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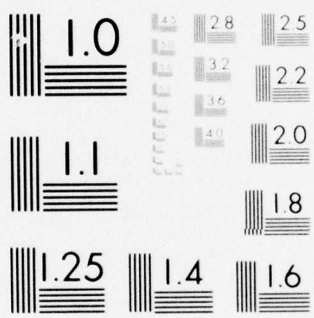
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Report SAM-TR-77-22

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OLFACTORY THRESHOLD OF CHLORINE IN OXYGEN

September 1977

Final Report for Period August 1974-June 1976

USAF SCHOOL OF AEROSPACE MEDICINE
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

NOTICES

This final report was submitted by personnel of the Crew Environments Branch, Crew Technology Division, USAF School of Aerospace Medicine, Aerospace Medical Division, AFSC, Brooks Air Force Base, Texas, under job order 7930-11-02.

The voluntary informed consent of the subjects used in this research was obtained in accordance with AFR 80-33.

This technical report has been reviewed and is approved for publication.

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: SAM-TR-77-22
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:
4. TITLE (and Subtitle): OLFACTORY THRESHOLD OF CHLORINE IN OXYGEN.
5. TYPE OF REPORT & PERIOD COVERED: Final rept. Aug 1974 - June 1976
6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): Gene A. Dixon, B.S.; Kenneth G. Ikels, Ph.D.

8. CONTRACT OR GRANT NUMBER(s):

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
USAF School of Aerospace Medicine (VNL)
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 62202F; 7930-11-02

11. CONTROLLING OFFICE NAME AND ADDRESS:
USAF School of Aerospace Medicine (VNL)
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

12. REPORT DATE: Sep[redacted] 1977

13. NUMBER OF PAGES: 10

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): 13p.

15. SECURITY CLASS. (of this report): UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report):

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):

18. SUPPLEMENTARY NOTES:

19. KEY WORDS (Continue on reverse side if necessary and identify by block number):

Chlorine, threshold, oxygen, olfactory

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The odor threshold of chlorine in oxygen was determined. Measurements were conducted in an altitude chamber, which provided an odor-free and noise-free background. Human male volunteers, with no previous olfactory acuity testing experience, served as panelists. Threshold values were affected by time intervals between trials and by age differences. The mean threshold value for 11 subjects was 0.08 ppm obtained by positive responses to the lowest detectable level of chlorine in oxygen, 50% of the time.

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OLFACTORY THRESHOLD OF CHLORINE IN OXYGEN

INTRODUCTION

Chlorate oxygen generators, such as those used on the C-5 transport, produce chlorine and other contaminants under certain conditions. During ignition the rapid increase in candle temperature may release sufficient chlorine to cause passenger rejection of the mask if the olfactory threshold is exceeded to a large degree. A requirement was established to formulate criteria for the maximum allowable concentration for chlorine in chlorate-generated oxygen. The literature contained a wide variability in published results for the odor threshold values (OTV) of chlorine in air. Sax (11) reported the OTV of 3.5 ppm; Leonardos et al. (7) reported a value of 0.3 ppm. However, nothing has been reported on the OTV of chlorine in oxygen.

This report describes results of experiments conducted to determine the OTV of chlorine in oxygen. The study was done with human volunteers, who were required to indicate the presence or absence of low levels of chlorine in oxygen presented in randomized sequence, in a situation approximating the use conditions of chlorate oxygen generators.

RATIONALE FOR EXPERIMENTAL DESIGN

Measurement of olfactory threshold involves several factors which may include the physical method of sample presentation, subject-to-subject variation in olfactory acuity, and day-to-day variation in individual subjects. In this study the odor threshold value was defined as the lowest concentration of chlorine in oxygen that could be detected and recognized by an individual subject at least 50% of the time. The end point for each subject was attained when he was able to provide reproducible evaluations of the chlorine odor within two concentration steps over a specified number of presentations (usually ten). The concentration steps employed were deltas of 0.1 ppm over the range from 2.0 to 0.1 ppm, and 0.02 ppm at concentrations less than 0.1 ppm.

