

SENSORY EVALUATION OF DIESEL EXHAUST ODORS



U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

Environmental Health Service

SENSORY EVALUATION OF DIESEL EXHAUST ODORS

Amos Turk, Ph. D.
Professor, Department of Chemistry
The City College of the City University of New York

Janet T. Wittes
Department of Statistics
Harvard University

and

L. R. Reckner and R. E. Squires
Scott Research Laboratories, Inc.

Prepared under Public Health Service Contracts
No. PH 27-66-96 and No. CPA-69-528

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service
National Air Pollution Control Administration
Raleigh, North Carolina
February 1970

The AP series of reports is issued by the National Air Pollution Control Administration to report the results of scientific and engineering studies, and information of general interest in the field of air pollution. Information reported in this series includes coverage of NAPCA intramural activities and of cooperative studies conducted in conjunction with state and local agencies, research institutes, and industrial organizations. Copies of AP reports may be obtained upon request, as supplies permit, from the Office of Technical Information and Publications, National Air Pollution Control Administration, U.S. Department of Health, Education, and Welfare, 1033 Wade Avenue, Raleigh, North Carolina 27605.

National Air Pollution Control Administration Publication No. AP-60

FOREWORD

Exhaust gases emitted by diesel engines are characterized by odors that are offensive in varying degrees to many members of the general public. The increasing use of diesel-powered trucks and buses in urban environments has resulted in widespread public awareness of the diesel exhaust odor problem.

It has not been established at this time whether any health hazards are involved; nevertheless, because the odors are unpleasant and irritating to people, studies of their origin and possible elimination are a necessary part of the over-all program of automotive air pollution research conducted by the National Air Pollution Control Administration (NAPCA).

Several research organizations, working under NAPCA sponsorship, are conducting programs of engine testing and chemical analysis designed to establish the identity and relative concentrations of all products of incomplete combustion present in diesel engine exhaust.

To correlate these chemical analyses with the presence of odors, one must devise means of rating the odors, both as to quality and intensity, on some sort of numerical scale. Satisfactory correlations, once accomplished, would make it possible to evolve criteria for readily enforceable standards for control of diesel exhaust odors standards based on chemical composition rather than odor ratings and hence less subject to human error or bias.

This publication consists of two parts: (1) a revision of Selection and Training of Judges for Sensory Evaluation of the Intensity and Character of Diesel Exhaust Odors (PHS No. 999-AP-32), a report prepared in 1967 under Public Health Service Contract No. 27-66-96, and (2) a subsequent report prepared by Scott Research Laboratories, Inc., under Public Health Service Contract No. CPA-69-528.

Part 1 outlines the development of training methods and chemical odor standards by which human panelists can measure the quality and intensity of diesel exhaust odors. These techniques are being applied in much of the PHS-sponsored research involving air pollution by diesel engines.

Part 2 summarizes further work undertaken to develop and extend the earlier studies. It describes the physical arrangement of an exhaust dilution and panel exposure system and presents instructions for conducting odor evaluation tests. It also discusses design of test programs and statistical analysis of test data.

ABSTRACT

Exhaust gases emitted by diesel engines are characterized by offensive odors, which can be rated numerically by human judges. Correlation of such ratings with the chemical composition of diesel exhaust will aid in (1) establishing Federal standards for diesel exhaust emissions and (2) developing methods of diesel odor control.

Part 1 presents instructions for the training of judges to rate the odors in terms of intensity and quality standards provided to them for reference. Part 2 describes the physical arrangement of an exhaust dilution and panel exposure system. It describes the performance of odor evaluation tests, design of test programs, and statistical analysis of test data.

Appendices describe (A) the theoretical basis for air purification requirements in test chambers, (B) composition and makeup of diesel odor standards, and (C) mathematical derivations of the statistical procedures.

CONTENTS

PART 1. SELECTION AND TRAINING OF JUDGES FOR SENSORY EVALUATION OF THE INTENSITY AND CHARACTER OF DIESEL EXHAUST ODORS	1
INTRODUCTION	3
ENVIRONMENTAL CONDITIONS FOR SENSORY TESTING	5
SELECTION OF JUDGES FOR DIESEL EXHAUST ODOR STUDIES	7
The Triangle Test.	7
The Intensity Rating Test	10
The Multicomponent Odor Identification Test.	13
Demonstration of Satisfactory Test Behavior.	15
TRAINING OF JUDGES FOR DIESEL EXHAUST ODOR STUDIES	17
Initial Improvement of Performance	17
Exposure to Diesel Exhaust	18
Learning the Diesel Odor Standards.	19
ACKNOWLEDGMENTS	20
PART 2. SENSORY EVALUATION OF DIESEL EXHAUST ODOR INTENSITY	21
INTRODUCTION	23
EXHAUST DILUTION AND PANEL EXPOSURE SYSTEM	25
TRAINING OF JUDGES FOR DIESEL EXHAUST ODOR- INTENSITY MEASUREMENTS.	29
Learning the Diesel Odor Intensity Standards	30
Program to Test Judges' Performance	31
Exposure to Diesel Exhaust	32
PANEL PROCEDURES DURING TEST PROGRAMS	35
DESIGN OF TEST PROGRAMS	37
STATISTICAL ANALYSIS OF TEST DATA	39
ACKNOWLEDGMENTS	41
APPENDIX A. Concentrations of Odorous Vapors in Test Chambers	45
APPENDIX B. Sensory Standards for Diesel Exhaust Odor Study	51
APPENDIX C. Statistical Derivations.	59

PART 1.
SELECTION AND TRAINING OF JUDGES
FOR SENSORY EVALUATION
OF THE INTENSITY AND CHARACTER
OF DIESEL EXHAUST ODORS

Amos Turk, Ph. D.
Professor, Department of Chemistry
The City College of the City University of New York

Janet T. Wittes
Department of Statistics
Harvard University

Prepared under Public Health Service
Contract No. PH 27-66-96
1967

PART 1.

SELECTION AND TRAINING OF JUDGES FOR SENSORY EVALUATION OF THE INTENSITY AND CHARACTER OF DIESEL EXHAUST ODORS

INTRODUCTION

When a person is exposed to diesel exhaust on the street or highway, he may sense odor, chemical irritation in the nose or eyes, sound, velocity pressure of moving air, temperature gradients, impaction of small particles and the sight of smoke, moving vehicles, and other associated actions. When the aggregate of such experience becomes sufficiently unpleasant, the threshold for individual action is exceeded and the affected person may voice a complaint or react in some other relevant manner.

Odor is undoubtedly the prime sensory attribute of diesel exhaust under the typical circumstances of human exposure. The sensory evaluation of diesel exhaust odor under different conditions of dilution, engine type, engine operation, fuel, fuel additives, and exhaust control devices will therefore provide part of the basis for specifying permissible conditions of exposure.

The sensory evaluations will be made by human judges. Taken as a group to increase the precision of the evaluations, the judges constitute a sensory odor panel. In serving on the panel, the individuals will be called upon to rank diesel exhaust samples to which they are exposed according to odor intensity and according to the quality, character, or type of odor. Depending on dilution of the exhaust, some samples will be chemically irritating (in the sense of "pungent") and odorous at the same time, even though the senses of irritation and odor are physiologically distinct. In some cases, therefore, the evaluation continuum will, in effect, comprise both types of sensations.

The judges in these tasks express their evaluations of intensity and quality in a quantitative way; they do not assume the role of individuals who express their personal preferences of "like" or "dislike." The following general requirements are imposed for the selection and performance of such judges.

1. They must have satisfactory sensory ability to distinguish among odors of different intensities and to discriminate among different odor qualities.
2. They must be emotionally receptive to tasks that involve quantitative and discriminatory judgments without expressions of preference.
3. They must be trained for the specific tasks to be accomplished.
4. A nondistracting environment must be provided for the sensory tests
5. Standards should be established to provide a quantitative basis for sensory measurements and to provide replicable anchoring points that will facilitate interlaboratory comparisons.

ENVIRONMENTAL CONDITIONS FOR SENSORY TESTING

A space for sensory testing should be free of competing distractions. In-and-out visits and socialization by non-participants should be restricted, except in demonstration exercises. The area for preparation and coding of test samples or make-up and dilution of exhaust gas streams should be separated from the panel members and not visible to them. Extraneous sounds, especially the sounds of operation of test vehicles, should be inaudible during the tests. Color schemes should be neutral.

The test area should have some means for space odor control, especially for odors introduced from the samples being tested. This may be accomplished either by local exhaust of vapors from the test samples, or by general purification of the room air through a recirculating device, preferably an activated carbon unit, or by some combination of both methods. If a considerable volume of air containing odorous diluted vehicle exhaust is spilled into the space during the tests, then the effectiveness of odor control by general recirculation through an air purifying device will be limited. The nature of this limitation is described in detail in Appendix A.

When the tests are to be conducted and reported on an individual basis without communication among judges, it is desirable to have separate booths or enclosures for the individual panel members. When the tests are to be cooperative, with discussion and comparisons among the judges, then a conference table setup is convenient.

The panel moderator or chairman should be able to communicate readily and conveniently with all of the judges. The general atmosphere should be comfortable and relaxing, but also should encourage the judges to be attentive and serious.

Several simple rules for conduct should be imposed. No smoking, eating, or drinking that is not associated with tests should be allowed in the test area. Judges should be discouraged from the use of perfumes or perfumed cosmetics just prior to a test session. A period of half an hour or more should be allowed after smoking, eating a meal, or drinking coffee, before participation in a test exercise.

SELECTION OF JUDGES FOR DIESEL EXHAUST ODOR STUDIES

There is no magic number of panel members. Many panels number five to fifteen judges, and a number close to ten is probably suitable for diesel exhaust sensory work. A large number of panelists should be available for testing so that no interruptions need be caused by temporary absenteeism or personnel turnover. The panel members should not be divided, however, into "regulars" and "standbys." Some rotation scheme should be set up so that no trained panel member is allowed to go "stale."

The major tasks that the odor judges will be expected to perform are:

1. To judge the relative intensity of diesel exhaust odors at different dilutions.
2. To discriminate among the different qualities of diesel exhaust odors.
3. To combine (1) and (2) to give a composite profile.

The judges will be expected to follow instructions, and at the same time to render independent judgments reflecting their own sensations and report their findings.

Four main tests for selection of judges are recommended:

1. The triangle test.
2. The intensity rating test.
3. The multicomponent odor identification test.
4. Demonstration of satisfactory test behavior.

These tests are described in detail in the following sections. Statistical derivations of these tests are presented in Appendix C.

THE TRIANGLE TEST

Three test samples are presented at the same time. Two are identical, the third is different. The candidate is requested to identify the different or "odd" sample.

In dealing with untrained candidates, the moderator should avoid strange or objectionable materials. It is convenient to use dilute aqueous solutions of food flavors. These are easy to administer, and they produce a minimum of initial shock to the candidate. The solutions may be smelled or tasted; in both cases, olfactory discrimination is actually being used to make the identification. Materials that are recommended are:

<u>Flavorant</u>	<u>Approximate concentrations</u>
Vanilla extract	To one quart of water add 1 or 2 drops of extract to achieve a detection threshold at a level such that about 75 percent of the triangle scores will be correct answers.
Lemon extract	
Pineapple extract	
Almond extract	
Rum extract	
Rose extract	
Mint extract	

The samples should be presented at ambient temperature in small throw-away paper cups.

Instructions are given as follows: "The object of this test is to distinguish differences between food flavors that are very weak in intensity. The samples given to you consist of 1 or 2 drops of a common food extract, such as vanilla, almond, or mint, in a quantity of pure drinking water. You may smell or taste the samples, or both. Each test consists of three samples, two of which are the same and one of which is different. Your task is to pick out the different or odd one. You do not have to identify the flavor, just choose which one is different from the other two. Enter on your score sheet the code number of the sample that you choose as the odd one."

Present a trial test to familiarize the candidate with the procedure. This trial should be conducted at a higher level of intensity so that the distinction is easy. Do not ask for a score. State the correct answer verbally to the candidate. Answer any questions regarding procedure. The purpose of this trial is to concentrate most of the learning into the first experiment and to make the subsequent tests independent of each other to a greater degree. Now administer and score five triangle tests.

Select the candidates on the following basis:

List the candidates and their scores (number of correct answers) in order, highest score first.

Refer to Table 1 to determine which differences between scores are significant.

