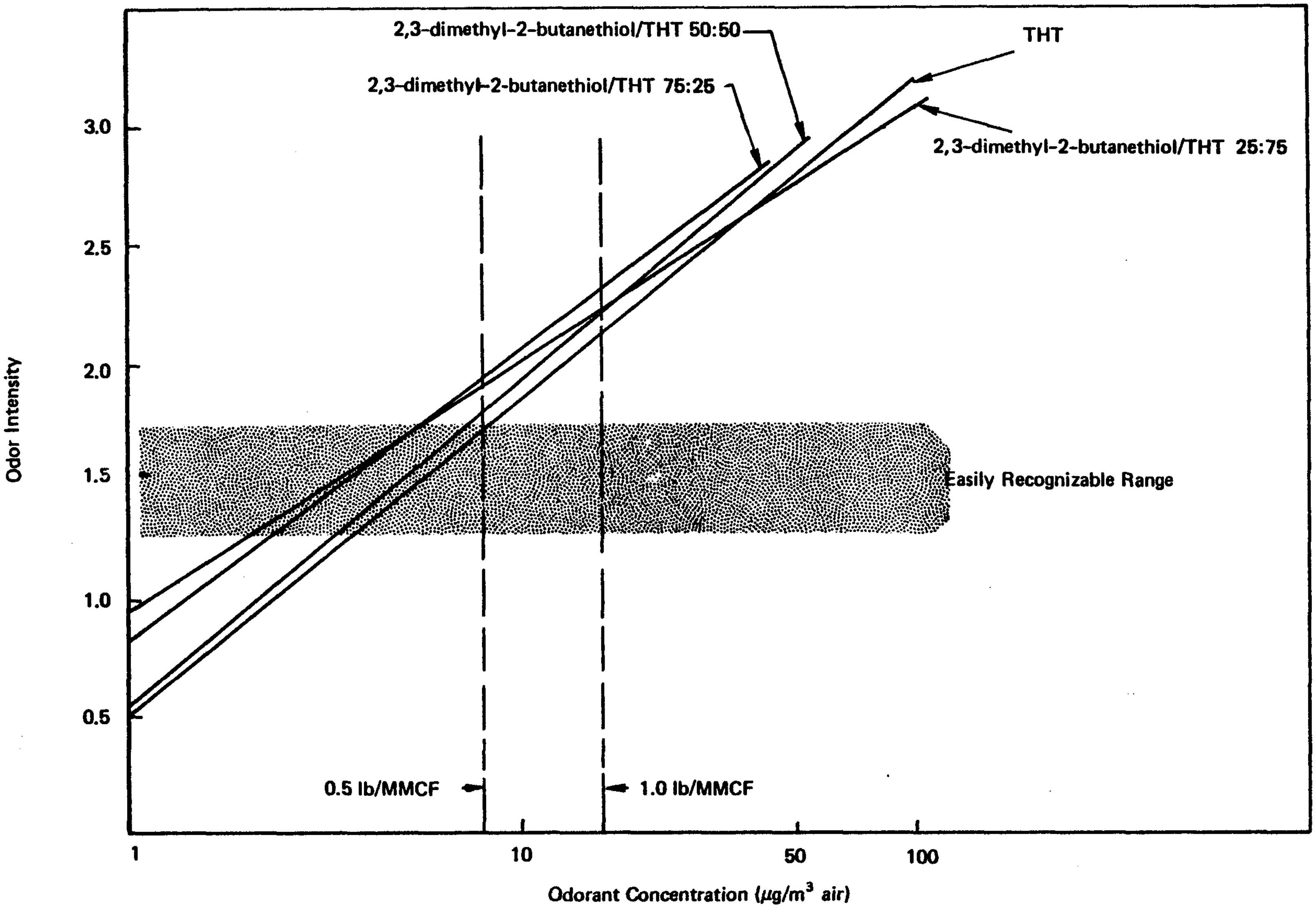


FIGURE 16 DOSE RESPONSE CURVES – ODORANT BLENDS

odorant level of 8 $\mu g/m^3$ in air. As in our previous work, the following seven-point scale was used to denote odor intensity (TIA = Total Intensity of Aroma):

0 = not detected
0.5 = very slight
1.0 = slight
1.5 = slight-moderate
2.0 = moderate
2.5 = moderate-strong
3.0 = strong

On the basis of previous experience, intensity levels of 1.25 and above on this scale are easily recognizable by most individuals.

TABLE 9

DESCRIPTION OF ODORANTS AND ODORANT BLENDS

Odorant or Odorant Blend	Ratio	Odor Descriptors
2,3-dimethyl-2-butanethiol/THT	25:75	Pungent, gassy, cabbagy
2,3-dimethyl-2-butanethiol/THT	50:50	Gassy, cat box
2,3-dimethyl-2-butanethiol/THT	75:25	Pungent, gassy, mercaptan, cat box
tetrahydrothiophene (THT)	–	Gassy, pungent, garlicky
2,3-dimethyl-2-butanethiol	–	Mercaptan, sulfidy, burnt rubber
2,3-dimethyl-2-butanethiol/DMS	25:75	Cabbagy, mercaptan
2,3-dimethyl-2-butanethiol/DMS	50:50	Cabbagy, cat box
2,3-dimethyl-2-butanethiol/DMS	75:25	Gassy, mercaptan, cabbagy, cat box
dimethyl sulfide (DMS)	–	Cabbagy, sulfidy
3-methyl-3-pentanethiol/DMS	25:75	Pungent, cabbagy, cat box
3-methyl-3-pentanethiol/DMS	50:50	Pungent, cabbagy, mercaptan, cat box
3-methyl-3-pentanethiol/DMS	75:25	Pungent, cabbagy, mercaptan
3-methyl-3-pentanethiol	–	Gassy, oniony, cat box