The physical method of sample presentation was designed to provide a highly reproducible concentration of chlorine to each subject in a distraction-free environment. Because of the reactivity and density of chlorine, a dynamic gas mixing apparatus was employed to accurately produce known concentrations of chlorine in oxygen, which were continuously monitored.

Although expert subjects are used by some investigators in their measurements of odor thresholds, Kendall et al. (5) reported that subjects with no experience in olfactory testing are as reliable as expert panelists in establishing a valid odor threshold value.

A brief discussion of errors in difference testing, as relates to our study, is deemed important in order to show how they affect the data. False-positive responses are considered errors of the first kind; i.e., chlorine odor is reported when in fact none is presented. In our study these types of errors were not of sufficient number to bias the data as shown by Figure 1.

Errors of the second kind, i.e., the lack of a positive response to the presence of a stimuli, represented that concentration at which the subject was not able to correctly identify the odor of chlorine, at least 50% of the time after repeated exposures. We then assumed that this concentration was below the threshold, as defined in our definition of odor threshold.

TEST METHODS

Panel Composition

The volunteer working panel consisted of 13 male subjects who passed a class II physical examination and were determined to have a normal sense of smell. The preliminary screening tests included examination by an otolaryngologist to eliminate general anosmics and examination by the investigator to eliminate subjects who were specifically anosmic to the odor of chlorine. The composition of the odor panel is shown in Table 1. The entire panel consisted of personnel employed at the USAF School of Aerospace Medicine. All possessed a scientific background and were considered to be motivated in the area of scientific research. None of the panelists had any prior experience with olfactory testing.

TABLE 1. ODOR PANEL COMPOSITION

Age group	Nonsmokers	Smokers	Total
18-35	7	3	10
36-55	1	2	3
Totals	8	5	13

Gas Composition and Delivery

Dynamic mixtures of chlorine in oxygen gas were generated through the use of a calibration system (AID Model 309). The calibration system utilized a thermostated oven containing a permeation tube (P-tube) of pure liquid chlorine enclosed in FEP Teflon. Carrier gas (100% O_2) from a liquid oxygen source was passed over the tube to produce a known concentration of chlorine as a function of oxygen flow and temperature of the permeation tube (12).

The permeation tubes were purchased from Analytical Instrument Development, Inc., and were certified to be individually calibrated using gravimetric procedures. The tubes were maintained at a constant and accurately controlled temperature. The permeation rates of the P-tubes (ng/min) were converted to parts per million by volume (ppmv) by the following formula:

$$C = \frac{PR}{F} \times \frac{22.4}{M} \times \frac{T}{273} \times \frac{760}{P}$$

where:

C = Exit gas concentration, ppmv

PR = Permeation rate, ng/min

F = Gas flow rate, ml/min

22.4 = Molar gas volume at STP, L

M = Molecular wt of chlorine

T = Temperature at which gas flow was measured, ^{o}K

P = Pressure at which flow was measured, mmHg

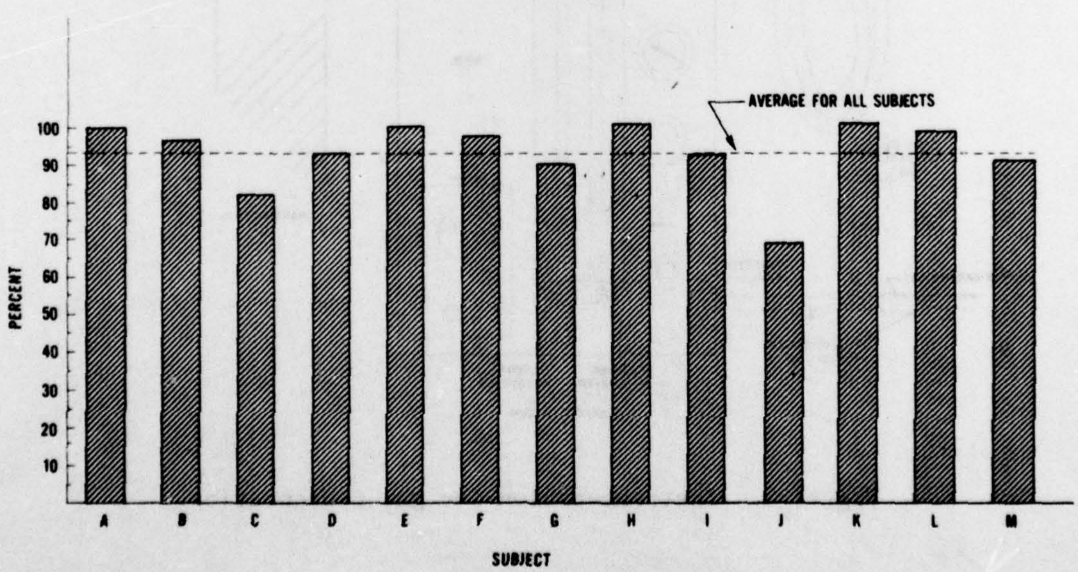

Figure 1. Percent efficiency for zero odor level.

The subject was presented with the gas for evaluation as shown in Figure 2.

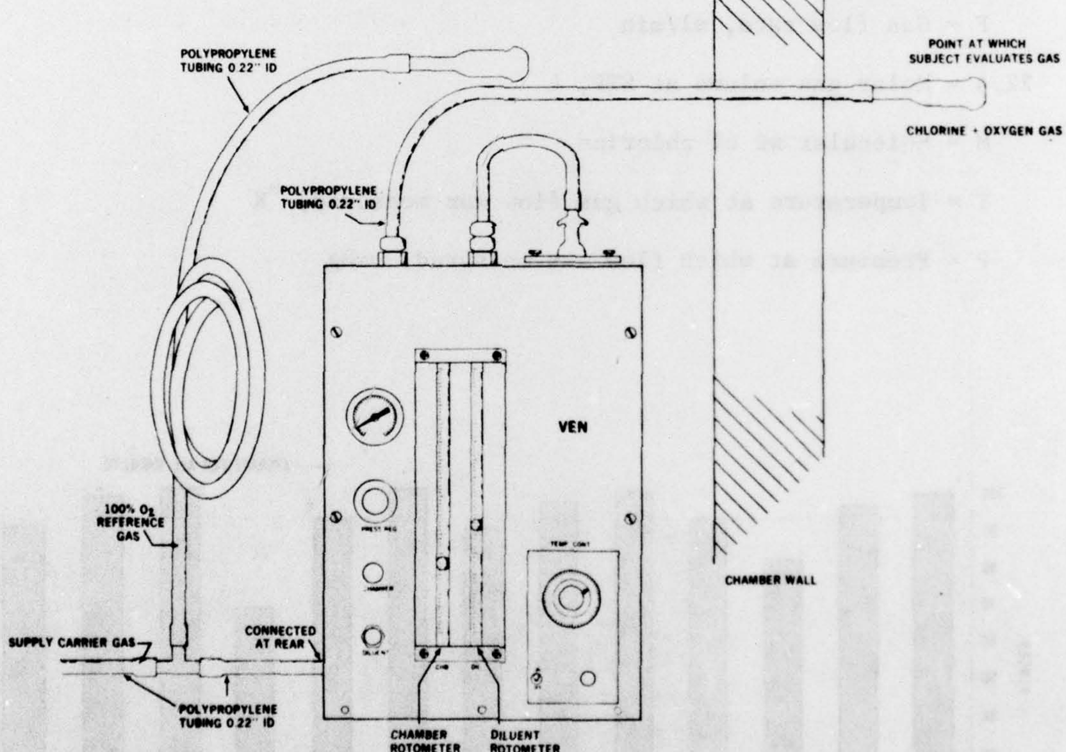

Figure 2. Instrumentation for gas presentation.

Method of Exposure

To provide an environment devoid of any extraneous noise or odors, the odor threshold test was conducted in a 7 x 6 x 8 ft (2.13 x 1.83 x 2.44 m) altitude chamber containing 300 ft^3 (8.49 m^3) of interior volume. Temperature and humidity were controlled inside the chamber at 23.1°C ± 0.5 and 50% ± 5% respectively. All equipment, instruments, and monitoring devices were external to the chamber to minimize subject distraction during the test.