Decide how many panel members you should select from the candidates available. Determine from the table at what levels there are statistically significant differences between candidates and make your selection accordingly. For these rough screening operations, it is recommended that confidence limits be set at about 25 or 30 percent, rather than the usual 5 percent. This will have the effect of initial rejection of most of the candidates that are likely to be unsuitable.*

*The procedure of this and some later examples does not describe a series of independent selections between randomly chosen pairs of candidates. Instead, the candidates among whom we are discriminating are ranked according to their scores. Consequently, tables of the distribution of difference between any two scores are not strictly appropriate to choosing among more than two candidates. Exact significance levels should be based on the distribution of the range of scores. This would require separate tables for each number of candidates being screened. Such a procedure would be unwieldy, and we feel that the tests based on the difference between two scores serve as satisfactory approximations to the exact significance levels.

Example 1. There are ten candidates, who take five triangle tests each. We need about five or six panel members from among these candidates. Their scores are:

<u>Candidate</u>	<u>Number of correct answers</u>
A	5
B	2
C	3
D	0
E	0
F	2
G	3
H	5
I	5
J	4

Table 1. SIGNIFICANCE OF DIFFERENCES AMONG SCORES IN TRIANGLE TESTS

<u>Number of tests</u>	<u>Difference between two candidates in number of correct answers</u>	<u>Probability that at least this difference could have been obtained by chance, %</u>
1	0	100
	1	44
2	0	100
	1	59
	2	10
3	0	100
	1	66
	2	19
	3	2
4	0	100
	1	71
	2	26
	3	5
	4	0.5
5	0	100
	1	74
	2	31
	3	9
	4	2
	5	0.1

Step 1. Choose an acceptable significance level. In this case we will choose 0.20 to 0.30 (70 to 80 percent confidence levels).

Step 2. List the candidates in order of the number of correct answers they gave.

<u>Candidates</u>	<u>Number of correct answers</u>
A, H, I	5
J	4
C, G	3
B, F	2
D, E	0

Step 3. Check Table 1 to determine how much of a difference in the scores of two candidates is needed to give confidence that they are significantly different from each other. In this example, the number of tests equals 5; therefore, a difference of 2 or more in score indicates a significant difference in performance.

Step 4. Choose the candidates required. Starting from the top, A, H, and I have a score of 5. But the scores of candidates A, H, I, and J differ by less than 2; therefore this difference is not significant, and we can consider these candidates to be "equal." If we need five or six panelists and have no other candidates, we must add C and G to the panel. (J, C, and G can be considered "equal.") The panel will then consist of the first six: A, H, I, J, C, and G.

Note that we could establish higher confidences in our selections by giving more tests, say 20 or 25 instead of five. This is not recommended because the extra effort can be more profitably expended in the screening of additional candidates.

THE INTENSITY RATING TEST

A series of dilutions of an odorant in an odorless diluent is set up. One sample is removed from the series. The candidate is asked to replace it according to its odor intensity in the position from which it was taken.

For use in selecting candidates, the odorant should be fairly strong when it is in pure form, and not toxic, unpleasant, or strange. Any of a number of fruity or fragrant odors is acceptable. Some possibilities are amyl acetate, eucalyptol, oil of wintergreen, and heptaldehyde.

In the example that follows, the odorant is amyl acetate in propylene glycol (low-odor perfumer's grade). Amber 2-ounce glass bottles with plastic screw caps are used.

<u>Bottle No.</u>	<u>Procedure</u>	<u>Concentration (fraction by volume of amyl acetate in the solution)</u>
1	Add 10 ml amyl acetate.	1
2	Add 10 ml amyl acetate plus 10 ml propylene glycol. Mix. Using a 10 ml pipet, remove 10 ml of the mixture and transfer to bottle 3.	1/2
3	Contains 10 ml of material from bottle 2. Add 10 ml propylene glycol. Mix. Remove 10 ml of mixture and transfer to bottle 4.	1/4
4	Contains 10 ml of material from bottle 3. Add 10 ml propylene glycol. Mix. Remove 10 ml of mixture and transfer to bottle 5.	1/8

Continue this procedure until 20 bottles are prepared. The odor should be detectable by a sensitive person as far as Bottle 19 or 20 in the dilution series.

If the bottle number is designated n , then the concentration in any bottle equals 2^{1-n} .

The bottles must appear identical and must be consecutively numbered so that the numbers are not visible to the candidates. Labels can be put on the bottoms of the bottles or on the face of the bottle if the label is obscured by wrapping with aluminum foil during the test. The bottles are lined up in sequence in front of the candidate.

The following instructions are given: "The 20 bottles lined up in front of you all contain solutions of amyl acetate, which is a synthetic banana oil. They differ from each other in odor strength; the most intense odor is on the left, and the intensity gradually decreases from bottle to bottle toward the right. The last bottle on your right has so little banana oil odor that it may not be detectable at all. In the test you are about to perform one of these bottles will be removed from the series, from a position unknown to you. The task will be to replace it in the proper location in the series, the location from which it was taken. If it is replaced in its proper position, it will smell stronger than the bottle on its right and weaker than the bottle on its left. Proceed as follows. First familiarize yourself with the odors of the bottles in the series. Start from the right (number 20) remove the cap, sniff gently and recap. Then do the same for every other bottle going to your left. Remember, the odors will be getting stronger toward the left and you will fatigue your sense of smell temporarily if you sniff too long at the more intense odors. You need not smell every bottle in the series at this stage of the test." (After a brief time for familiarization ...) "Now leave the room." (The tester removes one bottle, and rearranges the others to obscure the gap. The removed bottle is placed in front of the remaining 19). "Now come back into the room and replace the bottle in its proper place in the series."

Statistical scoring procedure: The same procedure, consisting of four tests, is used for each candidate. The bottles are successively removed in the standard order: 12, 8, 16, 3.

Step 1. Score as follows:

<u>Positions removed from correct location</u>	<u>Score (higher number is worse score)</u>
0	0
<u>+1</u>	1
<u>+2</u>	4
<u>+3</u>	9
<u>+4 or more</u>	16

Step 2. Refer to Table 2 to determine which differences between scores are significant.

**Table 2. SIGNIFICANCE OF DIFFERENCES
AMONG SCORES IN INTENSITY RATING TEST**

Differences between scores of any two candidates	Probability that at least this difference could have been obtained by chance, %
18	30
20	25
23	20
25	15
29	10
34	5
44	1
56	1/10

Example 1. A candidate performs as follows:

<u>Missing bottle</u>	<u>Replaced in position</u>
12	12
8	7
16	6
3	5

What is the candidate's score?

<u>Bottle number</u>	<u>Positions removed from correct location</u>	<u>Score</u>
12	12 12 = 0	0
8	8 7 = 1	1
16	16 6 = 10	16
3	3 5 = -2	4
		<hr/>

Total score 21

Example 2. Two candidates show the following performances. Is one better than the other? What confidence is there in the selection?

Candidate A

<u>Bottle missing</u>	<u>Replaced in position</u>
12	15
8	13
16	12
3	1

Candidate B

12	15
8	10
16	13
3	3

A's score		Score
12	15 = -3	9
8	13 = -5	16
16	12 = 4	16
3	1 = 2	<u>4</u>
		45

B's score		Score
12	15 = -3	9
8	10 = -2	4
16	13 = 3	9
3	3 = 0	<u>0</u>
		22

$$A - B = 45 - 22 = 23$$

Therefore B scored better than A. From the significance table (Table 2), this could have been due to chance alone 20 percent of the time. We have, therefore, a confidence of 80 percent in our selection of B over A. If we demand a confidence of 90 percent before making a decision, then we cannot rule out A as a possible panel member before further testing.

THE MULTICOMPONENT ODOR IDENTIFICATION TEST

This test presents three mixtures to the candidate. These mixtures contain, in sequence, 2, 3, and 4 odors out of a possible total of 8 known standards. The candidate is told how many components to look for, and is asked to identify them.

The following materials are recommended as standards:

1. Oil of cade (burnt)
2. Cassia (cinnamon)
3. Eucalyptus
4. Amyl acetate (banana)
5. Clove oil
6. Orange oil
7. Almond oil (benzaldehyde)
8. Vanillin or vanilla extract

Instructions are given as follows: "You have in front of you eight labeled common odors. They are (state which). These will be your reference standards and you may smell them whenever you wish. Now, you will be given an unknown odor sample. This sample contains a mixture of two of the standard odors. Write down on your score sheet which two odors are present in the test sample." When this test is finished, repeat the instructions but state that the new sample contains a mixture of three standards.

Then repeat the instructions again for the third test explaining that the sample contains a mixture of four odors.

The multicomponent odor identification test is scored as follows:

Step 1. Administer the same test sequence, consisting of three tests, to each candidate.

Test 1. Two components

Test 2. Three components

Test 3. Four components

Step 2. Calculate the score of each individual candidate according to the following procedure.

$$\text{Total score} = \left(\frac{\text{Number correct}}{\text{in test 1}} \right)^2 + \left(\frac{\text{Number correct}}{\text{in test 2}} \right)^2 + \left(\frac{\text{Number correct}}{\text{in test 3}} \right)^2$$

Step 3. Refer to Table 3 to determine which differences between scores are significant.

Table 3. SIGNIFICANCE OF DIFFERENCES BETWEEN SCORES IN MULTICOMPONENT ODOR IDENTIFICATION TEST

Difference between scores of any two candidates	Probability that at least this difference could have been obtained by chance, %
6	25
7	20
8	15
9	10
11	5
15	1

Example 1. Candidates A and B scored as follows in the multicomponent odor identification test. Are the scores significantly different?

Test	Number correct	
	Candidate A	Candidate B
1	2	0
2	3	1
3	1	4

$$\text{Score of A} = 2^2 + 3^2 + 1^2 = 14$$

$$\text{Score of B} = 0^2 + 1^2 + 4^2 = 17$$

Difference = 3. The probability that this difference could have been obtained by chance is greater than 25%. Therefore, we do not attach any

significance to this difference, and the two candidates should not be differentiated from each other.

Example 2. Choose the best four candidates from the following:

Test	Number correct obtained by each candidate								
	A	B	C	D	E	F	G	H	I
1	0	2	1	1	1	0	2	0	2
2	3	3	2	0	1	0	1	1	3
3	4	2	4	1	3	4	0	2	3

The scores are computed on the basis of the sum of the squares of the correct answers and are then listed in order of magnitude. The order is

Candidate	Score
A	25
I	22
C	21
B	17
F	16
E	11
G,H	5

Now, referring to Table 3, we can say with a confidence of 80 percent that any candidates whose scores differ by no more than 7 points are considered "equal." By this criterion of confidence, candidates A, I, and C could be considered to be equal and could be selected for the panel. Candidate B differs from Candidate A by more than 7 points and is, therefore, ruled out at this confidence level. At a confidence level of 90 percent, however, which implies a lower probability (10 percent) that the observed differences of scores could have been obtained by chance, we could have selected all of the candidates except the last three.

DEMONSTRATION OF SATISFACTORY TEST BEHAVIOR

During the phases of candidate selection, the panel leader or moderator should be attentive to various aspects of the candidates' test behavior. These aspects are:

Speed. The best behavior is purposeful and deliberate, neither excessively hasty nor slow.

Interest level. The candidate should feel challenged and motivated. Candidates who find the work distasteful or uncomfortable should not be selected.

Domination. In group testing, the candidate should be helpful when asked, but should not try to push his opinions on others.

Independence. The candidate should be willing to consider the suggestions of others, but should not be influenced to change score against his own judgment.

Honesty. Candidates who try (successfully or not) to decode labels or peek under bottles should be rejected.

The panel leader should observe the candidates' behavior in these matters carefully but unobtrusively. No specific numerical scoring system is recommended; the leader should rely on his own judgment with regard to the sensitive question of whether to reject, on the basis of poor test behavior, any otherwise acceptable candidates.

TRAINING OF JUDGES FOR DIESEL EXHAUST ODOR STUDIES

Training should be scheduled according to the following procedure.

1. Improve the performance of the judges in the same tests that were administered for panel selection. (Estimated time: 3 to 4 days.)
2. Expose the judges to diesel exhaust under the conditions to be used in the testing and under conditions of random ambient air dilution, to diesel fuel, and to components of diesel exhaust condensate if such are available. Discuss the four diesel odor descriptors (see Appendix 3) during each of these exposures. (Estimated time: 2 to 3 days.)
3. Introduce the judges to the kit of diesel odor reference standards. Explain how the standards will be used in measuring intensity and quality of diesel exhaust odor. Train the panel members in recognizing individual samples in the kit and in recognizing multicomponent samples. Establish minimum requirements for these tasks. During this training, intersperse exercises that relate the diesel quality standards to the sensory quality of diesel exhausts. (Estimated time: 1 to 2 weeks.)
4. Eliminate panel members as necessary in phases A, B, and C for reasons of poor performance or motivation, emotional problems, excessive domination or dependence, or other difficulties apparent to the moderator.
5. The panel may now operate according to whatever experimental design is adopted as the original research program. The continued conduct of the work will, in effect, continue the training of the panel. The panel members should be checked periodically to insure that the level of the performance with the kit components obtained in phase 3 is maintained.