TABLE 10

INTENSITY VALUES VERSUS ODORANT CONCENTRATION
(all odorants and odorant blends 0.1% in reagent grade nonane)

Test Chamber Concentration ($\mu g/m^3$)	Intensities		
	DMS	THT	3M-3-PT
2.8	0.22	1.03	0.81
5.3	0.46	1.59	1.38
16.3	1.03	2.06	1.63
	3M-3-PT/DMS 25:75	3M-3-PT/DMS 50:50	3M-3—PT/DMS 75:25
2.8	1.06	1.16 (1.33)*	0.88 (1.34)
5.3	1.47	1.47 (1.46)	1.50 (1.78)
16.3	2.0	2.0 (2.0)	1.71 (2.13)
	2,3DM-2-BT	2,3DM-2-BT/DMS 25:75	2,3DM-2-BT/DMS 50:50
2.8	1.25	0.42	0.84
5.3	1.53	1.06	1.13
16.3	2.22	1.75	1.91
	2,3DM-2-BT/THT 25:75	2,3DM-2-BT/THT 50:50	2,3DM-2-BT/THT 75:25
2.8	1.41	1.03	1.41
5.3	1.75	1.72	1.66
16.3	2.22	2.16	2.34

*Numbers in parentheses are replicate tests.

TABLE 11

ODORANT DOSE RESPONSE DATA

	3M-3PT 100 –	3M-3PT 75 DMS 25	3M-3PT 50 DMS 50	3M-3PT 25 DMS 75	– DMS 100
Correl. Coeff.	0.93	0.91	0.999	0.996	0.997
Slope	1.01	1.01	1.10	1.21	1.07
Intercept	0.47	0.56	0.67	0.55	-0.28
Mean	1.27	1.36	1.54	1.51	0.57
Std. Dev.	0.42	0.43	0.42	0.47	0.41
TIA					
10 $\mu g/m^3$	1.48	1.57	1.76	1.76	0.79
1 $\mu g/m^3$	0.47	0.56	0.67	0.55	-0.28

Legend: 3M-3PT = 3-methyl-3-pentanethiol
DMS = dimethyl sulfide

TABLE 12

ODORANT DOSE RESPONSE DATA

	2,3DM-2BT 100 –	2,3DM-2BT 75 DMS 25	2,3DM-2BT 50 DMS 50	2,3DM-2BT 25 DMS 75	– DMS 100
Correl. Coeff.	0.996	0.998	0.995	0.991	0.997
Slope	1.28	1.16	1.42	1.70	1.07
Intercept	0.64	0.47	0.16	-0.28	-0.28
Mean	1.67	1.39	1.29	1.08	0.57
Std. Dev.	0.49	0.44	0.55	0.66	0.41
TIA					
10 $\mu g/m^3$	1.93	1.62	1.59	1.43	0.79
1 $\mu g/m^3$	0.64	0.47	0.16	-0.28	-0.28

Legend: 2,3DM-2BT = 2,3-dimethyl-2-butanethiol
DMS = dimethyl sulfide

TABLE 13

ODORANT DOSE RESPONSE DATA

	2,3DM-2BT 100 –	2,3DM-2BT 75 THT 25	2,3DM-2BT 50 THT 50	2,3DM-2BT 25 THT 75	– THT 100
Correl. Coeff.	0.997	0.995	0.959	0.997	0.975
Slope	1.28	1.24	1.411	1.05	1.34
Intercept	0.64	0.82	0.515	0.96	0.51
Mean	1.67	1.80	1.63	1.79	1.57
Std. Dev.	0.49	0.48	0.57	0.41	0.53
TIA					
10 $\mu g/m^3$	1.93	2.05	1.92	2.01	1.84
1 $\mu g/m^3$	0.64	0.82	0.52	0.96	0.51

Legend: 2,3DM-2BT = 2,3-dimethyl-2-butanethiol
THT = tetrahydrothiophene

Two cases of unusual enhancement, or synergism, were found. The first is a 50:50 blend of 3-methyl-3-pentanethiol and DMS which was examined repeatedly, and the second is a 25:75 3-methyl-3-pentanethiol/DMS blend. The synergistic effect is shown in Figure 14 and Table 10 where the odorant blends are appreciably stronger in intensity than either of the individual odorants at their respective concentrations. Table 11 lists additional dose response data and demonstrates the synergism of these odorant blends at a concentration of 10 $\mu g/m^3$. No such synergistic effects were observed when 2,3-dimethyl-2-butanethiol was blended with THT or DMS (Tables 10, 12 and 13).

b. Statistical Analysis of Dose Response Tests

The data were analyzed statistically and results of these examinations confirm that there is a synergistic effect in blends of 3-methyl-3-pentanethiol and DMS.

Dose response experiments were conducted for several odorant blends of DMS and 3M-3PT. Concentration levels ranging from 2.8 $\mu g/m^3$ to 16.3 $\mu g/m^3$ were presented independently and in random order to each of several profile-trained subjects. The basic experiment was replicated so that each subject provided two independent observations for each odorant blend/concentration level considered. Odor intensity was measured according to the standard seven-point scale described in Section E-5.a. Average intensities are summarized in Table 14.