The test protocol was conducted over a period of 7 months. Subjects were excused from testing on any days in which an upper respiratory ailment was apparent. However, each subject, once starting a series, completed the series with no more than a three-day interval between each successive exposure test. The number of exposure tests varied from subject to subject depending on their nasal acuity and judgment as discussed later.

Each subject was tested on a one-per-day basis to avoid any effects of adaptation in odor acuity (2). The subjects were presented with varying concentrations of chlorine in oxygen, using a modification of the up-and-down method of obtaining sensitivity data (3). This technique involved presentation of the odorant in a concentration dependent on the subject's previous response. If a subject was correct in his response at the starting concentration, he was given the next lower concentration. If the response was incorrect, he was given the previous higher concentration. All subjects were initially started at a concentration of 1-2 ppm. This technique had the primary advantage of automatically concentrating test presentations near the threshold. The subjects were required to attempt detection of a mixture of chlorine in oxygen presented in conjunction with a reference gas (100% O_2) and were told to indicate the presence or absence of the chlorine odor by a yes or no response. Subjects were instructed to evaluate the chlorine odor in the same manner during each test. Although the sniff varied from subject to subject, each panelist employed the same sniff with the chlorine plus oxygen mixture as he did with the 100% oxygen reference gas. Hence the presentations were equivalent for each subject.

Within each series of tests, the subjects were given three samples for evaluation; one of four possibilities existed: (a) none contained chlorine, (b) all contained chlorine, (c) one contained chlorine, and (d) two contained chlorine. Each subject was further instructed that if chlorine appeared in any one of the three samples, it would appear at the same concentration if detected in any of the two remaining samples within the same series. This instruction was given to eliminate any possibility of anticipation or guess on the subject's part.

Testing was conducted on a midmorning-midafternoon schedule to offset any olfactory effects of breakfast or lunch (1). Each subject was allowed to sniff the gas presented without restriction as to time.

Normally, the subjects gave a response (positive or negative) within 15 s of the presentation. The flow rate of the presentation gas was 7 to 8 l/min for both the chlorine plus oxygen mixture and the reference gas. This measure was taken to prevent the possibility of impingement velocity influencing subject response (10).

The study was conducted in a double blind design. Neither the subject nor the investigator within the altitude chamber was aware of the presentation sequence. Only the technician outside the chamber, who prepared the chlorine concentration levels, was aware of the manner in which the subject received the samples.

Analytical Measurement

Analytical measurement of the chlorine concentration of the presentation gas mixtures was done by two methods. Primary measurement was done by microcoulometry (Dohrmann Model C-200B) using a continuous sampling adaptation (8,9). Confirmatory analysis was done with a chemiluminescence instrument (Geomet Model 401B) originally developed for detection of hydrogen chloride gas. The chemiluminescent analyzer, with only minor modification, was found to be highly accurate in measuring chlorine as well. The modification involved removal of the alumina inlet tube to allow passage of the chlorine-oxygen mixture directly into the chemiluminescent cell reaction chamber in the instrument. Both the microcoulometer and chemiluminescent analyzers gave a linear response over the range of chlorine concentrations employed in this study (Fig. 3).

The flow rates of the carrier gas were monitored by use of a wet test meter which was calibrated against a 120-l chain-compensated gasometer. Measurements from both the Geomet HCl monitor and the microcoulometer were recorded on strip chart recorders.

RESULTS

Data are summarized in Table 2. The variability of the panel responses to the chlorine odor increased as the chlorine concentration decreased (Fig. 4). However, at least 50% of the panel was able to detect the odor of chlorine in oxygen at concentrations of 0.08 ppm at least 50% of the time. Odor threshold level range was 0.06 - 0.20, as determined by the panel of 11 diversified human volunteers used in this study.

The data acquired from two of the subjects were incomplete, according to the criteria of consistent judgments as outlined for purposes of this study. Therefore, data for these subjects were not included in establishing the odor threshold of chlorine.

The oldest subject tested exhibited wide variability in response, accompanied by a high threshold when compared with the group. This may be explained by the possible deterioration of the sense of smell with age (6), and the difficulty associated with establishing a stable response criterion.