Some of these phases of panel training are considered in more detail in the following sections.

INITIAL IMPROVEMENT OF PERFORMANCE

The tests used for the selection of panel members should be repeated, with one important difference. In training, no errors are ignored. As soon as a trainee or group of trainees scores a test, the correct answers are disclosed; the trainee repeats the exercise with attention focused on elimination of the error, with the help of the leader.

Example 1. Trainee: "I detect eucalyptus, banana, clove, and cinnamon in this mixture."

Leader: "The mixture contains eucalyptus, banana, almond, and cinnamon. That means you misidentified one element. Refer to the almond and clove standards, recheck them, and then smell your mixture again."

(Note — The leader must not be deprecatory. Say "misidentified" to express the facts, not "confused" or "made an error" or "goofed" to express disapproval.)

Trainee: "Well, that almond is overpowered by the other odors. It didn't come through for a while."

Leader: "That's all right, it may happen that way. A four-component mixture is a difficult task. Focus your attention on one component at a time, take only short sniffs so you do not get fatigued, and refer to the standards whenever you have to."

During training, allow trainees to work together and help each other by suggestions and exchange of comments and samples. Keep records of the trainees' progress.

Training should be continued until there is a noticeable levelling-off in performance. Prolonged continuation of training on known mixtures is wasteful, because the diesel work will involve new materials and, of necessity, new training.

An important aspect of training, and, later, of panel utilization is the question of whether the panel should work on an individual or on a group basis. The individual basis eliminates social influences; each panelist's score is purely his own judgment. The group basis allows for cooperative suggestions that will call a panelist's attention to something that he himself senses only after his attention is properly focused. The decision between the two methods is best made on a statistical basis. It will be appropriate to use the t-test to determine whether the difference between the average panel scores obtained on an individual and on a group basis is significant.

EXPOSURE TO DIESEL EXHAUST

The panel members must be exposed to diesel exhaust under various conditions that are likely to be experienced in the proposed testing program and also under typical conditions expected on the street or highway. The panelists should also be exposed to diesel fuel and/or fuel components, diesel exhaust condensate, and other relevant odor sources. Explain to the panel members that the quality of an odor can be described in terms of quality components. The explanation can be an expansion of remarks such as the following:

"You have identified the components of mixtures of two, three, or four odorants in the tests you have been conducting during the last few days. This identification is also a description of odor quality. You may say that the odor of a given sample is a mixture of lemon and vanilla. This statement describes the quality of the odor mixture, just as the same statement would be a description of flavor if the sample were a piece of cake. We are going to describe diesel exhaust in terms of four qualities:

1. Burnt/smoky. This is the quality in which diesel exhaust is related to the odors of other products of burning or combustion.
2. Oily. This quality is the oiliness related to the presence of the odor of the heavy components of unburned fuel.

3. Pungent/acid. This is the quality associated with pungency in high concentration, gradually changing to an acid or sour quality with greater dilution.

4. Aldehydic/aromatic. This is the quality related to what may be thought of as the "fragrant" aspect of diesel exhaust. It may also be thought of, in most instances, as that quality not represented by smokiness, oiliness, or pungency."

LEARNING THE DIESEL ODOR STANDARDS

(Refer to Appendix B for details of the composition and preparation of the diesel odor kit.)

The following introductory remarks may be appropriate:

"You will be given a kit of standard odors to which you will refer in making your odor judgments. Standard odors D-1 through D-12 represent the intensity levels of diesel exhaust odor, without regard to quality. Standards B-1 through B-4 represent four intensity levels of burnt odor; O-1 through O-4 represent intensity levels of oily odor. (The moderator at this point should explain the entire kit.) Before using these standard odors to measure diesel exhaust, it will be necessary for each of you to learn the various standards and to get some familiarity with mixtures of the standards."

The training for recognition of odor standards should now proceed along the following lines.

1. The judges should be trained in the intensity levels of the D-1 through D-12 series. Judges should be able to identify any unknown sample to within ± 1 or 2 intensity levels.

2. The judges should learn each of the quality components at the "extreme" concentration (B-4, O-4, P-4, and A-4). They should then learn to identify each intensity of each quality, 16 bottles in all. They should be able to identify all unknowns as to quality and intensity about 90 percent of the time.

3. The compositions of standard mixtures are shown in Tables 4 and 5. The leader should specify to the judges the number of components in each training mixture. The judges should practice identifying two- and three-component mixtures until performance levels off. They should reach a level at which they identify mixtures correctly about 80% of the time. Correct identification is much more difficult when the number of components is unspecified. The probabilities of obtaining correct identifications by chance are shown in Table 6.

**Table 4. COMPOSITION OF COMPONENTS
FOR ODOR STANDARD MIXTURES**

Quality	Code (t = training)	Composition
Burnt	B-t	B-4 (See Appendix 3)
Oily	O-t	100 % octylbenzene
Pungent	P-t	P-4
Aldehydic	A-t	1 % A in mineral oil

**Table 5. COMPOSITION OF ODOR STANDARD
MIXTURES FOR TRAINING**

Number of components	Code (t = training)	Composition
2	AB-t	1 : 1 mixtures of the solutions of Table 4. About ½ to 1 ml of solution is placed in a wad of cotton in a plastic squeeze bottle.
	AO-t	
	AP-t	
	BO-t	
	BP-t	
	OP-t	
3	ABO-t	1 : 1 : 1 mixtures as above.
	ABP-t	
	AOP-t	
	BOP-t	
4	ABOP-t	1 : 1 : 1 : 1 mixture as above.

**Table 6. PROBABILITY OF CORRECT IDENTIFICATION OF TRAINING
STANDARDS BY CHANCE ALONE**

Number of components stated to be in mixture	Number of training standards	Probability per test of correct identification of standard by chance alone
1	4	1/4
2	6	1/6
3	4	1/4
4	1	1
Not disclosed	15	1/15

ACKNOWLEDGMENTS

The following chemists participated in the development of the odor standards: Louis Reckner, Robert Squires, and Z. Tomaras, all of the Scott Research Laboratories; Stanley Mehlman and Elizabeth Wolf, both of the City University of New York; and Jonathan Turk, of Brown University.

PART 2.
SENSORY EVALUATION
OF DIESEL EXHAUST ODOR INTENSITY

L. R. Reckner and R. E. Squires
Scott Research Laboratories, Inc.

Prepared under Public Health Service
Contract No. CPA-69-528
1969

PART 2.

SENSORY EVALUATION OF DIESEL EXHAUST ODOR INTENSITY

INTRODUCTION

The need for a reliable method to measure the intensity of diesel exhaust odor has increased in recent years as greater attention has been given to the reduction of air pollution from motor vehicles. Accurate, reproducible, chemical or physical tests would be the ideal answer to this need. However, the validity of any instrumental method for odor measurement must first be verified by comparison with results obtained from human responses. Odor-panel techniques are, therefore, a prerequisite to this ultimate goal, as well as a tool that can be used to advantage until adequate instrumental procedures have been established.

The primary considerations in developing panel sensory techniques are the presentation of the stimulus in a manner that stimulates realistic environmental exposure and the objectivity of the resulting panel responses. The five basic requirements for achieving these goals in diesel exhaust odor studies are as follows:

1. Construction of an exhaust dilution and panel exposure system that simulates on-the-street exposure.
2. Selection of panelists with superior olfactory ability.
3. Training of the selected panelists to rate the intensity of dilute diesel exhaust.
4. Formulation of diesel odor intensity standards.
5. Design of test programs.

These requirements are discussed in detail in succeeding sections.

EXHAUST DILUTION AND PANEL EXPOSURE SYSTEM

A system that can be used to dilute exhaust and present it to the odor panel is essential for conducting experimental and research programs involving the measurement of diesel exhaust odor intensity. The system should meet the following criteria:

1. The system should present diluted exhaust to the panelists in a manner simulating on-the-street exposure.
2. The concentration of exhaust odorants should not be altered, except by dilution, between the exhaust source and the odor judge. Condensation, absorption, chemical reaction, or oxidation of exhaust odorants within the system must be minimized.
3. Additional dilution of the exhaust should not occur during the odor appraisal.
4. The system should be suitably equipped to control and monitor a broad range of exhaust concentrations.

The system illustrated in Figure 1 meets the above criteria and can be used to perform all of the programs described herein. It has been successfully employed to rate exhaust intensity at a number of engine, fuel, dilution, and steady-state operating-condition combinations. This system is described in detail to demonstrate the precautions necessary to maintain the integrity of exhaust odor. Other systems that fit specific needs and situations may be substituted if they meet the stated criteria.

The system delivers freshly diluted diesel exhaust to a sniff box at manually controlled dilution ratios. Stainless steel and Teflon* lines are used throughout. Exhaust flows from the center of the engine exhaust pipe into the dilution air stream through a short length of heated tubing containing a valve that controls the exhaust flow rate. An extended stem permits the operator to control the flow rate while observing the dilution monitoring equipment. A back-pressure valve in the engine exhaust pipe is used, when necessary, to create pressure (6 inches H₂O) to drive the exhaust into the dilution air stream. Ambient air from a compressor is passed through condensate, charcoal, and silica gel traps and used as the dilution air at a constant flow rate of 2 cubic feet per minute.

The diluted exhaust is transferred to the sniff box through 1-inch-diameter tubing. Heated stainless steel is employed in the vicinity of the mixing point while the remainder is Teflon, which minimizes hangup of odorous compounds. A baffle plate is used to diffuse the diluted exhaust entering the sniff box. The box is constructed of stainless steel with a transparent Mylar back, which prevents the panelist from feeling closed-in while

*Mention of company or product names does not constitute endorsement by the National Air Pollution Control Administration.

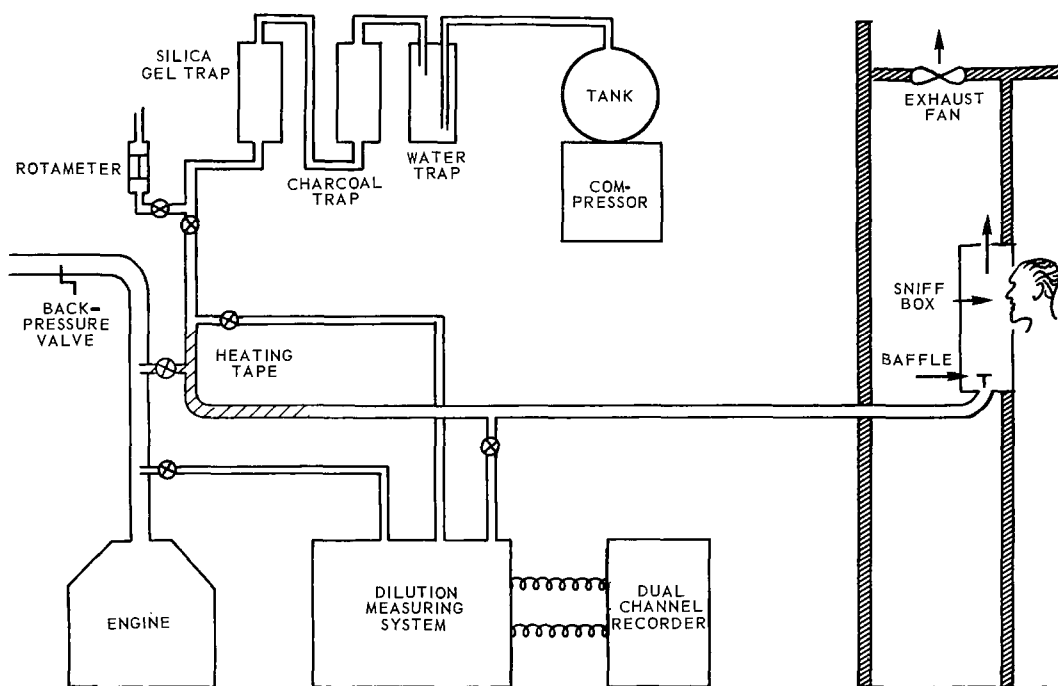


Figure 1. Exhaust dilution and panel exposure system.

he is sniffing. The box is illuminated by a 25-watt bulb in the adjacent exhaust chamber. A sheet of paper, held in place by cellophane tape, is used to seal the face opening when the box is not being used. The box has a volume of 1/2 cubic foot. The transfer time from the exhaust pipe to the sniff box is approximately 4 seconds, and the residence time in the box is 15 seconds.

