

UNCLASSIFIED

AD NUMBER

AD016993

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

**Distribution authorized to U.S. Gov't. agencies and their contractors;
Administrative/Operational Use; 06 AUG 1953.
Other requests shall be referred to Chemical Corps Medical Labs., Army Chemical Center, MD.**

AUTHORITY

ECBC memo dtd 20 Jun 2016

THIS PAGE IS UNCLASSIFIED

CB-111906

CHEMICAL CORPS MEDICAL LABORATORIES RESEARCH REPORT

Report No. 206

THE MEDIAN DETECTABLE CONCENTRATION OF DIBORANE, PENTABORANE AND DECABORANE BY ODOR FOR MAN

by

Charles C. Comstock
Fred W. Oberst

with the technical assistance of

Lorraine Lawson
Ernest E. Ozburn



August 1953

Copy No. _____

SEP 11 1953

LIBRARY AND FILES SECTION
THE CHEMICAL CORPS SCHOOL
FORT MCCLELLAN, ALA.

Cy-2

ARMY CHEMICAL CENTER, MARYLAND

CHEMICAL CORPS
MEDICAL LABORATORIES
ARMY CHEMICAL CENTER
MARYLAND

CMLRE-ML-52

Medical Laboratories Research Report No. 206

THE MEDIAN DETECTABLE CONCENTRATION OF DIBORANE, PENTABORANE
AND DECABORANE BY ODOR FOR MAN

by

Charles C. Comstock
Fred W. Oberst

with the technical assistance of

Lorraine Lawson
Ernest E. Ozburn

August 1953

Medical Laboratories Research Report No. 206

The Median Detectable Concentration of Diborane, Pentaborane
and Decaborane by Odor for Man

ABSTRACT

OBJECT.

The object of this work was to determine the median detectable concentration (MDC) of diborane (B_2H_6), pentaborane (B_5H_9), and decaborane ($B_{10}H_{14}$) by odor for man.

RESULTS.

Human subjects were used to determine the threshold concentrations for odors of three boron hydrides by means of the Fair-Wells osmoscope. Concentrations of diborane vapor in a chamber were determined by chemical analysis and those for penta- and decaborane were determined by a nominal method.

CONCLUSIONS.

1. The median detectable concentrations of diborane and pentaborane by odor are in the same range of 3.7 (3.3-4.2) $mg./m^3$ (analytical) and 2.5 (1.7-3.6) $mg./m^3$ (nominal), respectively. None of the subjects could detect diborane at 1.5 $mg./m^3$. For decaborane the MDC is 0.35 (0.24-0.49) $mg./m^3$ (nominal).

2. The odor of diborane was described by the majority of the subjects as "an odor of rotten eggs". Pentaborane was described by several subjects as either "garlic", "acetylene-like" or "slightly sweet". Decaborane was said to be either "unpleasant", "foul" or "chocolate-like".

3. There were no aftereffects from smelling the vapors of diborane, pentaborane or decaborane in concentrations ranging from 0.2 to 6 $mg./m^3$.

RECOMMENDATION.

None.

Medical Laboratories Research Report No. 206

The Median Detectable Concentration of Diborane, Pentaborane and Decaborane by Odor for Man

I. INTRODUCTION.

A. Object.

The object of this work was to determine the median detectable concentration (MDC) of diborane (B_2H_6), pentaborane (B_5H_9), and decaborane ($B_{10}H_{14}$) by odor for man.

B. Authority.

Authorized by the Chief Chemical Officer, under Project 4-61-14-002, Health Hazards of Military Chemicals, Cml C Research and Development Program for fiscal year 1952.

II. THEORETICAL.

In order that the odor of any substance may be detected the material must be present as a vapor (2,3). The smallest concentration of a substance required to stimulate the olfactory nerves and to obtain a perception of odor is called the threshold value of the odor. The Fair-Wells osmoscope (Type B) used in the following study, is designed to detect threshold odors.

The boron hydrides have characteristic odors in relatively low concentrations in air. Since these compounds are quite toxic by inhalation, their presence may constitute a health hazard. The MDC values for each agent may be useful in determining the approximate concentration of the agent present in air by odor when approximately one-half of the personnel recognize its presence. The time of exposure may then be restricted by the degree of the hazard involved.