The absence of a significant number of subjects who were smokers does not permit a valid examination of the influence of smoking on olfactory acuity. The literature is not clear on the question of a deleterious influence of smoking on olfactory acuity (4, 13).

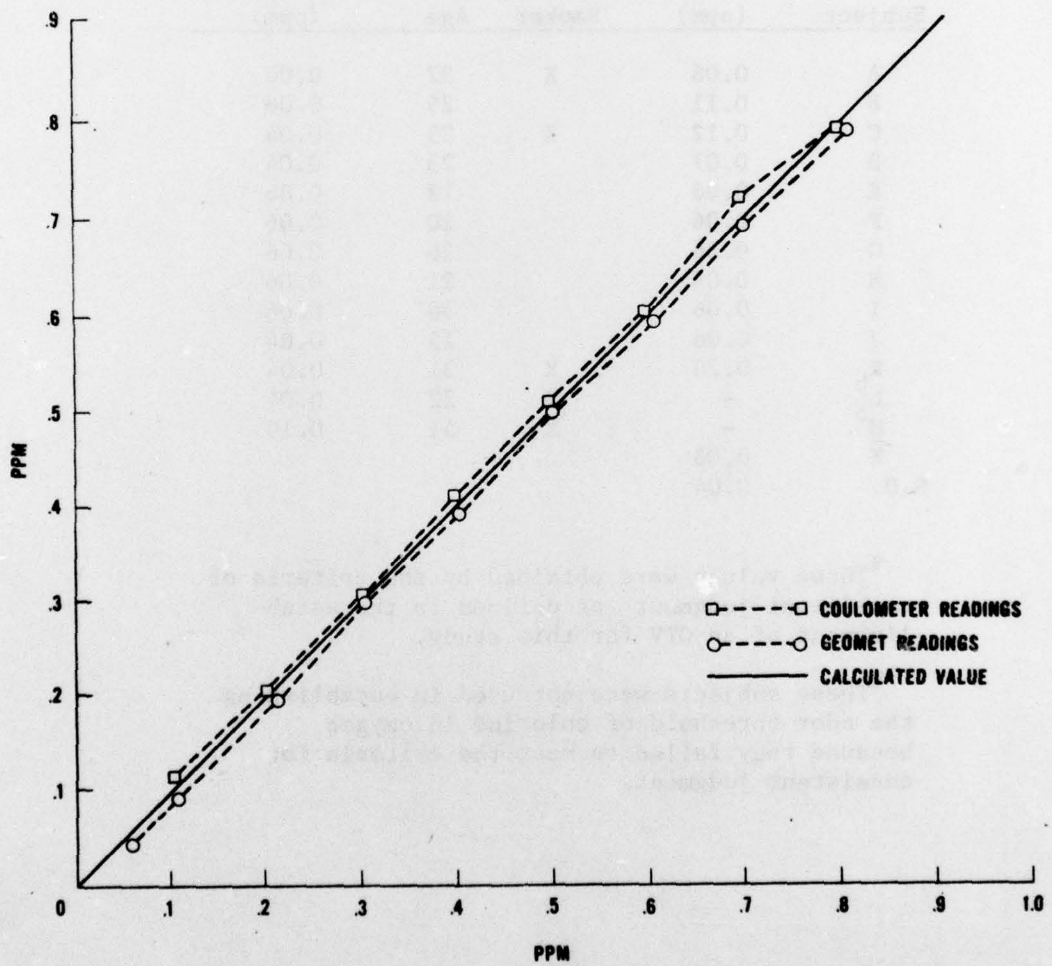

Figure 3. Comparability of coulometer-Geomet.

TABLE 2. SUMMARY OF DATA

Subject	Odor threshold[a] (ppm)	Smoker	Age	Lowest detectable concentration (ppm)
A	0.06	X	37	0.06
B	0.11		25	0.06
C	0.12	X	25	0.04
D	0.07		23	0.04
E	0.06		18	0.06
F	0.06		20	0.06
G	0.06		26	0.06
H	0.06		21	0.06
I	0.06		38	0.06
J	0.06		25	0.04
K	0.20	X	31	0.04
L[b]	-	X	22	0.04
M[b]	-	X	51	0.10
$\bar{X}$	0.08			
S.D.	0.04			

[a]These values were obtained by the criteria of consistent judgment as defined in the establishment of an OTV for this study.