The odor room is constructed in accordance with the criteria specified in Part 1. The temperature of the room is controlled at $72^{\circ} \pm 1^{\circ}$ F. Charcoal-filtered air is blown into the room to maintain a slight positive pressure (0.02 inch H_2O), which prevents the diluted exhaust in the sniff box and other contaminated air from entering the room.

The exhaust dilution ratio is continuously measured and recorded using nondispersive infrared analyzers sensitized to carbon dioxide (CO_2). The exhaust-gas-analysis system is shown schematically in Figure 2. The CO_2 concentration in the diesel exhaust pipe is measured by a 0 to 10 percent analyzer that is spanned with a close-tolerance (± 2 percent) analyzed gas mixture containing 10 percent CO_2 in nitrogen. The CO_2 in the diluted exhaust stream is measured differentially with an analyzer having a nominal range of 0 to 100 parts per million. A dual range (0 to 100 and 0 to 500 ppm) instrument is recommended. Dilution air flows through the reference cell while diluted exhaust (dilution air plus exhaust) flows through the sample cell. In this differential analysis, the instrument response decreases as the CO_2 in the cells increases even though the difference in concentrations between the two cells remains constant. For example, a concentration of 100 ppm in one cell and 0 in the other gives approximately twice the response given by 500 ppm in one cell and 400 ppm in the other. For this reason, calibration

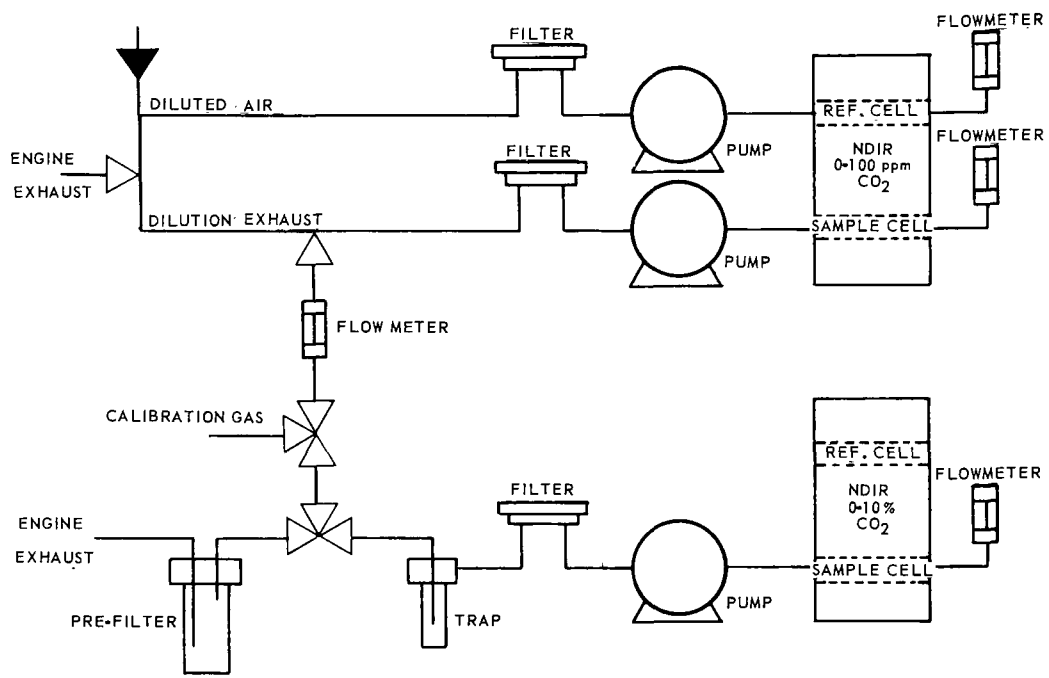


Figure 2. Dilution measuring system.

without a representative amount of CO_2 in the reference cell is not valid. Calibration curves are obtained for this instrument by adding low flows of a calibration standard through a calibrated rotameter into the dilution air stream at a point near where exhaust is ordinarily added. This simulates actual use conditions. The readings from both infrared analyzers are recorded on a dual-channel recorder.

TRAINING OF JUDGES FOR DIESEL EXHAUST ODOR INTENSITY MEASUREMENTS

The diesel odor panel should consist of approximately ten judges. At least 40 candidates should be screened in order to obtain a panel with the required level of olfactory acuity.

Three tests are recommended for the selection of judges for diesel exhaust odor intensity measurements.

1. The triangle test.
2. The intensity rating test.
3. Demonstration of satisfactory test behavior.

Statistical derivations and detailed descriptions of each test are given in Part 1.

Part 1 also gives valuable information on the training of judges for sensory evaluations, with details on the composition and preparation of the odor standards. The procedures for training judges for intensity measurements are presented here with additional detail based on experience acquired after the initial work was published.

Training for intensity measurements is accomplished according to the following procedure.

1. Improve the performance of the judges by repeating the tests that were administered for panel selection. No errors should be ignored. As soon as a test is scored, the correct answer is disclosed, and the trainee repeats the exercise with attention focused on elimination of the error. Training should be continued until there is a noticeable leveling in performance.

(Estimated time: two 2-hour sessions)

2. Introduce the judges to the kit of diesel odor intensity standards. Explain how they will be used. Train the panel members to recognize the 12 standards in the series.

(Estimated time: six to eight 2-hour sessions)

3. Test the judges' ability to identify the standards.

(Estimated time: three 1-hour sessions)

4. Introduce the judges to dilute diesel exhaust. Train the judges to rate the exhaust odor in terms of the intensity standards.

(Estimated time: four to six 2-hour sessions)

5. Eliminate panel members as necessary for reasons of poor performance or motivation, emotional problems, or other difficulties apparent to the moderator during Phases 1, 2, 3, and 4.

6. The panel may now operate according to the experimental design adopted. Individual performance during each program should indicate when retraining is necessary. Performance may also be monitored periodically by employing the test administered during Phase 3 above.

Some of these phases of training are considered in detail in the following sections.

LEARNING THE DIESEL ODOR INTENSITY STANDARDS

The following introductory remarks may be appropriate:

"In front of each of you are 12 plastic bottles, each of which contains an odor standard. The odorant in each bottle is the same, but the concentrations are different. Each bottle has a number on its base. The bottle numbered 1 contains the weakest odor, and the bottle numbered 12 contains the strongest. During the next few weeks you will be trained to identify each of the standards by number. Following this phase of training, you will learn to rate the odor intensity of dilute diesel exhaust in terms of the 12 odor standards."

Training should now proceed along the following lines:

1. Train the judges to handle the standards. The routine handling procedure is to remove the standard from its rack, shake it gently, remove the cap, place the bottle 1 to 2 inches below the nose, squeeze the bottle gently and sniff the gas expelled, replace the cap, and return the standard to its original position in the rack. Care must be exercised to prevent spillage or contact of the bottle with the nose. The same procedure must be used regardless of the concentration of the standard being sniffed.
2. Familiarize the trainees with the standards by administering intensity ranking tests using the standards as the odorant. No errors should be ignored, and emphasis should be placed upon association of the odor intensity with the number on the base of the bottle.

The procedures are nearly identical to those employed during trainee selection. The standards are lined up with the weakest (No. 1) on the left and the strongest (No. 12) on the right. One bottle is selected at random and removed from the series. The remaining bottles are shifted to obscure the gap. The trainee is instructed to find the proper location of the bottle that was removed. When the proper location is found, the bottle will smell stronger than the one on its left and weaker than the one on its right. The trainee counts from left to right and records the number of the standard. After everyone has recorded his answer, the correct identity is revealed, and judges in error repeat the exercise with attention focused upon elimination of the error.

This exercise is repeated at 3-minute intervals until the trainees can consistently identify any unknown standard to within ± 1 intensity unit with confidence and without having to sniff more than two bottles in the series before making the identification.

3. Train the judges to identify the intensity standards to ± 1 unit from memory. Remove the odor standards from in front of the trainee.

Randomly select standards and present them as unknowns at 3-minute intervals. After each judge has recorded his response, reveal the correct identity of the unknown. Instruct judges in error by greater than one unit to re-sniff the samples. Continue this exercise until 90 percent of the responses are correct to ± 1 unit.

PROGRAM TO TEST JUDGES' PERFORMANCE

The judges' performance should be checked following initial training and periodically thereafter to ensure that the performance level obtained during training is maintained. The recommended test program consists of three sessions, held on separate days. Two intensity standards are presented as knowns at the start of each session. The 12 intensity standards are then presented in random order as unknowns. The standards are presented at 5-minute intervals to prevent olfactory fatigue. Each judge works independently, and the identities of the unknowns are not revealed during the test.

At least 90 percent of the responses obtained during this program should be within ± 1 unit of the true value. Responses in error by greater than one unit should be randomly distributed among the judges and intensity standards. Failure to achieve this level of performance should result in re-training the judge or judges in the area indicated necessary by the data analysis.

Example: Ten odor judges each evaluated 12 intensity standards that were presented as unknowns on 3 separate days. The data were tabulated in Table 1 below, and the percentage of responses in each class was calculated. Over 90 percent of the responses were correct to within ± 1 unit of the true value, indicating satisfactory overall panel performance.

Table 1. DISTRIBUTION OF RESPONSES

Error, odor units	Frequency	Total response, %
0	223	62
± 1	119	33
± 2	18	5
± 2	0	0
Total	360	100

Errors greater than one unit were tabulated in a matrix (Table 2) to determine their distribution among judges and intensity standards.

A relatively high number of total errors were recorded in the D and F judge columns and in the 4 and 5 intensity standard columns. Judge D failed to identify standards 4 and 5 within ± 1 unit on two of the three evaluations. Judge F recorded two errors for standard 5 and one error each for standards 4 and 6. These errors account for the relatively high totals. This shows that judges D and F should be re-trained in the area of standards 4, 5, and 6.

Table 2. DISTRIBUTION OF ERRORS GREATER THAN ONE UNIT

Standard number	Judge										Total
	A	B	C	D	E	F	G	H	I	J	
1											0
2				X							1
3		X									1
4	X			XX		X		X			5
5				XX		XX					4
6						X				X	2
7	X										1
8		X									1
9						X					1
10											0
11						X					1
12								X			1
Total	2	2	0	5	0	6	0	2	0	1	18

EXPOSURE TO DIESEL EXHAUST

When the judges have been trained to indentify the intensity standards presented as unknowns to within ± 1 unit 90 percent of the time, they are ready to rate diesel exhaust. A variety of exhaust concentrations and engine operating conditions should be presented. Emphasis should be placed upon identification of the exhaust-odor intensity in terms of the odor standards.

An expansion of the following remarks is an appropriate introduction to this phase of training:

"We are about to begin the final phase of training. The procedures employed at the termination of this phase will be used during future evaluation programs. The odorant will be dilute diesel exhaust presented in a sniff box. Your task will be to sniff the exhaust and record the number of the odor standard that has the same apparent intensity as the exhaust sample."

Training may now proceed along the following lines:

1. Familiarize the judges with the exposure procedure. Dilution air is passed through the sniff box. The trainee is instructed to approach the box, lift the door, press his face snugly against the box, and sniff the contents in a normal manner. The judges approach the box in a sequence specified by the panel moderator until everyone has sniffed the sample. The entire group should sniff the dilution air at least twice using the same sequence and with the moderator answering any questions that arise.
2. Introduce the judges to dilute diesel exhaust. The procedures of step 1 above are repeated with two exceptions. First, dilute exhaust instead of dilution air is passed through the sniff box. Second, the judges are instructed to record the number of the standard that has the same apparent odor intensity as the sample. The panel moderator determines the average response for the group and presents that standard to the judges for reference. The judges re-evaluate the sample and when all answers have been recorded, they are displayed on a

blackboard. Judges with responses two units or more from the panel average are instructed to re-sniff the exhaust and record their final impressions.

The procedure is repeated using a number of exhaust concentrations and engine operating conditions. The time between exhaust presentations must be long enough to prevent olfactory fatigue. Individual performance should be monitored closely. If a judge consistently disagrees with the group average by two or more units, the reason for the low or high responses must be determined and corrective action taken.

As the trainees become familiar with the task, the deviation of individual response from the group average will decrease until there is a noticeable leveling in performance. At this time displaying the results and repeating exposure to the same sample is discontinued. Standards are then selected at random and presented as unknowns between exhaust samples. The true identity of the standard and the average response for the exhaust samples are not revealed. This procedure should be continued for at least one 2-hour session or until individual responses are consistently less than two units from the panel average.

During the final phase of training the alternate presentation of standards with exhaust is discontinued and two randomly selected standards are presented as unknowns at the start of each session only. After the judges have recorded their responses, the true identity is revealed and those in error by greater than one unit are instructed to re-sniff the standard. Exhaust samples covering a broad range of concentrations and engine operating conditions are presented to the panel. Judges work independently, and the results are not discussed. Samples are presented until individual responses are consistently less than two units from the panel average.