TABLE 14

DOSE RESPONSE TESTS OF ODORANT BLENDS

Odorant Blend		Concentration ($\mu g/m^3$)	Number of Observations	Average Odor Intensity
% DMS	% 3M-3PT			
100	0	2.8	8	0.2
		5.3	8	0.5
		16.3	8	1.0
75	25	2.8	8	1.1
		5.3	8	1.5
		16.3	8	2.0
50	50	2.8	16	1.3
		5.3	16	1.5
		9.9	8	2.1
		16.3	16	2.0
25	75	2.8	14	1.3
		5.3	14	1.8
		9.9	8	1.8
		16.3	14	1.9
0	100	2.8	8	1.0
		5.3	8	1.4
		9.9	8	1.9
		16.3	8	2.0

A statistical technique known as regression analysis was then used to analyze the dose response data for each blend tested. It is well known that perceived intensity tends to be linearly related to log concentration. Therefore, it seemed reasonable to assume that the observed intensity values obtained for repeated presentations to several subjects were normally distributed about some true (but unknown) average value at each concentration level tested.

By applying regression theory to the experimental data, it was then possible to perform the following analyses:

(i) Test for linearity; i.e., determine whether or not the average TIA (total intensity of aroma) values were linearly related to log concentration over the range of concentration considered;

(ii) Determine the precision associated with the estimated mean TIA values; i.e., calculate confidence interval estimates;

(iii) Examine the slopes for the various blends to measure rate of increase in TIA;

(iv) Establish significant differences among blends at various concentration levels.

In general, the assumed linear relationship appeared to be verified by the data obtained for each blend. Regression lines are given for each blend in Figures 17 through 21, and 95% confidence intervals about the regression line are also exhibited for each data set. These intervals are also given in Figure 22 at three different concentration levels to clarify their interpretation. For example, the experimental data of Figure 22 indicate that the probability is 0.95 that the interval 0.05 to 0.47 includes the true, mean intensity of DMS when 3 $\mu g/m^3$ are presented to the panel.

As shown in Figure 22, the addition of 3M-3PT significantly enhances detection when compared with DMS alone over the entire range of concentrations tested.