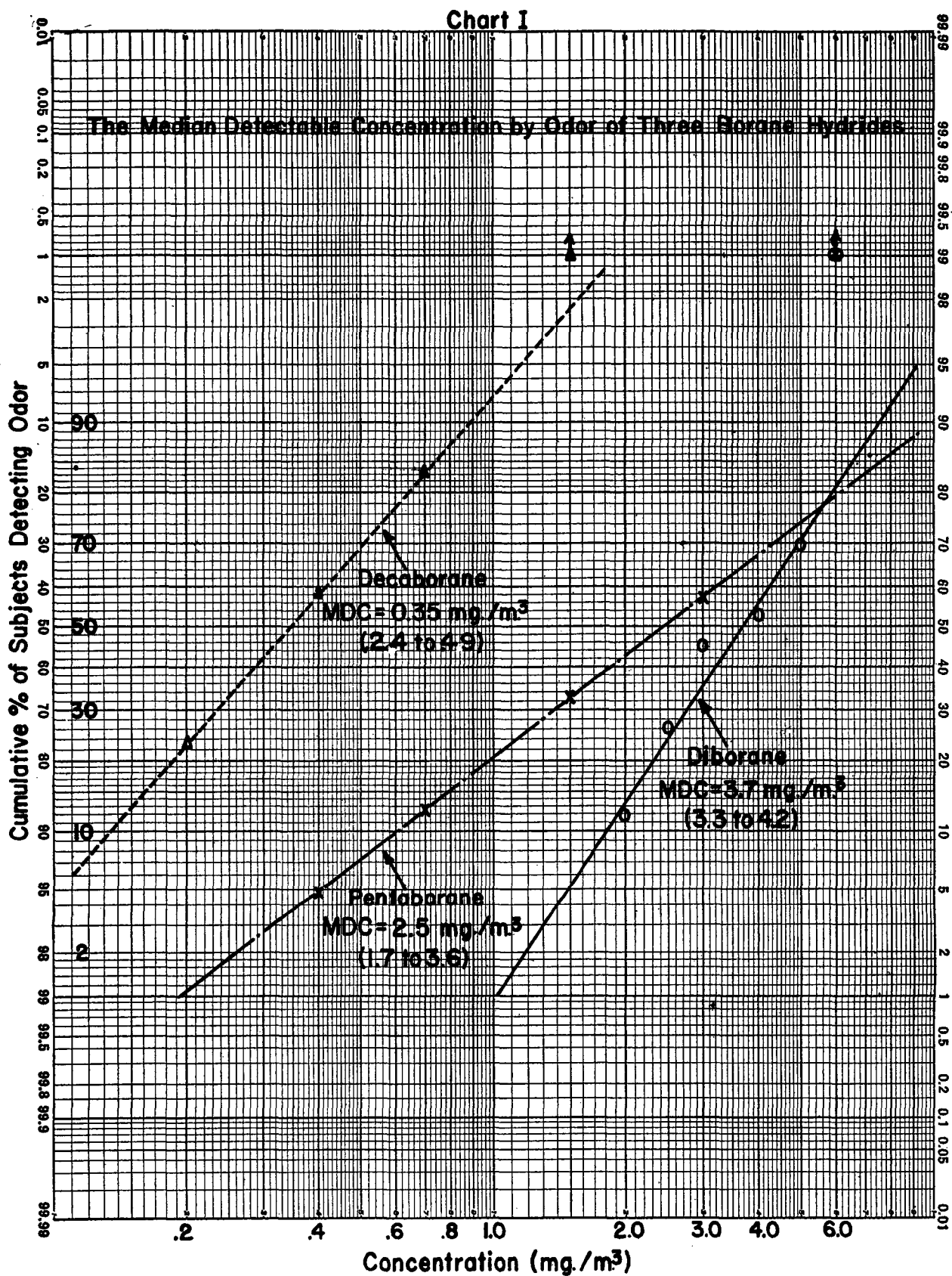
III. EXPERIMENTAL.

A. Subjects.

Each compound was tested 2 to 4 times on 10 to 15 subjects. In most instances the same subject volunteered for the repeated tests which always were made on succeeding days. In calculating the MDC the results of all runs on a given compound were pooled according to the concentration level at which the odor was detected.

B. Method for Detection of Odor.

A Fair-Wells osmoscope (Type B), attached to the gassing chamber, was used (3). The data from the sniff tests on the three compounds were plotted on log-probability paper from which the MDC (Chart 1) was obtained. The 19/20 confidence limits were calculated by the method of Litchfield (4).



C. Procedures.

1. Diborane.

Diborane gas was metered into an 0.4 m^3 gassing chamber at a constant rate. For chemical analysis a sample of chamber air was drawn at a flow rate of 0.001 m^3 per minute through an absorption tube which contained water and glass beads. The boric acid which formed in the tube was titrated in the presence of mannitol using 0.01 N NaOH and phenolphthalein indicator (1).

2. Pentaborane.

Pentaborane vapor was drawn from a cylinder by a calibrated syringe and the contents were injected into an 0.4 m^3 static gassing chamber to which the osmoscope was attached. From the amount of pentaborane in the syringe, the nominal chamber concentration was calculated to be 6 mg./m^3 . The procedure for determining the MDC by odor was the same as that described for diborane.