The training is complete, but the decision must be made whether the judges should or should not physically refer to the odor standards during formal exhaust evaluation programs. Physical reference may result in olfactory fatigue and no improvement in panel performance. The decision is best made on a statistical basis. The use of a t-test is appropriate to determine whether the average panel response and deviation between replicate responses obtained using the two methods are significantly different. Unless there is a significant improvement in performance, physical reference to the standards should not be made during an evaluation program.

PANEL PROCEDURES DURING TEST PROGRAMS

During formal programs, judges with colds or other disorders that might affect their sensory ability should not participate. Judges should allow a period of at least 1/2 hour after smoking, eating a meal, or drinking coffee before participating in a test exercise. The use of perfumes or perfumed cosmetics must be discouraged.

Two randomly selected intensity standards are presented as unknowns at the start of each session. After the judges have recorded their answers, the true identities are revealed. Judges in error by greater than 1 unit should re-sniff the standard.

Dilute exhaust is presented in the order specified by the program design. Individual judgements are made at intervals sufficient in length to prevent olfactory fatigue. Intervals of 3 to 5 minutes are recommended. The judges work independently, and the results are not discussed during the test session.

The judges do not sniff the odor standards during the test program unless this has been shown to be beneficial in the final training phase. If the judges refer to the standards during the test, it is recommended that the reference be made only to confirm a predetermined answer and that the sniffing of standards be minimized in order to reduce the possibility of olfactory fatigue.

DESIGN OF TEST PROGRAMS

Statistically valid conclusions concerning the effects of variables such as engines, fuels, exhaust devices, operating conditions, and exhaust concentrations can be obtained only through formal test programs that are designed to meet specific test requirements. The complexity of the statistical design and subsequent data analysis is determined by the number of test variables to be studied and the statistical precision desired. The following recommendations apply to the general design of test programs.

1. Selection of test variables. The number of variables investigated during each program should be minimized in order to decrease the likelihood of obtaining interaction effects that may mask the effect of the variables of interest. Only variables pertinent to the evaluation should be included in the design. All test conditions should be controlled at realistic levels.
2. Order of sample presentation. The order of sample presentation may affect an individual's response to the odorant. Such influences are commonly referred to as time error and contrast effect. These influences may be avoided by balancing the order of presentation so that over the entire program each test condition will precede and follow each other test condition an equal number of times. In addition to the balanced order of presentation, partially balanced or randomized-block, and paired-observation designs have been employed with success under various test situations. When only two levels of a single variable are of primary interest, the paired-observation design is considered ideal because of the precision of the results obtained and the simplicity of data analysis.
3. Number of replicate observations per test condition. Sufficiently large numbers of replicate observations should be made in order that conclusions concerning the test variables can be drawn with a high degree of confidence. It is recommended that initial randomized-block and paired-observation designs include 5 and 8 replicate observations per test condition, respectively. Statistical procedures, beyond the scope of this publication, may be employed to predict from initial data the number of replicate observations that would be required to draw conclusions at specified confidence levels during subsequent tests.
4. Number of observations per test session. The number of observations per test session should be between 12 and 15, and should not exceed 18. Presentation of a greater number of samples may result in the loss of sensory ability because of either physical or psychological factors.

A program design that has wide practical application is given in Table 3. The program was designed to test the intensity difference produced by two levels of a variable at three engine operating conditions and one exhaust concentration. The program follows a paired design with a random order

of presentation. Operating conditions are randomized within blocks. The term "block" refers to two time periods within a test session.

The two levels of variable (1 and 2) may be two fuels of different composition, a fuel with and one without an additive, exhaust before and after a device, two engines of different design, or any other pair of variables that realistically fit the design. F, H, and I may be any conditions pertinent to the evaluation of 1 and 2, such as three engine operating conditions.

Table 3. DESIGN FOR INTENSITY RATING PROGRAM

Day	Block	Test condition (engine condition, fuel)					
		(H, 1)	(H, 2)	(F, 1)	(F, 2)	(I, 1)	(I, 2)
1	1	(H, 1)	(H, 2)	(F, 1)	(F, 2)	(I, 1)	(I, 2)
	2	(H, 2)	(H, 1)	(I, 2)	(I, 1)	(F, 2)	(F, 1)
2	1	(I, 2)	(I, 1)	(H, 2)	(H, 1)	(F, 2)	(F, 1)
	2	(F, 2)	(F, 1)	(I, 1)	(I, 2)	(H, 2)	(H, 1)
3	1	(F, 2)	(F, 1)	(H, 1)	(H, 2)	(I, 2)	(I, 1)
	2	(H, 1)	(H, 2)	(F, 1)	(F, 2)	(I, 1)	(I, 2)
4	1	(F, 2)	(F, 1)	(H, 2)	(H, 1)	(I, 1)	(I, 2)
	2	(I, 2)	(I, 1)	(F, 2)	(F, 1)	(H, 1)	(H, 2)

Notes: The design emphasizes definition of the difference between variables 1 and 2, but the relationship between variables F, H, and I are also subject to analysis of variance.

F, H, and I may be any engine operating conditions. 1 and 2 may be any two levels of a variable such as two fuels or two engines.

STATISTICAL ANALYSIS OF TEST DATA

Many kinds of hypotheses concerning the odor intensity of diesel exhaust can be made and statistically tested through the use of panel response data. The "null hypothesis" is the only one that will be discussed here. This hypothesis states that there is no real difference in odor intensities produced during specified operating conditions. Tests are applied to determine how reasonable the hypothesis is. This is stated in terms of significance level (α). The significance level indicates the probability of finding a difference when actually there is none. Significance is often expressed as a confidence level that is the complement of significance. For example, a 95 percent confidence level corresponds to a 5 percent significance level.

Two methods of analysis, analysis of variance and t-tests, are commonly used to test hypotheses concerning the odor intensity of diesel exhaust. Both methods may be used to test the difference in intensity produced at two or more exhaust conditions. However, the t-test may be used to test hypotheses concerning only two exhaust conditions at one time. For example, if it is desired to test the difference between five exhaust conditions, it is necessary to compute ten t values. There are a number of reasons why this is not good statistical practice. There is no restriction as to the number of conditions that may be evaluated simultaneously using an analysis of variance. Therefore, analysis of variance techniques are recommended when multiple tests of significance are desired.

Detailed descriptions of the above analytical techniques go beyond the scope of this publication, and only the analytical procedure pertaining to the program design given in Table 3 will be illustrated. Reference to statistical tests is recommended for those interested in obtaining a knowledge of analysis of variance and/or diversified t-test techniques.

Panel results obtained during a program employing the design given in Table 3 are shown in Table 4. The program tested the intensity difference produced by two fuels (1 and 2) at three engine operating conditions, idle (I), half load (H), and full load (F) and one exhaust concentration. A short method of analysis, t-by-difference, was employed to test whether the difference between fuel intensities was significant at the 95 percent confidence level ($\alpha = 0.05$) for each operating condition independently. The 95 percent confidence limits for the difference between means were also calculated. A summary of the analyses is given in Table 5. Actual computations for the half-load operating condition are given below to illustrate the calculation procedure.

1. Test of significance

- a. $H: \bar{F}_2 - \bar{F}_1 = 0$. That is, the mean intensity rating for Fuel 1 = mean intensity rating for Fuel 2. The hypothesis is accepted or rejected by comparing t values computed from the data with t values obtained from tables published in statistics texts.

Table 4. PANEL INTENSITY RATINGS OF DILUTED DIESEL EXHAUST

Day	Block	I			H			F		
		Fuel 2	Fuel 1	D ^a	Fuel 2	Fuel 1	D ^a	Fuel 2	Fuel 1	D ^a
1	1	4.88	5.75	-0.87	7.00	5.25	1.75	5.63	6.75	-1.12
	2	7.75	6.50	1.25	6.38	5.00	1.38	6.75	6.25	0.50
2	1	6.25	5.13	1.12	6.63	5.00	1.63	7.75	6.25	1.50
	2	5.88	5.63	0.25	6.63	5.88	0.75	6.50	5.38	1.12
3	1	7.75	5.88	1.87	5.75	4.63	1.12	6.38	5.63	0.75
	2	8.00	5.38	2.62	6.00	5.00	1.00	6.38	6.75	-0.37
4	1	8.13	6.00	2.13	7.13	5.25	1.88	6.25	6.13	0.12
	2	8.25	6.88	1.37	6.63	5.88	0.75	6.88	6.25	0.63
Average		7.11	5.89	1.22	6.51	5.23	1.28	6.56	6.15	0.41

^aD = Fuel 2 - Fuel 1 panel rating.

Table 5. SUMMARY OF STATISTICAL ANALYSIS OF DATA IN TABLE 4

Engine operating condition	I	H	F
Fuel intensity difference (F ₂ - F ₁)	1.22	1.28	0.41
95 % confidence interval	0.30, 2.14	0.91, 1.65	-0.31, +1.11
t for fuel difference (calculated)	3.13	8.16	1.39
t _{0.975} (α = 0.05, d.f. = 7)	2.36	2.36	2.36

- b. α = 0.05. This is the chance of finding a significant difference between F₁ and F₂ when there is none.
- c. Degrees of freedom (d.f.) = 7. That is, number of paired observations minus one.
- d. Critical t - t_{1/2α} and t_{1-1/2α} = ±2.365 as read from a published t-table for the level of significance (α) specified and the d.f. of the actual test.
- e. Calculated $t = \frac{\bar{d}}{S/\sqrt{N}} = \frac{1.28}{0.44/2.83} = 8.23$

Where: \bar{d} = average difference between responses,

$$s^2 = \frac{\sum d_i^2 - \frac{(\sum d_i)^2}{N-1}}{N} = \text{variance of the differences between responses,}$$

d_i = difference between responses, and

N = number of paired observations.

- f. Calculated t (8.23) is greater than critical t (2.365), and the hypothesis of equal intensity produced by the two fuels at this operating condition is rejected. Therefore, it is concluded with 95 percent confidence that Fuel 2 produced a greater intensity than Fuel 1.

2. Confidence limits for the difference between two means

- a. It is often desirable to express the difference between population means in terms of confidence limits. The confidence limits between means are

$$\bar{d} \pm t_{1/2\alpha} S \sqrt{\frac{1}{N}} \quad \text{and} \quad \bar{d} \pm t_{1-1/2\alpha} S \sqrt{\frac{1}{N}}$$

Where : \bar{d} = average difference between population means,
 S = square root of the variance of the difference between population means,
 N = number of paired observations,
 α = level of significance, and
 $t_{1/2\alpha}$ = a value obtained from a table for the level of significance specified and the degrees of freedom for the test ($N - 1$).

- b. The 95 percent confidence limits for the difference between fuel intensities are:

$$\bar{d} \pm t_{1-1/2\alpha} S \sqrt{\frac{1}{N}} = 1.28 - (2.365 \times 0.44 \times 0.354) = 0.91, \text{ and}$$

$$\bar{d} \pm t_{1/2\alpha} S \sqrt{\frac{1}{N}} = 1.28 + (2.365 \times 0.44 \times 0.354) = 1.65, \text{ or the}$$

intensity of exhaust produced by Fuel 2 is between 0.91 and 1.65 odor-standard units greater than the intensity of exhaust produced by Fuel 1 at this engine operating condition and exhaust concentration.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Amos Turk, consultant, of Danbury, Connecticut, and Dr. S. K. Katti, of Florida State University, for their invaluable assistance in the development of the techniques described herein.

APPENDICES

- A. CONCENTRATIONS OF ODOROUS VAPORS IN TEST CHAMBERS**
- B. SENSORY STANDARDS FOR DIESEL EXHAUST ODOR STUDY**
- C. STATISTICAL DERIVATIONS**

APPENDIX A. CONCENTRATIONS OF ODOROUS VAPORS IN TEST CHAMBERS

Odor test chambers are used either for evaluation of odor-reducing devices or to provide odor-free environments in which a jury can measure the odors of materials, products, or foods. It is important to consider the factors that determine the changing or equilibrium concentrations in such chambers.

Processes that tend to increase the concentration of odorous vapors are:

1. The generation of vapor within (or injection into) the space.
2. The introduction of vapor by replacement of chamber air by ventilation or infiltration with outdoor air of higher vapor concentration.

Processes that tend to decrease the concentration of odorous vapor are:

1. The treatment of the chamber air by a vapor-reducing device (e. g., activated carbon recirculator).
2. The removal of vapor by replacement of chamber air by ventilation or infiltration with outdoor air of lower vapor concentration.