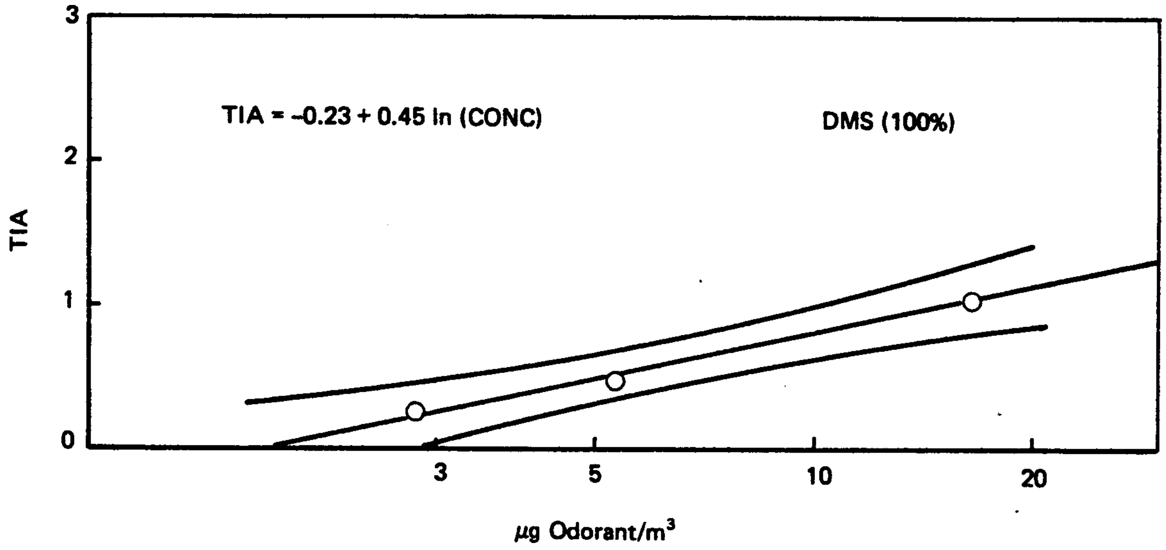


FIGURE 17 95% CONFIDENCE INTERVALS

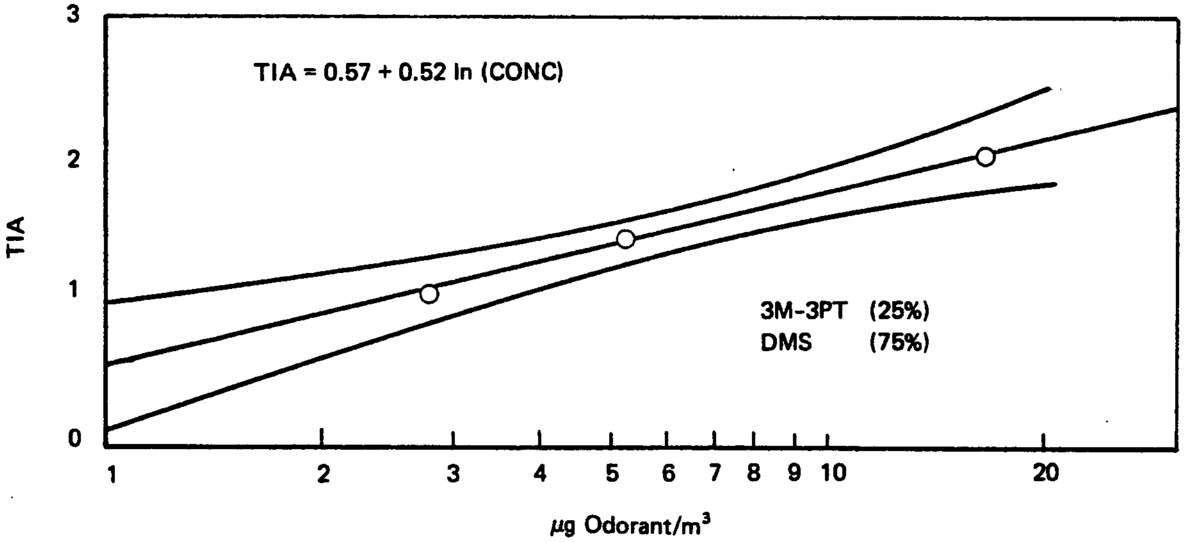


FIGURE 18 95% CONFIDENCE INTERVALS