3. Decaborane.

As this compound is a solid which has a comparatively high vapor pressure, it was possible to weigh out the required amount of material which on vaporization would produce a concentration of 6 mg./m^3 in an 0.4 m^3 static chamber. The material was vaporized by placing it on the floor of the gassing chamber and heating it with an electric light bulb until it was completely volatilized. At this point the procedure for determining the MDC by odor was the same as that described for diborane.

D. Results.

1. Diborane.

The MDC by odor of diborane is $3.7 (3.3-4.2) \text{ mg./m}^3$. The results are based on a series of tests (Table 1) in which a total of 49 determinations was used. All subjects detected the odor of diborane at 6 mg./m^3 , and none were able to detect it at 1.5 mg./m^3 . The odor was distinct at each threshold level for the subject and was described by the majority as "an odor of rotten eggs". No aftereffects occurred from sniffing diborane.

Table 1
Detection of Diborane by Odor
n = 49 determinations

Osmoscope Concentration		Subjects	Detecting Odor
mg./m^3	ppm	no.	cumulative %
2.0	1.8	6	12
2.5	2.2	7	26
3.0	2.7	9	45
4.0	3.6	4	53
5.0	4.5	8	69
6.0	5.4	15	100

MDC = $3.7 (3.3-4.2) \text{ mg./m}^3$
S = $1.76 (1.50-2.06)$

2. Pentaborane.

The MDC of pentaborane based on 40 determinations is 2.5 (1.7-3.6) mg./m³. The odor of this compound was the most difficult of the three boron hydrides for the subjects to describe. Descriptive terms were given such as, "garlic-like", "acetylene-like", and "pungent". The chamber concentration of pentaborane vapor was 6 mg./m³; all subjects were able to detect this concentration level. The detailed data are shown in Table 2.

Table 2
Detection of Pentaborane by Odor
n = 40 determinations

Osmoscope Concentration		Subjects	Detecting Odor
mg./m ³	ppm	no.	cumulative %
0.4	0.2	2	5
0.7	0.3	3	12.5
1.5	0.6	8	32.5
3.0	1.0	10	57.5
6.0	2.0	17	100.0

MDC = 2.5 (1.7-3.6) mg./m³

S = 3.0 (2.65-3.39)

3. Decaborane.

The results from 17 determinations on decaborane are shown in Table 3. The MDC found is 0.35 (0.24-0.49) mg./m³. The odor was readily described as either "unpleasant", "foul", or chocolate-like".

Table 3
Detection of Decaborane by Odor
n = 17 determinations

Osmoscope Concentration		Subjects	Detecting Odor
mg./m ³	ppm	no.	cumulative %
0.2	0.4	4	24
0.4	0.8	6	59
0.7	1.4	5	88
1.5	3.0	2	100

MDC = 0.35 (0.24-0.49) mg./m³

S = 2.09 (1.55-2.70)

IV. DISCUSSION.

The vapor concentrations at which the three boron hydrides can be detected by odor are not injurious to laboratory animals for relatively short exposures of a few hours but these concentrations probably would be harmful to human beings over prolonged exposure periods (1). As the sense of smell is easily fatigued, personnel detecting traces of boron hydrides should leave the contaminated area immediately or don a gas mask until assurance is made that decontamination measures have been completed. Fortunately, the odors of the three boron hydrides are easily detected at very low concentrations, which

reduces the hazards of these compounds and serves as a warning that danger is present. In the manufacturing of these compounds there may be other chemical substances present in the air which also emit odors that may mask the odor of a boron hydride. Should this be the case, then the identification by odor of any one of the boron hydrides at low levels may not be made easily.

In establishing the prescribed chamber concentration only diborane was determined by an analytical procedure. Pentaborane and decaborane concentrations were obtained by nominal methods. The extent to which these two substances may have been adsorbed on the walls of the chamber is not known. Depending upon the degree that this may have occurred, the actual MDC of these compounds would be lower than the values reported. Particularly may this be true of decaborane, which is a solid at room temperature. In this case vaporization was induced by heating and considerable loss on the chamber walls may have occurred.

V. CONCLUSIONS.

1. The median detectable concentrations of diborane and pentaborane by odor are in the same range of 3.7 (3.3-4.2) mg./m³ (analytical) and 2.5 (1.7-3.6) mg./m³ (nominal), respectively. None of the subjects could detect diborane at 1.5 mg./m³. For decaborane the MDC is 0.35 (0.24-0.49) mg./m³ (nominal).

2. The odor of diborane was described by the majority of the subjects as "an odor of rotten eggs". Pentaborane was described by several subjects as either "garlic", "acetylene-like" or "slightly sweet". Decaborane was said to be either "unpleasant", "foul" or "chocolate-like".