The concentration of odorous vapor in a chamber will approach an equilibrium point at which the rates of vapor-reducing and vapor-increasing processes are equal. If it is assumed that air introduced into the chamber by ventilation, infiltration, or recirculation through a treatment device is completely and instantaneously mixed with the chamber air, then the concentrations of vapors at any time and at equilibrium are given by the general equations:*

$$C = C_o e^{-(Q_i + EQ_r)t/V} + \left(\frac{C_i Q_i + G}{Q_i + EQ_r} \right) \left[1 - e^{-(Q_i + EQ_r)t/V} \right]$$

$$C_\infty = \frac{C_i Q_i + G}{Q_i + EQ_r}$$

SPECIAL CASES OF THE GENERAL EQUATIONS

Consider the following possibilities:

1. Ventilation air is pure. ($C_i = 0$)
2. No vapor is being generated or injected. ($G = 0$)

*See page 49 for definition of terms.

3. The vapor reducing device is 100% efficient.
($E = 1$ and $C_r = 0$)
4. The chamber is originally pure. ($C_o = 0$)
5. The room is tight. ($Q_i = 0$)
6. Combination of (1) and (2)
7. Combination of (1) and (3)
8. Combination of (2) and (5)
9. Combination of (1), (2), and (3)

For each possibility, 1 through 9, the equation for the vapor concentration at any time (C) or at equilibrium (C_∞) is derived directly from the general equations:

Possibility 1: $C_i = 0$

$$C = C_o e^{\frac{-(Q_i + EQ_r)t}{V}} + \frac{G}{(Q_i + EQ_r)} \left[1 - e^{\frac{-(Q_i + EQ_r)t}{V}} \right]$$

$$C_\infty = \frac{G}{(Q_i + EQ_r)}$$

Possibility 2: $G = 0$

$$C = C_o e^{\frac{-(Q_i + EQ_r)t}{V}} + \frac{C_i Q_i}{(Q_i + EQ_r)} \left[1 - e^{\frac{-(Q_i + EQ_r)t}{V}} \right]$$

and

$$C_\infty = \frac{C_i Q_i}{(Q_i + EQ_r)}$$

Possibility 3: $E = 1$ and $C_r = 0$

$$C = C_o e^{\frac{-(Q_i + Q_r)t}{V}} + \left(\frac{C_i Q_i + G}{Q_i + Q_r} \right) \left[1 - e^{\frac{-(Q_i + Q_r)t}{V}} \right]$$

and

$$C_\infty = \frac{C_i Q_i + G}{(Q_i + Q_r)}$$

Possibility 4: $C_o = 0$

$$C = \frac{C_i Q_i + G}{Q_i + EQ_r} \left[1 - e^{\frac{-(Q_i + EQ_r)t}{V}} \right]$$

Note that the concentration rises to the equilibrium value expressed by the general equation.

Possibility 5: $Q_i = 0$

$$C = C_o e^{-EQ_R t/V} + \frac{G}{EQ_R} \left(1 - e^{-EQ_R t/V} \right)$$

and $C_\infty = G/EQ_R$

Possibility 6: Combination of (1) and (2). C_i and $G = 0$

$$C = C_o e^{-(Q_i + EQ_R)t/V}$$

and $C_\infty = 0$

Possibility 7: Combination of (1) and (3). $C_i = 0$, $E = 1$, and $C_R = 0$

$$C = C_o e^{-(Q_i + Q_R)t/V} + \frac{G}{(Q_i + Q_R)} \left(1 - e^{-(Q_i + Q_R)t/V} \right)$$

and $C_\infty = \frac{G}{Q_i + Q_R}$

Possibility 8: Combination of (2) and (5). $G = 0$, and $Q_i = 0$

$$C = C_o e^{-EQ_R t/V}$$

and $C_\infty = 0$

Possibility 9: Combination of (1), (2), and (3). $C_i = 0$, $G = 0$, $E = 1$, and $C_R = 0$

$$C = C_o e^{-(Q_i + Q_R)t/V}$$

and $C_\infty = 0$

EXPRESSION IN TERMS OF AIR CHANGES

An air change is the addition to the chamber of a volume of air equal to the volume of the chamber. Then the number (N) of air changes (dimensionless) per unit time is given by:

$$N/t = Q/V, \text{ or} \\ N = Qt/V$$

MIXING FACTOR

In any expression of the general form $e^{-Qt/V}$ or e^{-N} , a mixing factor, m, may be applied to account for the fact that dilution of air is not instantaneous, and that concentration fall-off rates are actually smaller than the ideal values given by the equations developed here. Brief² suggests that m commonly ranges between 1/3 and 1/10.

SENSORY TESTING

The efficiency of a vapor-reducing device may be measured by sensory methods that obviate the need for determination of material concentrations. If we select a sealed chamber in which no odor is being generated, then the ratio of concentrations C_1/C_2 corresponding to any two times t_1 and t_2 during the operation of the device is

$$C_1/C_2 = e^{(EQ_r m/V)(t_2 - t_1)}$$

It is possible to measure the ratio of two supra-threshold concentrations of odorous vapor C_1/C_2 by either a dilution or a matching technique. Let

$$P = \frac{\text{Volume of air sample diluted to threshold}}{\text{Volume of original air sample}} = C/C_t$$

Then, the ratio of P values for any two concentrations C_1/C_2 is:

$$\frac{P_1}{P_2} = \frac{C_1/C_t}{C_2/C_t}, \text{ or}$$

$$P_1/P_2 = C_1/C_2$$

We may therefore write:

$$P_1/P_2 = e^{(EQ_r m/V)(t_2 - t_1)}$$

and

$$\log_{10} P_1/P_2 = 0.434 (EQ_r m/V)(t_2 - t_1)$$

Solving for E ,

$$E = \frac{2.303 \log_{10} P_1/P_2}{(Q_r m/V)(t_2 - t_1)}$$

The latter equation tells us that for a room of known volume and air mixing characteristics, it is possible, by sensory determination of odor in the room at different times, to measure the efficiency of a vapor-reduction device operating within the room.

Example: In a 1000-cubic-foot sealed room, 50 cubic feet per minute of air is recirculated by an air purifier of 60 percent efficiency. The mixing factor in the room is $1/3$. Some diesel exhaust vapor is spilled into the room. How long must the air purifier operate if the vapor concentration in the room is to be reduced by 90 percent?

Solution: $C_2 = C_1 - 0.9C_1$, and $C_1/C_2 = 10$

$$\begin{aligned} t_2 - t_1 &= \frac{2.303 \log C_1/C_2}{EQ_r m/V} = \frac{2.303 \log 10}{0.60 \times 50 \times 1/3 / 1000} \\ &= 230 \text{ min. , or } 3 \text{ hr. } 50 \text{ min.} \end{aligned}$$

NOTATION

V	=	Volume of chamber
t	=	Time
C	=	Concentration of vapor in chamber at any time
C_0	=	Initial concentration of vapor in chamber
C_∞	=	Concentration of vapor in chamber at equilibrium
C_1	=	Concentration of vapor in ventilation or infiltration air
C_r	=	Concentration of vapor delivered by the air treatment device
E	=	Efficiency of vapor reduction by the air treatment device
Q_i	=	Volume rate of ventilation or infiltration
Q_r	=	Volume rate of air delivery by the air treatment device
G	=	Quantity rate of generation of vapor within (or injected into) chamber
N	=	Number of air changes
m	=	Mixing factor

REFERENCES

1. A. Turk, Measurements of Odorous Vapors in Test Chambers: Theoretical. ASHRAE J., Oct. 1963.
2. R. S. Brief, Simple Way to Determine Air Contaminants, Air Engineering, Vol.2, p. 39 (1960).

APPENDIX B. SENSORY STANDARDS FOR DIESEL EXHAUST ODOR STUDY

This Appendix describes the composition and method of preparation of sensory standards for a diesel exhaust odor study. The standards are designed to serve as sensory references for (1) the intensity of diesel exhaust odor, without regard to the quality of the odor, (2) the quality of diesel exhaust odor, expressed in terms of the intensities of each of four odor quality descriptors, and (3) the intensity of odor-modifying agents that are designed to improve diesel exhaust odor by odor masking or odor counteraction.

The intensities of the individual odor qualities, taken together, constitute a "quality-intensity profile," or "QI profile." The profile is not designed so that the sum of its intensity scores should be related to the overall diesel exhaust odor intensity.

Descriptors are used to designate diesel exhaust odor quality.

The descriptors are:

Name	Code
Burnt/smoky	B
Oily	O
Pungent/acid	P
Aldehydic/aromatic	A
Masking	M

BURNT/SMOKY (B)

Burnt quality or smokiness is a typical odor component of the products of combustion of organic matter. There is considerable variation in the quality of burnt odors, however, among different conditions of combustion, different materials being burned, and different states of molecular or aerosol aggregation of the airborne combustion products. Many of the primary combustion products are unstable and therefore unsuitable for use as sensory reference standards. The chemical makeup of materials that have a burnt odor includes products of decomposition and partial oxidation. Oil of cade (juniper tar) is included in the B standard because this oil has a typical burnt odor and is readily available from commercial sources. Guaiacol and carvacrol impart the phenolic odor component that is contributed in part by the oxidation of benzenoid aromatic matter. Acetylene dicarboxylic acid is a commercially available chemical, the odor of which somewhat resembles that of a dilute mixture of carbon suboxide in air. Carbon suboxide is a likely product of partial oxidation that contributes to burnt odor. Benzyl benzoate is an almost odorless diluent that solubilizes the other components.

Composition of B

Component	Percent by weight	
	Including solvent	Excluding solvent
Oil of cade (Juniper tar)	16.8	84.3
Guaiacol	0.2	1.0
Carvacrol	0.9	4.2
Acetylene dicarboxylic acid	2.1	10.5
Benzyl benzoate	80.0	(solvent/odorant, 4:1)
	100.0	

Intensity series (diluent: as noted)

Odor intensity	Code	Concentration (B/B + diluent)			
		Diluent	Fraction	Decimal	Percent
Slight	B-1	min. oil	1/720	0.00139	0.139
Moderate	B-2	min. oil	1/180	0.00556	0.556
Strong	B-3	min. oil	1/45	0.0222	2.22
Extreme	B-4	benz. ben.	1/4	0.25	25.0

Procedure

Make up the stock mixture B.

To make B-4, mix 1 part of B with 3 parts of diluent.

To make B-3, mix 1 part of B-4 with 14 parts of diluent.

To make B-1, mix 1 part of B-2 with 3 parts of diluent.

Notes: 1. The dilutions can be made on a volume basis without introducing any significant error.

2. Stock solution B should be shaken before dilutions are made to bring into suspension any component of the oil of cade that might have settled.

3. Note the change in diluent between B-4 and B-3.

OILY (O)

Oiliness is an odor quality generally associated with organic chemicals, the molecular structure of which is characterized by long saturated hydrocarbon chains. Among materials of plant origin, such substances are typically esters of long-chain fatty acids. In diesel exhaust, oily quality is believed to be associated with the presence of high-boiling-point components of unburned fuel, in the boiling range approximately 300° C (1 atm). The most satisfactory standard found to represent this odor quality is n-octylbenzene.

Composition of O

n-octylbenzene, 100 percent

Intensity series (diluent: mineral oil)

Odor intensity	Code	Concentration, O/(O + diluent)			
		Exponent	Fraction	Decimal	Percent
Slight	O-1	2 ⁻⁷	1/128	0.0078	0.78
Moderate	O-2	2 ⁻⁵	1/32	0.0313	3.13
Strong	O-3	2 ⁻³	1/8	0.125	12.5
Extreme	O-4	2 ⁻¹	1/2	0.5	50.0

Procedure

The stock material O is pure n-octylbenzene.

To make O-4, mix 1 part of O with 1 part of diluent.

To make O-3, mix 1 part of O-4 with 3 parts of diluent.

To make O-2, mix 1 part of O-3 with 3 parts of diluent.

To make O-1, mix 1 part of O-2 with 3 parts of diluent.

Note: The dilutions can be made on a volume basis without introducing any significant error.

PUNGENT/ACID (P)

Diesel exhaust in high concentration can be perceived as an irritant. The word "irritant" is used here to denote a substance that can be detected by the common chemical sense, as distinguished from the specific olfactory sense. Such irritants are said to have a "pungent" quality. This type of common chemical sensation can coexist with odor. For example, a concentrated mixture of butyric acid vapor in air is both pungent and odorous. As the mixture is diluted, the common chemical irritation diminishes and then disappears at concentrations at which odor still persists. The sensation is then no longer said to be pungent; instead, it is described as "acid" or "sour." The existence of pungent, acid components in diesel exhausts is evidenced by (1) the interpretation of infrared spectra by Scott Research Laboratories to indicate the presence of organic acid (carboxyl function), (2) the sensory identification of "sour" substances among the column chromatographic fractions of diesel exhaust obtained by Scott Research Laboratories, and (3) the pungency experienced by direct exposure to concentrated diesel exhaust.