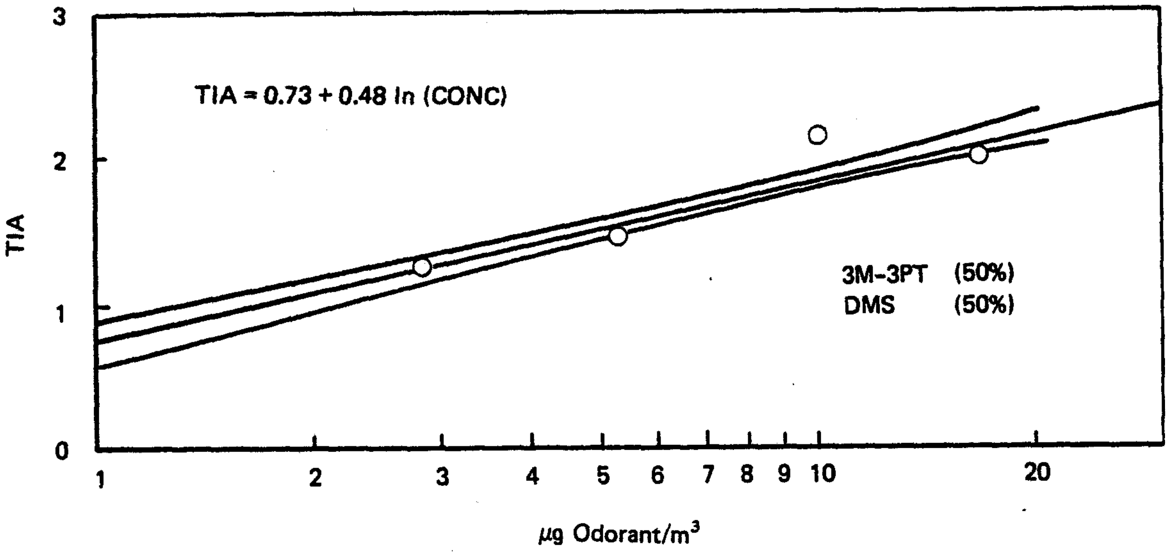


FIGURE 19 95% CONFIDENCE INTERVALS

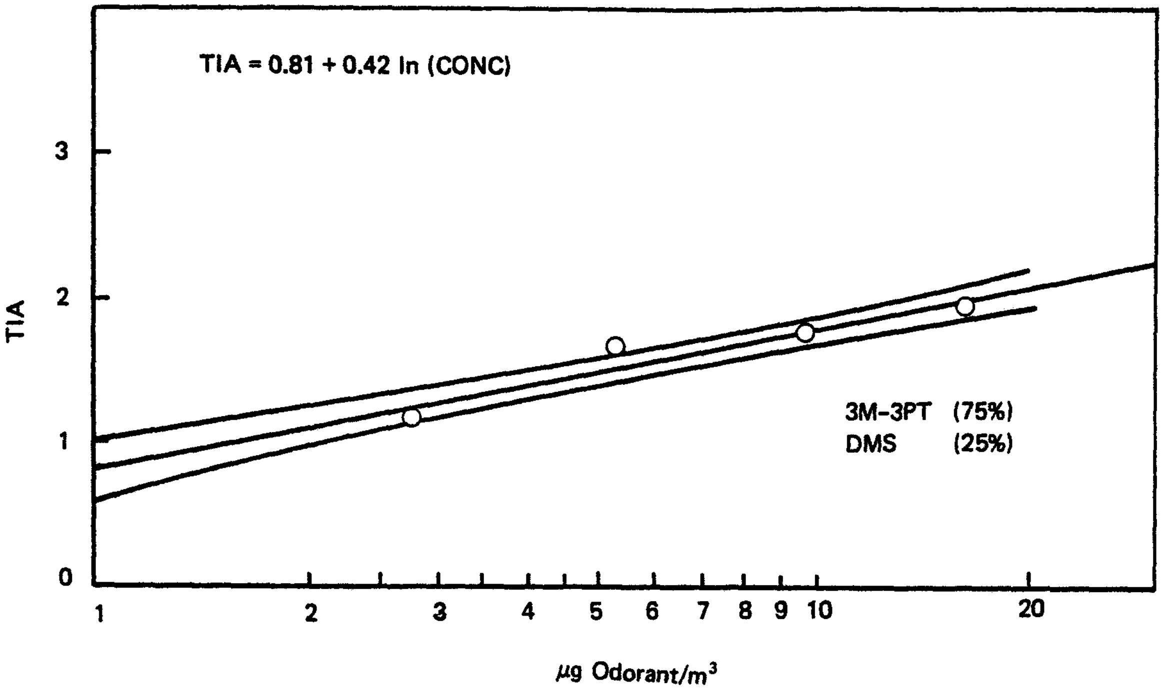


FIGURE 20 95% CONFIDENCE INTERVALS

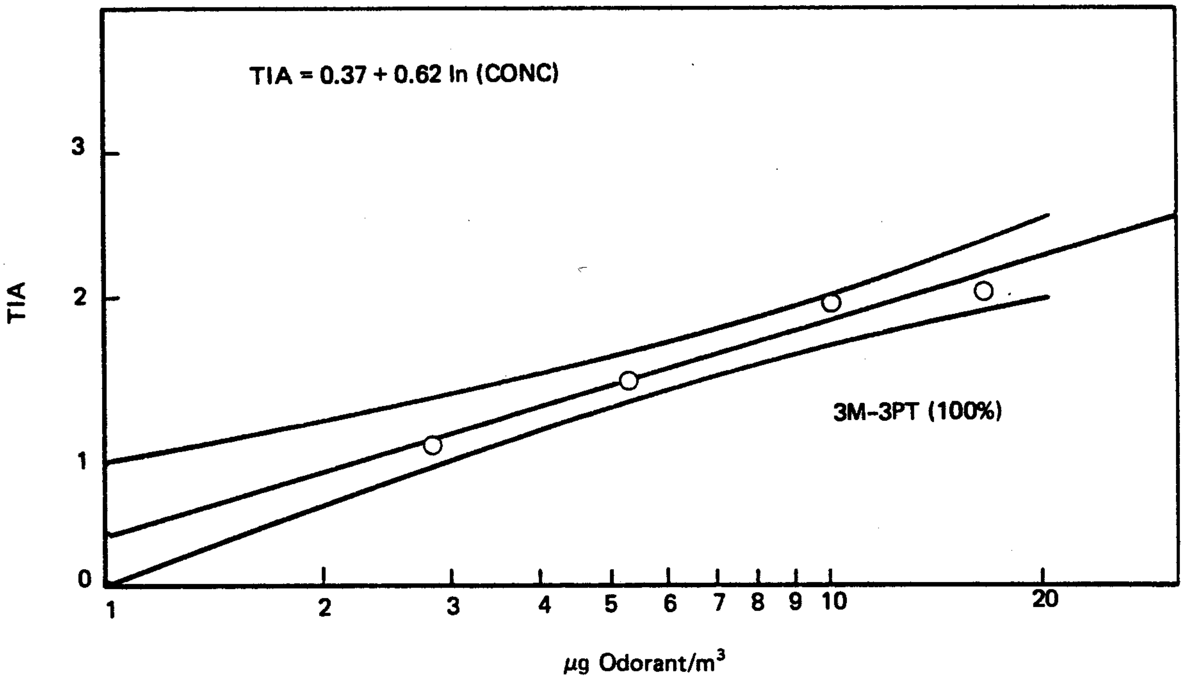