[b]These subjects were not used in establishing the odor threshold of chlorine in oxygen because they failed to meet the criteria for consistent judgment.

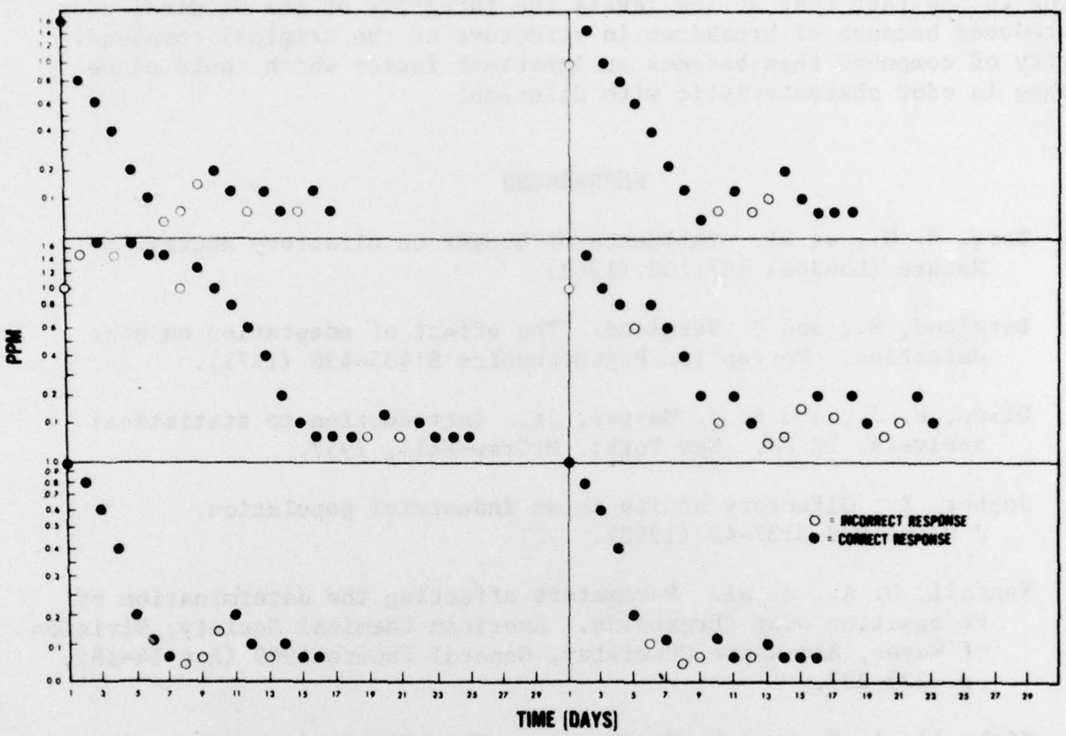

Figure 4. Typical responses of selected subjects.

CONCLUSIONS

The military specification which permits 0.20 ppmv of chlorine impurity in generated oxygen from chlorate candles seems to be satisfactory, since the odor threshold of 0.08 ppm indicates the point at which the subject first began to detect the presence of the odor chlorine.

Generally as a subject progresses to the point of his threshold, his ability to reproduce judgments of the prescribed concentration tends to decrease; at this point, we noted that the time interval between trials became significant in relation to the subject's ability to make consistent judgments. Judgmental difficulties arise when there is a lack of sharp onset of stimulation as in the instance of levels of odor sensation well above the threshold levels.

In this study, we noted that the character of the odor influences the validity of any odor threshold measurement. Compounds with distinct odors sometimes do not display the same odor at low concentrations, owing to the fact that at low levels the integrity of the original odor is reduced because of breakdown in structure of the original compound. Purity of compound then becomes an important factor which could cause change in odor characteristic with dilution.

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