3. There were no aftereffects from smelling the vapors of diborane, pentaborane or decaborane in concentrations ranging from 0.2 to 6 mg./m³.

VI. RECOMMENDATION.

None.

VII. BIBLIOGRAPHY.

1. Comstock, C.C., L. Feinsilver, L.H. Lawson and F.W. Oberst: Inhalation Toxicity of Diborane in Dogs, Rats and Guinea Pigs. MLRR in preparation.

2. Fair, G.M., Jr. 1933. The Determination of Odors and Tastes in Water. New Eng. Water Works Ass'n. 47:248-72.

3. Fair, G.M., Jr. and F. W. Wells. 1934. Determining Odors in Water. Water Works Eng., 87:1051-5.

4. Litchfield, J.J., Jr. 1949. A Method for Rapid Graphic Solution of Time-Per Cent Effect Curve. J. Pharmacol. & Exper. Therap. 97:399-408.

Medical Laboratories Research Report No. 206. SUBMITTED:
The Median Detectable Concentration of Diborane,
Pentaborane and Decaborane by Odor for Man.

Chasent
CHARLES C. COMSTOCK*
Gassing Branch

Authority:

Project No.: 4-61-14-002

Fred W. Oberst
FRED W. OBERST*
Chief, Gassing Branch

* Authors

APPROVAL RECOMMENDED:

Experimental Data:

Date Started: 11 May 1951
Date Completed: 29 June 1951
Notebook No.: MD 989, 891

S. D. Silver
S. D. SILVER
Chief, Toxicology Division

APPROVED:

David B. Dill
DAVID B. DILL
Scientific Director
Chairman, Editorial Committee

Typed: 6 August 1953
hy

CMLRE-ML-52
Publication Control No. 5030-206

Harold W. Wheeler
Major and C & O
for
NORMAN W. ELTON
Colonel, Medical Corps
Commanding

SUGGESTED HEADINGS FOR MEDICAL LABORATORIES RESEARCH REPORT NO. 206

- 1. Decaborane, analysis**
- 2. Decaborane, detect., odor**
- 3. Diborane, analysis**
- 4. Diborane, detect., odor**
- 5. Pentaborane, analysis**
- 6. Pentaborane, detect., odor**



DEPARTMENT OF THE ARMY
US ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
EDGEWOOD CHEMICAL BIOLOGICAL CENTER
5183 BLACKHAWK ROAD
ABERDEEN PROVING GROUND, MD 21010-5424

REPLY TO
ATTENTION OF

JUN 20 2016

RDCB-DSR-S

MEMORANDUM THRU Director, Edgewood Chemical Biological Center, (RDCB-D/Dr. Joseph L. Corriveau), 5183 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010-5424

FOR Defense Technical Information Center, 8725 John J. Kingman Road, Ft Belvoir, VA 22060

SUBJECT: Change in Distribution

1. This action is in response to an Edgewood Chemical Biological Center (ECBC) Internal Request for a Change in Distribution for the following documents:

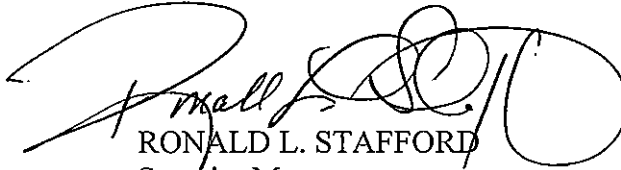
a. Comstock, C.C.; Oberst, F.W.; Lawson, L.; Ozburn, E.E. *The Median Detectable Concentration of Diborane, Pentaborane and Decaborane by Odor for Man*; Medical Laboratories Research Report No. 206; Chemical Corps Medical Laboratories: Army Chemical Center, MD, 1953, Unclassified, Distribution C. **CBRNIAC-CB-111906**

b. Comstock, C.C.; Feinsilver, L.; Lawson, L.H.; Oberst, F.W. *Inhalation Toxicity of Diborane in Dogs, Rats, and Guinea Pigs*; Medical Laboratories Research Report No. 258; Chemical Corps Medical Laboratories: Army Chemical Center, MD, 1954, Unclassified, Distribution C. **ADB032228 CBRNIAC-CB-113261**

c. Lawson, L.H.; Jacobson, K.H. *The Median Lethal Concentration of Diborane Vapor for Rats and Mice*; CWLR 2031; Chemical Warfare Laboratories: Army Chemical Center, MD, 1956, Unclassified, Distribution C. **AD0099186 CBRNIAC-CB-116024**

2. The above listed documents have been reviewed by ECBC Subject Matter Experts and deemed suitable for the change in distribution to read "Approved for public release; distribution unlimited."

3. The point of contact is Adana Eilo, ECBC Security Specialist, (410) 436-2063, adana.l.eilo.civ@mail.mil.


RONALD L. STAFFORD
Security Manager