FIGURE 21 95% CONFIDENCE INTERVALS

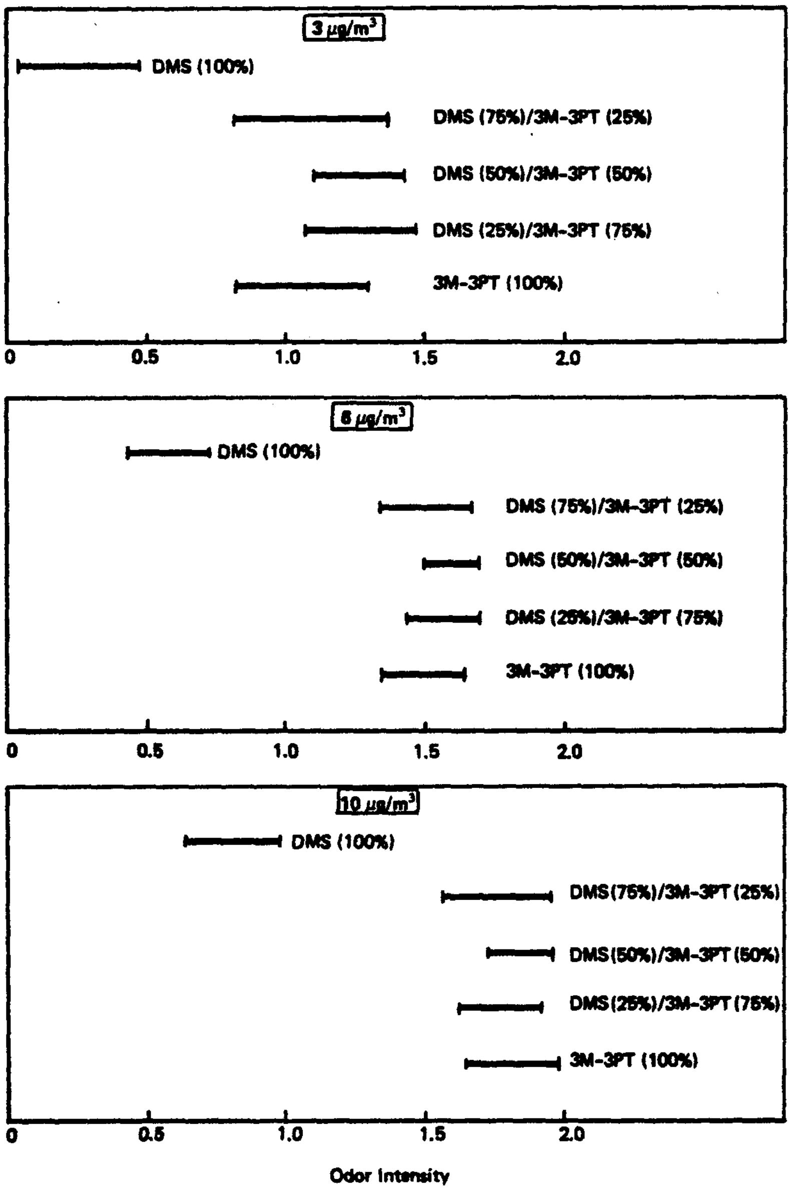


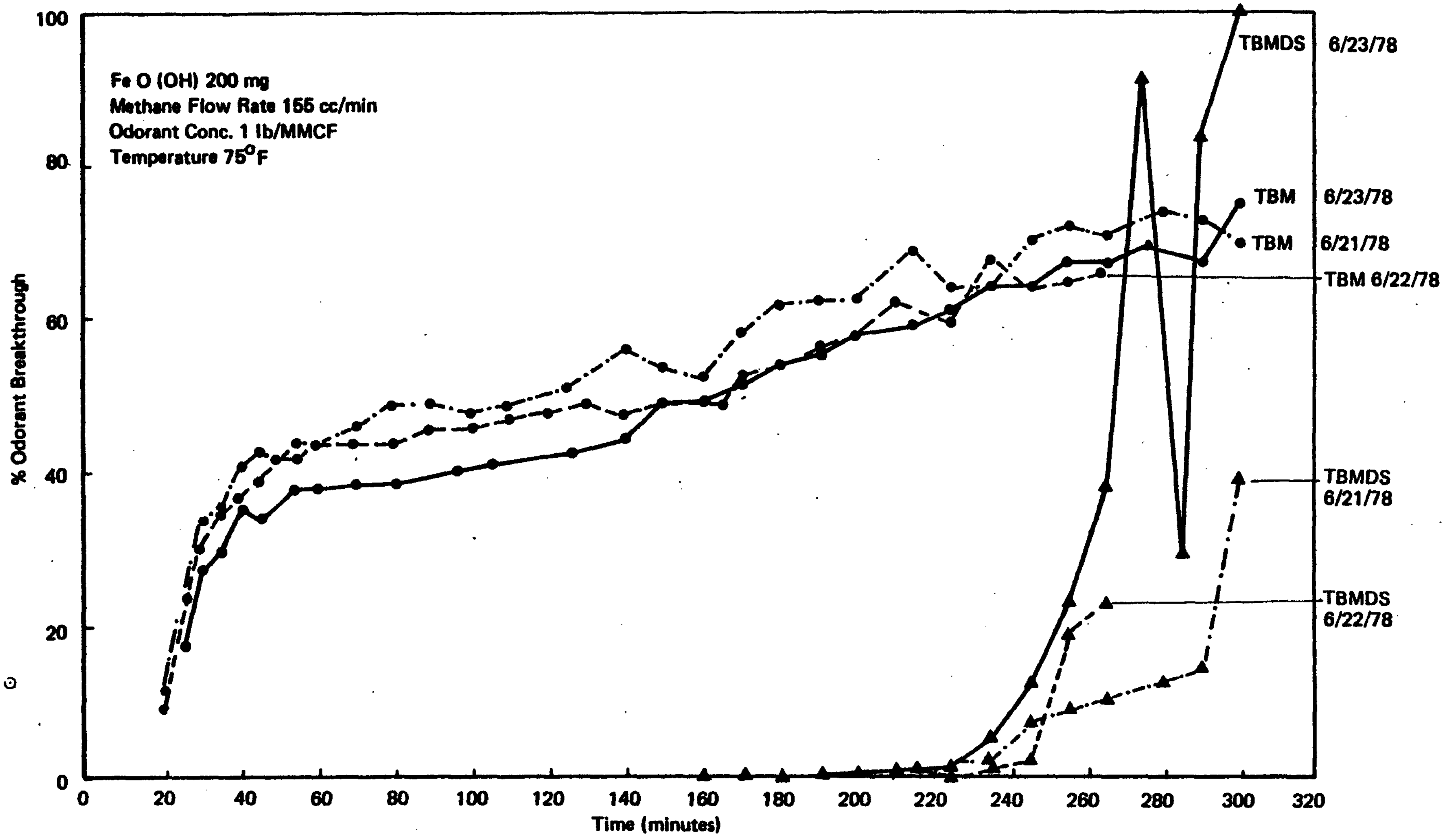
FIGURE 22 95% CONFIDENCE INTERVALS (Mean TIA)