The character of "sourness" or "acid odor" (as distinguished from pungency) varies among different sources. Butyric and valeric acid odors are characterized by sour odor qualities typical of rancidification of organic matter. An acidic odor quality more closely related to combustion products is associated with organic acids that have olefinic or acetylenic unsaturation.

Composition of P

Component	Percent by weight
Crotonic acid	3.3
Propiolic acid	2.9
Benzyl benzoate	93.8
	100.0

Intensity series (diluent: mineral oil)

Odor Intensity	Code	Concentration, P/(P + diluent)		
		Fraction	Decimal	Percent
Slight	P-1	1/720	0.0014	0.14
Moderate	P-2	1/180	0.0055	0.55
Strong	P-3	1/60	0.0167	1.67
Extreme	P-4	1/20	0.05	5.0

Procedure

Make up the stock solution P. The mixture will have to be warmed slightly to bring the components into solution. Allow the solution to cool to ambient temperature.

To make P-4, mix 1 part of P with 19 parts of diluent.

To make P-3, mix 1 part of P-4 with 2 parts of diluent.

To make P-2, mix 1 part of P-3 with 2 parts of diluent.

To make P-1, mix 1 part of P-2 with 3 parts of diluent.

Note: 1. The dilutions can be made on a volume basis without introducing any significant error.

2. The components of P-4 may have to be warmed to bring them into solution.

ALDEHYDIC/AROMATIC (A)

Aldehydes are known to exist as components of diesel exhaust. Some of the column chromatographic fractions of diesel exhaust obtained by Scott Research Laboratories were characterized as having "sweet" or "spicy" odors. A mixture used at Scott Research Laboratories for setting up odor intensity ratings of diluted diesel exhaust contained heptaldehyde as the major component. These circumstances, taken together, support the selection of a quality description of diesel exhaust odor that reflects aldehydic and other highly odorous, somewhat fragrant components. The intensity series that consists of these pervasive odorants is represented by comparatively dilute solutions.

Composition of A

Component	Percent by weight
n-Butylbenzene	16.6
sec-Butylbenzene	16.6
p-Cymene	16.6
Heptaldehyde	38.9
Nonaldehyde	9.7
Salicylaldehyde	0.4
Cinnamic aldehyde	0.4
alpha-Methylcinnamic aldehyde	0.4
p-Tolyl aldehyde	0.4
	100.0

Intensity series (diluent: mineral oil)

Odor intensity	Code	Concentration, A/(A + diluent)				
		Exponent	Fraction	Decimal	Percent	ppm
Slight	A-1	2-16	1/65536	0.00001525	0.0015	15
Moderate	A-2	2-14	1/16384	0.0000610	0.0061	61
Strong	A-3	2-12	1/4096	0.000244	0.0244	244
Extreme	A-4	2-10	1/1024	0.000976	0.0976	976

Preparation

Make up the stock solution A. The components are highly odorous and should be handled in the fume hood.

To make A-4, calibrate a pipet or dropper in milligrams per drop of stock solution A. Pipet a measured quantity of A into a Flask. Add mineral oil in the ratio 1.02 grams mineral oil per gram of A. Shake the mixture to dissolve the components.

To make A-3, mix 1 part of A-4 with 3 parts of diluent.

To make A-2, mix 1 part of A-3 with 3 parts of diluent.

To make A-1, mix 1 part of A-2 with 3 parts of diluent.

Note: The dilutions can be made on a volume basis without introducing any significant error.

MASKING (M)

Odor-modifying agents are designed to improve objectionable odors by admixture with another vapor that will change the malodorous quality (masking action) and/or reduce the intensity of the malodor (odor-counteracting action.) Agents of this type differ among manufacturers and are proprietary. When such agents are used for modification of diesel odor it will be helpful to have a general "masking" standard to use as a quality reference. Such a standard should contain components of the type likely to resemble the composition of

common diesel masking agents or to be associated in the experience of panel members with commercial products that contain mixtures of industrial essential oils.

Composition of M

Component	Precent by weight
Oil of wintergreen	10
Terpineol	20
Cedrene	20
Bornyl acetate	30
Phellandrene	20

Intensity series (diluent: mineral oil)

Odor intensity	Code	Concentration, M/(M + diluent)				
		Exponent	Fraction	Decimal	Percent	ppm
Slight	M-1	2 ⁻¹⁶	1/65536	0.00001525	0.0015	15
Moderate	M-2	2 ⁻¹³	1/8192	0.000122	0.0122	122
Strong	M-3	2 ⁻¹⁰	1/1024	0.000976	0.0976	976
Extreme	M-4	2 ⁻⁷	1/128	0.00781	0.781	

Preparation

Make up the stock solution M. The components are highly odorous and should be handled in the fume hood.

To make M-4, calibrate a pipet or dropper in milligrams per drop of stock solution M. Pipet a measured quantity of M into a flask. Add mineral oil in the ratio 0.127 grams of mineral oil per milligram of M. Shake the mixture to dissolve the components.

To make M-3, mix 1 part of M-4 with 7 parts of diluent.

To make M-2, mix 1 part of M-3 with 7 parts of diluent.

To make M-1, mix 1 part of M-2 with 7 parts of diluent.

Note: The dilutions can be made on a volume basis without introducing any significant error.

DIESEL (D)

As stated earlier, the intensity of diesel exhaust odor may be measured without regard to the quality of the odor. The intensity reference standards, therefore, could consist of a dilution scale of any convenient odorant. It is considered likely, however, that panel members will become proficient in QI odor profile work more easily if the overall intensity reference standard is related to the individual odor quality standards.

Composition of D

Component	Percent by volume
B-4	59.3
O-4	37.0
A-4	3.7
	100.0

Intensity series (diluent: mineral oil)

Odor intensity	Code	Concentration D/(D + diluent)				
		Exponent	Fraction	Decimal	Percent	ppm
Slight	D-1	2 ⁻¹¹	1/2048	0.000488	0.0488	488
	D-2	2 ⁻¹⁰	1/1024	0.000976	0.0976	976
	D-3	2 ⁻⁹	1/512	0.00195	0.195	
Moderate	D-4	2 ⁻⁸	1/256	0.00391	0.391	
	D-5	2 ⁻⁷	1/128	0.00781	0.781	
	D-6	2 ⁻⁶	1/64	0.0156	1.56	
Strong	D-7	2 ⁻⁵	1/32	0.0313	3.13	
	D-8	2 ⁻⁴	1/16	0.0625	6.25	
	D-9	2 ⁻³	1/8	0.125	12.5	
Extreme	D-10	2 ⁻²	1/4	0.25	25.0	
	D-11	2 ⁻¹	1/2	0.5	50.0	
	D-12	2 ⁻⁰	1	1	100.0	

Procedure

Make up the stock solution D.

D-12 is identical with stock solution D.

To make D-11, mix 1 part of D-12 with 1 part of diluent.

To make D-10, mix 1 part of D-11 with 1 part of diluent.

Continue in this manner until D-1 is prepared.

- Notes:
1. The dilutions can be made on a volume basis without introducing any significant error.
 2. Stock solution B should be shaken before dilutions are made to bring into suspension any component of the oil of cade that might have settled down.

SOURCES AND PURITY OF CHEMICALS

All of the chemicals used must be pure enough that any impurities present do not make a detectable contribution to odor. For highly odorous chemicals, such as aldehydes, this requirement normally poses no problem.

A suitable odorless mineral oil is Primol 325 available from Humble Oil & Refining Company, Hutchinson River Parkway, Pelham, New York

The benzyl benzoate should not have any of the cherry or almond odor that may be associated with the presence of some benzaldehyde impurity. Satisfactory grades are available from Mallinkrodt Chemical and from the Matheson Company.

The octyl benzene must not emit any of the sulfur odor that is sometimes associated with inferior samples. A satisfactory grade may be purchased from the Humphrey Chemical Company, in North Haven, Connecticut.

Acetylenic compounds are available from Farchan Research Laboratories, Willoughby, Ohio.

CONTAINERS

Twenty-five milliliters of each odorant reference solution is placed in a labeled 4-oz. polyethylene squeeze bottle, fitted with a screw cap having a conical polyethylene liner.

The entire kit comprises 32 bottles (12 of the intensity series and 4 each of the 5 components of the QI profile, including the masking standards). These bottles should be arranged in a metal rack in a metal box that has an internal activated-carbon panel to keep the atmosphere in the box odor-free. Porous materials of construction like wood or cardboard should be avoided because they absorb and retain odor. The activated carbon should be granular material of the type commonly used for air purification.

APPENDIX C. STATISTICAL DERIVATIONS

STATISTICAL DERIVATION OF TRIANGLE TEST SELECTIONS

A number of candidates are given m triangle tests each. On the basis of the number of correct answers, we wish to choose the "best" candidates. It is assumed (1) that the candidates act independently of each other, and (2) that the test has been demonstrated to them beforehand so that they are not learning during the test sequence. Each test is therefore independent of the other tests taken by the same candidate.

If a candidate answers purely by guesswork, the chance of getting a correct answer on any single test is $1/3$. The probability of getting x correct answers out of m is expressed by the probabilities of the binomial distribution:

$$P_x = \frac{m!}{x! (m-x)!} (1/3)^x (2/3)^{m-x}$$

where: P_x = probability that a candidate would give x correct answers.

m = number of triangle tests given.

x = number of correct answers.

The classical treatment of triangle tests uses a chi-square statistic to assess the candidate's sensory acuity for odor and flavor. However, the significance level computed by chi-square is an approximation to the true significance level. When the number of triangle tests is greater than 15, the approximation is quite satisfactory. In our screening procedures, we recommend only four or five triangle tests per candidate. Therefore, the chi-square is not valid, and our significance levels are based upon the following derivation.

Suppose we have two candidates, one who has x correct answers and one who has y , and we want to know whether the difference between the two is significant. We therefore want the distribution of $|x-y|$. According to distribution theory in probability, x and y are identically, independently distributed binomial random variables, where:

$$P_x = \frac{m!}{x! (m-x)!} (1/3)^x (2/3)^{m-x} \quad \text{and}$$

$$P_y = \frac{m!}{y! (m-y)!} (1/3)^y (2/3)^{m-y}$$

The expected value (E expectation) of any function $f(x)$ is defined as:

$$E(f(x)) = \sum_{x=0}^m P_x f(x)$$

By convention, we choose $f(x) = t^x$, where t is a dummy variable.

$$\text{Then, } \left. \begin{aligned} E(t^x) &= \sum_{x=0}^m t^x p_x \quad \text{and} \\ E(t^y) &= \sum_{y=0}^m t^y p_y \end{aligned} \right\} \begin{array}{l} \text{These are called the} \\ \text{"generating functions"} \\ \text{of } p_x \text{ and } p_y. \end{array}$$

To find $p_{|x-y|}$, the probability distribution of $|x-y|$, the expected value of $t^{|x-y|}$ is computed.

$$E(t^{|x-y|}) = E(t^x) E(t^{-y})$$

$$\begin{aligned} E(t^x) &= \sum_{x=0}^m t^x p_x = \sum_{x=0}^m t^x \left(\frac{m!}{x! (m-x)!} \right) (1/3)^x (2/3)^{m-x} \\ &= \sum_{x=0}^m \left(\frac{m!}{x! (m-x)!} \right) \left(\frac{1}{3}t \right)^x \left(\frac{2}{3} \right)^{m-x} \\ &= \left(\frac{1}{3}t + \frac{2}{3} \right)^m \quad (\text{by binominal expansion}) \end{aligned}$$

and similarly

$$\begin{aligned} E(t^{-y}) &= \sum_{y=0}^m \left(\frac{m!}{y! (m-y)!} \right) \left(\frac{1}{3t} \right)^y \left(\frac{2}{3} \right)^{m-y} \\ &= \left(\frac{1}{3t} + \frac{2}{3} \right)^m \quad (\text{by binominal expansion}) \end{aligned}$$

Then,

$$\begin{aligned} E(t^{|x-y|}) &= \left(\frac{1}{3}t + \frac{2}{3} \right)^m \left(\frac{1}{3t} + \frac{2}{3} \right)^m \\ &= \left[\left(\frac{1}{3}t + \frac{2}{3} \right) \left(\frac{1}{3t} + \frac{2}{3} \right) \right]^m \\ &= \left[\frac{5}{9} + \frac{2}{9} \left(t + \frac{1}{t} \right) \right]^m \end{aligned}$$

To find the distribution it is necessary to expand the generating function, gather like terms, and consider two competing candidates, A and B, whose respective scores are x and y . The probability that, by chance alone, the absolute difference between the two scores is z (or, that $|x-y| = z$), is the sum of the coefficients of the terms in t and $-t$. If two candidates take m triangle tests each, the maximum difference between scores is $\pm m$.