III. RECOMMENDATIONS FOR FUTURE WORK

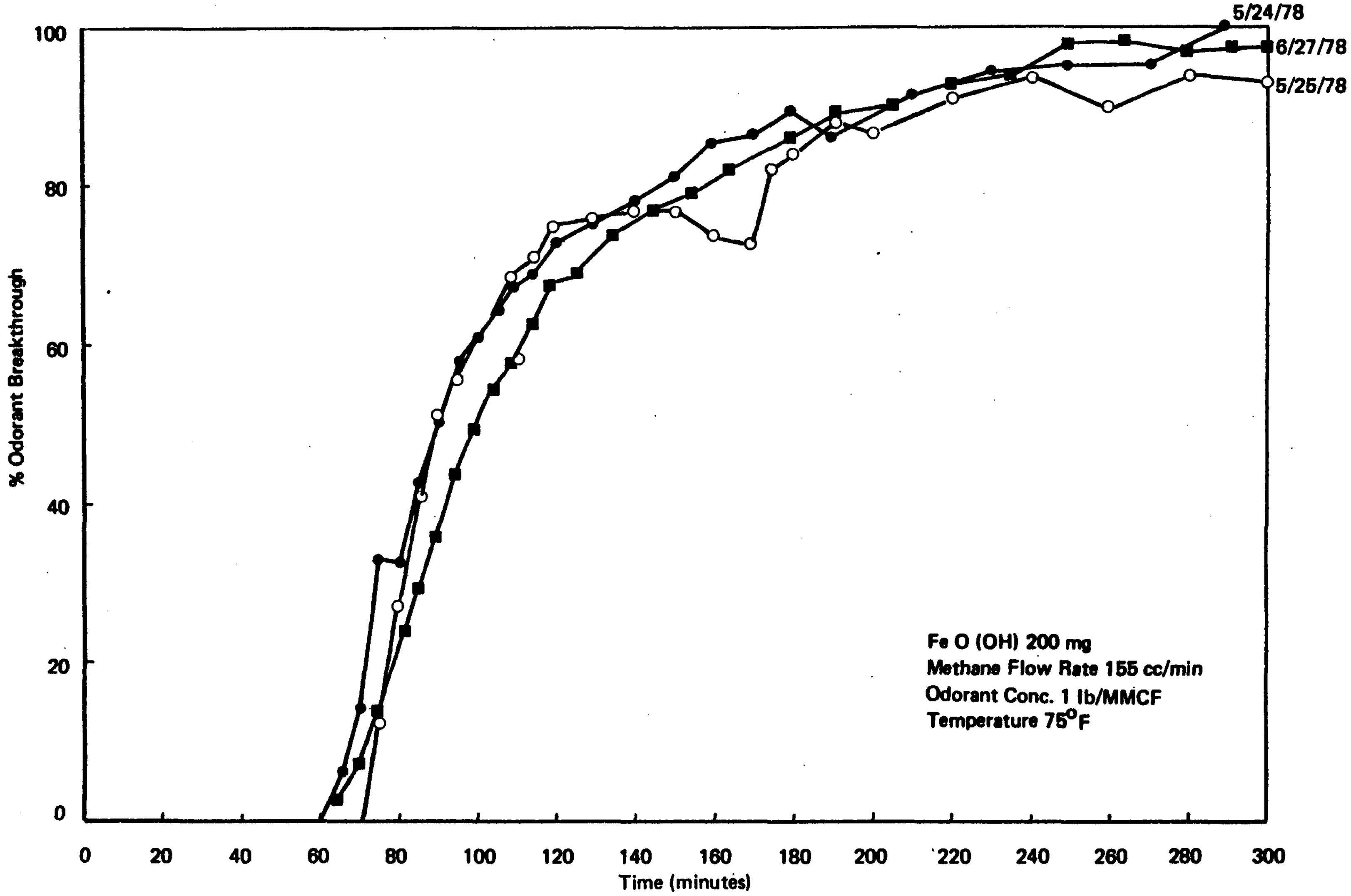
We feel that this study has resulted in significant contributions in the gas odorization field. As a logical extension of this work, we recommend the following program:

- Assess the benefits in terms of risk reduction offered by our new odorant 3-methyl-3-pentanethiol as opposed to currently used odorants. Cost comparisons should also be made.
- Further investigation of 3-methyl-3-pentanethiol/dimethyl sulfide blends to determine the concentrations where synergism and warning are most pronounced. The patentability of our new odorant should also be considered.
- Determine the influence of variables such as water vapor, oxygen, and temperature on pipeline fading.
- Develop a protocol for field testing our odorant candidate.
- Prepare an odorant attribute chart for the gas odorants we have studied, including our best candidates. This would contain information pertaining to odor intensity, type, impact, persistence, soil penetrability, and pipeline stability.

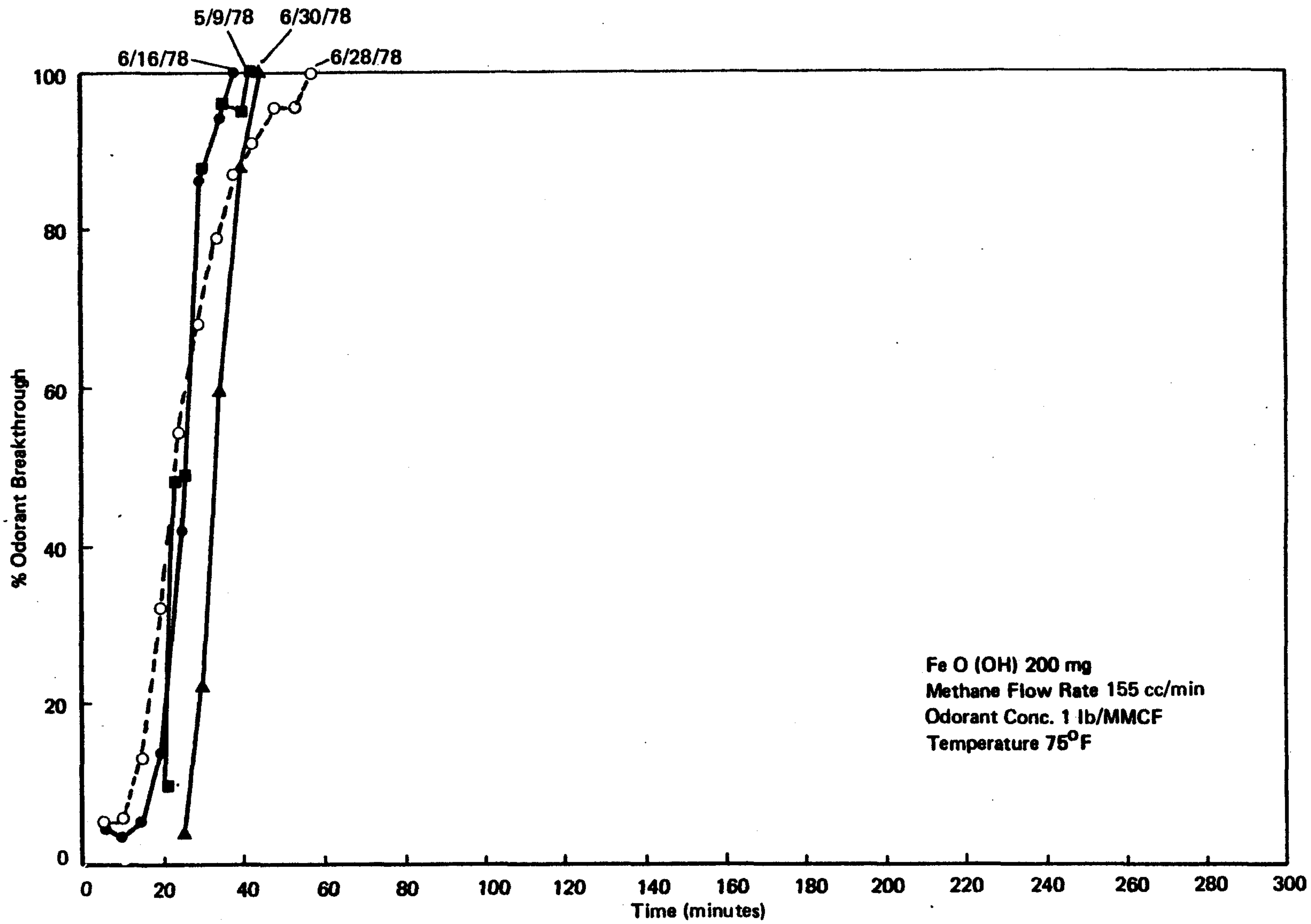
APPENDIX A



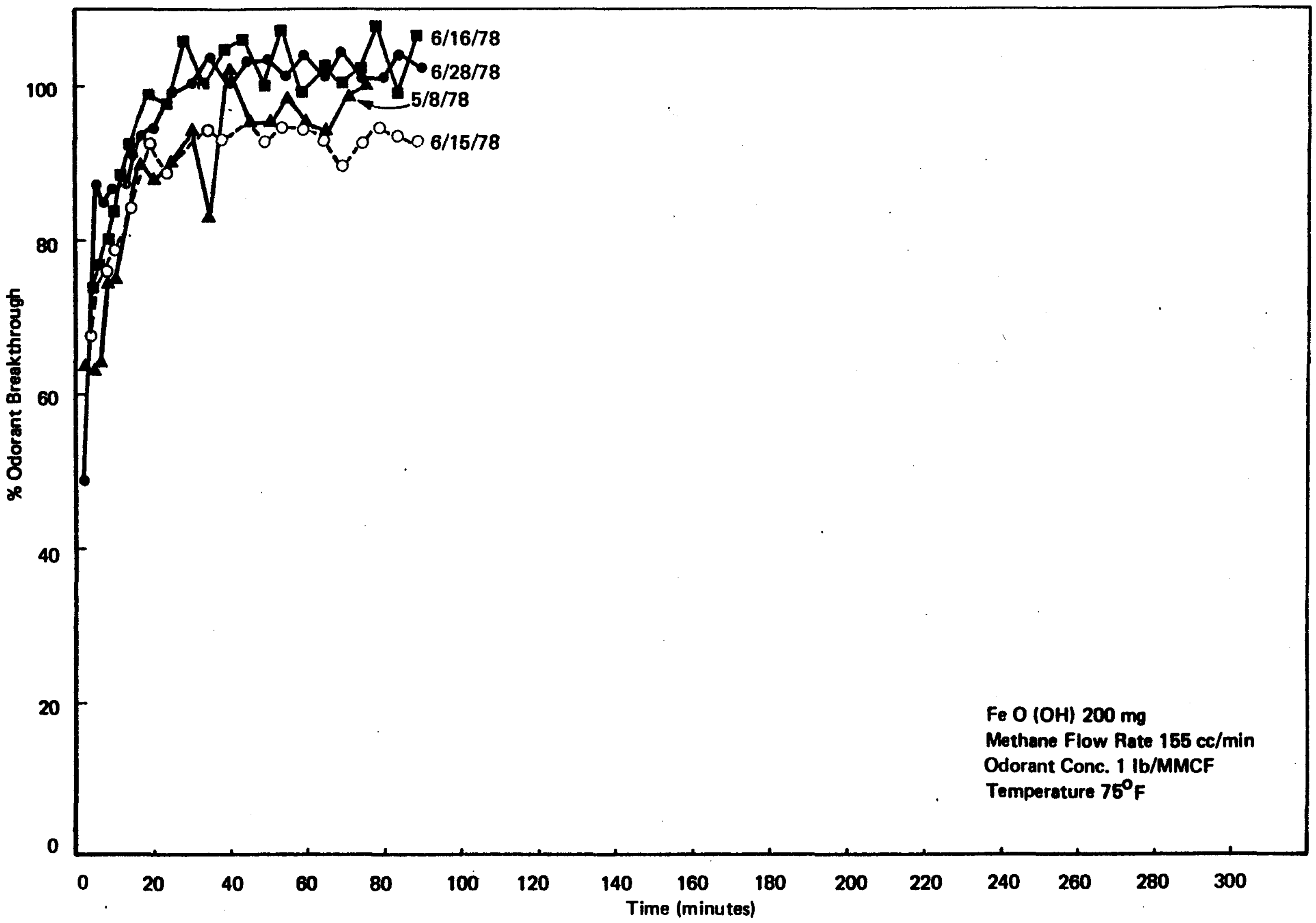
APPENDIX FIGURE A–1. REPLICATE TBM AND TBMDS TESTS



APPENDIX FIGURE A–2. REPLICATE 2,3 DIMETHYL-2-BUTANETHIOL TESTS



APPENDIX FIGURE A–3. REPLICATE THT TESTS



APPENDIX FIGURE A–4. REPLICATE DMS TESTS