Let $m = 0$. (There are no tests.)

Then,

$$\begin{aligned} E(t^{|x-y|}) &= 1 \\ &= t^0 \end{aligned}$$

and $P_0 = 1$. (The probability is 1 that the score is tied.)

Let $m = 1$. (One test is carried out.)

Then,

$$\begin{aligned} E(t^{x-y}) &= \frac{5}{9} + \frac{2}{9}t + \frac{2}{9t} \\ &= \frac{2}{9}t^{-1} + \frac{5}{9}t^0 + \frac{2}{9}t^1. \end{aligned}$$

Therefore,

$$P_0 = \frac{5}{9}$$

$$P_1 = \frac{2}{9} + \frac{2}{9} = \frac{4}{9},$$

for, the chances are $\frac{2}{9}$ that A will win over B, $\frac{2}{9}$ that B will win over A, and $\frac{5}{9}$ that A and B will tie.

Let $m = 2$

$$\begin{aligned} \text{Then, } E(t^{x-y}) &= \left[\frac{5}{9} + \frac{2}{9} \left(t + \frac{1}{t} \right) \right]^2 \\ &= \frac{4}{81}t^{-2} + \frac{20}{81}t^{-1} + \frac{33}{81}t^0 + \frac{20}{81}t^1 + \frac{4}{81}t^2 \end{aligned}$$

Therefore,

$$P_0 = 33/81$$

$$P_1 = 20/81 + 20/81 = 40/81$$

$$P_2 = 4/81 + 4/81 = 8/81$$

Calculations are similar for $m = 4$ and $m = 5$.

In a series of triangle tests taken by candidates A and B, the distribution of the differences in correct scores $|x-y|$ tells us what the probability is that any given difference in scores obtained by A and B is due to chance alone. These distributions appear in Table C-1.

STATISTICAL DERIVATION OF INTENSITY RATING TEST SELECTIONS

Assumptions

When two candidates replace a sample at or near the correct position, they are candidates who will be considered for favorable action and it is important to make a valid distinction between them.

Candidates who replace the samples very far from the correct position are not likely to be chosen and we do not care much about distinctions between "very bad" and "extremely bad."

For example: correct position = 3

Candidate A Replaces sample in position 3

Candidate B Replaces sample in position 4

Candidate C Replaces sample in position 17

Candidate D Replaces sample in position 18

Table C-1. TRIANGLE TESTS: PROBABILITY DISTRIBUTION AND CUMULATIVE DISTRIBUTION FUNCTION OF ABSOLUTE DIFFERENCE IN SCORES

Number of triangle tests m	Absolute difference between scores $ x-y $	$P_{ x-y }$	Cumulative distribution function (Probability that a difference in scores of at least $ x-y $ would be obtained by chance alone.) $\sum_{i=0}^{ x-y } P_i$
0	0	1.0000	1.0000
1	0	0.5556	1.0000
	1	0.4444	0.4444
2	0	0.4074	1.0000
	1	0.4938	0.5926
	2	0.0988	0.0988
3	0	0.3361	1.0000
	1	0.4774	0.6639
	2	0.1646	0.1865
	3	0.0219	0.0219
4	0	0.2928	1.0000
	1	0.4512	0.7072
	2	0.2024	0.2561
	3	0.0488	0.0537
	4	0.0049	0.0049
5	0	0.2629	1.0000
	1	0.4257	0.7371
	2	0.2234	0.3113
	3	0.0732	0.0878
	4	0.0135	0.0146
	5	0.0011	0.0011

Then A's score is slightly better than B's and we want to know how reliable this difference is. Candidates C and D are both very poor and we do not really care whether one is worse than the other.

Scoring

Position of replaced bottle	Score (the higher number is the worse score)
Correct position	0
Correct position ± 1	1
Correct position ± 2	4
Correct position ± 3	9
Correct position ± 4 or more	16

Each candidate must be given the same program; they must not communicate with each other.

Test number	Correct position of sample
1	12
2	8
3	16
4	3

Distribution of Possible Scores:

Correct answer	Possible scores	Probability of each score
3	0	1/20
	1	2/20
	4	2/20
	9	1/20
	16	14/20

Explanation:

Bottle

Position: 1 2 3 4 5 6 7 8 9 ----- 20

Deviation from

correct location: -2 -1 0 +1 +2 +3 +4 +5 +6 etc.

Score 4 1 0 1 4 9 16 16 16 ----- 16

Number of ways of getting a score of 0 is 1 out of 20.

Number of ways of getting a score of 1 is 2 out of 20.

Number of ways of getting a score of 4 is 2 out of 20.

Number of ways of getting a score of 9 is 1 out of 20.

Number of ways of getting a score of 16 is 14 out of 20.

Correct answer	Possible scores	Probability of each score
8, 12, or 16	0	1/20
	1	2/20
	4	2/20
	9	2/20
	16	13/20

Therefore, in the sum of the four tests, the lowest possible score (the best) is 0; the highest possible score (the worst) is 64.

Table C-2 gives the probability distribution of scores in the odor intensity tests.

STATISTICAL DERIVATION OF MULTICOMPONENT ODOR IDENTIFICATION TEST SELECTIONS

A candidate is given eight known odor standards, A, B, C, D . . . H. He is then asked to identify, in three successive tests, the components of a two-component mixture, a three-component mixture, and a four-component mixture.

Two-Component Mixture

Let the two components be A and B. The chance of guessing both correctly is:

$$\frac{1}{8} \quad \times \quad \frac{1}{7} \quad = \quad \frac{1}{56}$$

chance of guessing and guessing
A first B next

Table C-2. PROBABILITY DISTRIBUTION FUNCTION AND CUMULATIVE DISTRIBUTION FUNCTION OF DIFFERENCE IN SCORES OF TWO SUBJECTS ON ODOR-INTENSITY TEST

Difference in score	Probability of difference	Cumulative probability of difference	Nominal significance level
0	0.0899	1.0000	
1	0.0289	0.9101	
2	0.0140	0.8812	
3	0.0467	0.8672	
4	0.0372	0.8205	
5	0.0374	0.7883	
6	0.0124	0.7459	
7	0.0754	0.7335	
8	0.0465	0.6581	
9	0.0274	0.6116	
10	0.0165	0.5842	
11	0.0191	0.5677	
12	0.0834	0.5486	
13	0.0123	0.4652	
14	0.0175	0.4529	
15	0.0822	0.4354	
16	0.0466	0.3532	
17	0.0119	0.3066	
18	0.0111	0.2947	0.30
19	0.0333	0.2836	
20	0.0176	0.2502	0.25
21	0.0096	0.2326	
22	0.0259	0.2230	
23	0.0214	0.1971	0.20
24	0.0222	0.1757	
25	0.0051	0.1534	0.15
26	0.0063	0.1483	
27	0.0292	0.1423	
28	0.0156	0.1131	
29	0.0046	0.0975	0.10
30	0.0164	0.0929	
31	0.0182	0.0765	
32	0.0062	0.0583	
33	0.0021	0.0521	
34	0.0073	0.0500	0.05
35	0.0055	0.0427	
36	0.0033	0.0372	
37	0.0037	0.0339	
38	0.0040	0.0302	
39	0.0053	0.0262	
40	0.0024	0.0209	
41	0.0007	0.0185	
42	0.0038	0.0178	
43	0.0038	0.0140	
44	0.0012	0.0102	0.01
45	0.0015	0.0090	
46	0.0023	0.0075	
47	0.0013	0.0052	
48	0.0004	0.0039	
49	0.0005	0.0035	
50	0.0005	0.0030	
51	0.0004	0.0025	
52	0.0003	0.0021	
53	0.0002	0.0018	
54	0.0004	0.0016	
55	0.0003	0.0012	
56	0.0001	0.0009	0.001
57	0.0002	0.0008	
58	0.0002	0.0006	
59	0.0001	0.0004	
60	0.0001	0.0003	
61	0.0001	0.0002	
62	0.0001	0.0001	0.0001
63	0.0000	0.0000	
64	0.0000	0.0000	

$$\begin{array}{rclcl}
 \text{plus} & \frac{1}{8} & \times & \frac{1}{7} & = \frac{1}{56} \\
 & \text{chance of} & & \text{guessing} & \\
 & \text{guessing B first} & \text{and} & \text{A next} & \\
 & & & \text{Total} & = \frac{2}{56}
 \end{array}$$

The chance of guessing only one correctly is:

$$\begin{array}{rclcl}
 & \frac{1}{8} & \times & \frac{6}{7} & = \frac{6}{56} \\
 & \text{chance of guessing} & & \text{guessing C,} & \\
 & \text{A first} & & \text{D, E, F, G,} & \\
 & & & \text{or H next} & \\
 \text{plus} & \frac{6}{8} & \times & \frac{1}{7} & = \frac{6}{56} \\
 & \text{chance of guessing} & & \text{guessing} & \\
 & \text{C, D, E, F, G, or} & & \text{A next} & \\
 & \text{H first} & & &
 \end{array}$$

Similarly, chance of guessing only B is:

$$\begin{array}{rclcl}
 & 2 \times \frac{6}{56} & & & = \frac{12}{56} \\
 & \text{Total} & & & = \frac{24}{56}
 \end{array}$$

The chance of getting none correct is:

$$\begin{array}{rclcl}
 & \frac{6}{8} & \times & \frac{5}{7} & = \frac{30}{56} \\
 & \text{chance of guessing} & & \text{chance of guessing} & \\
 & \text{C, D, E, F, G, or} & & \text{C, D, E, F, G, or} & \\
 & \text{H first} & & \text{H next} & \\
 & & & \text{Grand total} & \frac{56}{56}
 \end{array}$$

Three-component mixture and four-component mixture are treated analogously. The results are:

Number of components in mixture	Number of components identified correctly	Probability of identifying this number of components by chance
2	0	30/56
	1	24/56
	2	2/56
3	0	60/336
	1	180/336
	2	90/336
	3	6/336
4	0	24/1680
	1	384/1680
	2	864/1680
	3	384/1680
	4	24/1680

Scoring

It is assumed that it is much better to get a score of j correct than a score of $j-1$. Therefore, a quadratic scoring system is used. In other words, there is no great trick in getting 1 out of 4 right, even if chance is not involved, but a candidate who gets 4 out of 4 right is doing very much better, and we therefore credit him with being not $(4/1)$ times better but $(4/1)^2$ times better. Therefore, the score is taken to be (the number of correct answers)².

The test program consists of giving each candidate three tests (the test components are the same for each candidate).

Test 1: two-component mixture
Test 2: three-component mixture
Test 3: four-component mixture

Candidates are selected on the following basis:

Let the score of candidate 1 equal X and the score of candidate 2 equal Y . Then the difference between scores is $X - Y$.

When is this difference significant? What is the basis for choice between candidates?

The lowest possible total score is $0 + 0 + 0 = 0$.

The highest possible total score is $2^2 + 3^2 + 4^2 = 29$; hence the maximum difference $(X - Y) = 29 - 0 = 29$.

Table C-3 lists all of the probabilities of difference between scores from 0 to 29.

**Table C-3. DISTRIBUTION FUNCTION AND CUMULATIVE DISTRIBUTION
FUNCTION FOR ABSOLUTE DIFFERENCE IN SCORES OF ANY TWO
SUBJECTS ON MULTICOMPONENT ODOR IDENTIFICATION TEST**

Difference in score	Probability of difference	Cumulative probability of difference	Nominal significance level
0	0.1132	1.0000	
1	0.1518	0.8868	
2	0.1025	0.7350	
3	0.1397	0.6325	
4	0.1278	0.4928	
5	0.0938	0.3650	
6	0.0647	0.2712	0.25
7	0.0511	0.2062	0.20
8	0.0570	0.1554	0.15
9	0.0370	0.0984	0.10
10	0.0139	0.0614	
11	0.0148	0.0475	0.05
12	0.0141	0.0327	
13	0.0062	0.0186	
14	0.0032	0.0124	
15	0.0037	0.0092	0.01
16	0.0027	0.0055	
17	0.0011	0.0028	
18	0.0008	0.0017	
19	0.0006	0.0009	0.001
20	0.0002	0.0003	
21	0.0001	0.0001	0.0001
22	0.0000	0.0000	
23	0.0000	0.0000	
24	0.0000	0.0000	
25	0.0000	0.0000	
26	0.0000	0.0000	
27	0.0000	0.0000	
28	0.0000	0.0000	
29	0.0000	0.0000	