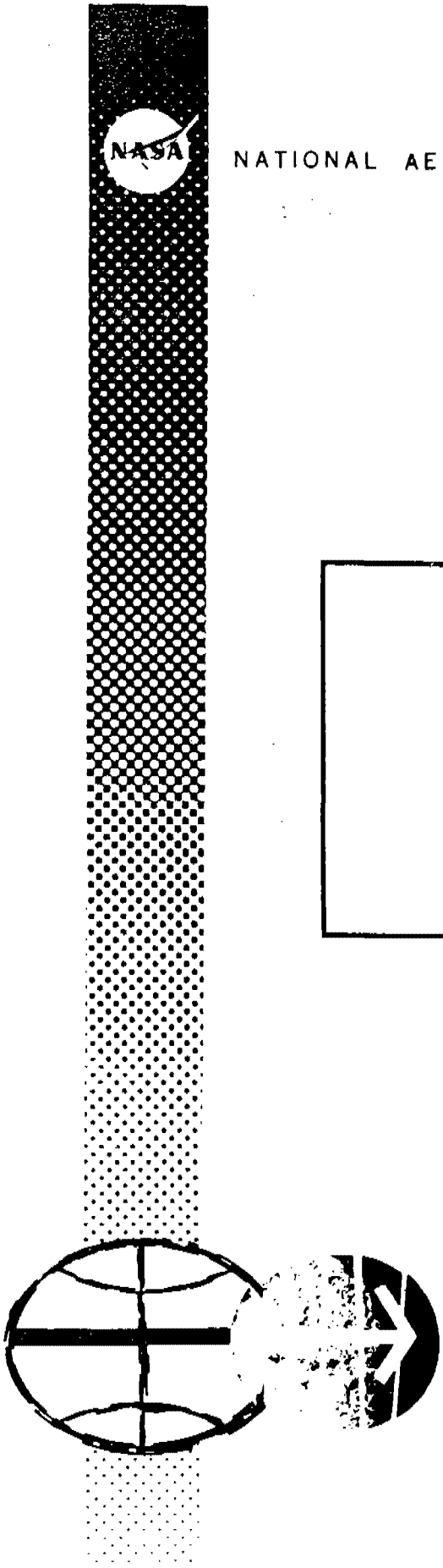


NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

DOCUMENT NO. TR-WSTF-140

DATE August 4, 1976

Test Report

Olfactory Response to Monomethylhydrazine

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WHITE SANDS TEST FACILITY
LAS CRUCES, NEW MEXICO

JSC FORM 2026A (SEPT. 14, 73)

Test Report

Olfactory Response

to

Monomethylhydrazine

Issued by

Laboratories Test Office

White Sands Test Facility

Johnson Space Center

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Abstract

A test was conducted to determine if personnel were capable of detecting the odor of 0.2 ppm monomethylhydrazine (MMH). A panel of forty-two volunteer individuals were selected and medically qualified to participate in the test. Preparation and analysis of the test atmosphere (0.2 ppm MMH) and odor test conduct are described. Test results indicated approximately two-thirds of the subjects were able to detect the odor. The results also indicated that routine exposure to MMH tends to decrease the ability of test subjects to detect the odor. Twelve panel members experienced irritation of the nasal mucosa.

1.0 Introduction

Personnel working in the rocket engine test stand areas at White Sands Test Facility (WSTF) are subjected to trace residues of monomethylhydrazine (MMH) fuel during their normal course of work. The residual fuel levels in the work areas are below the published threshold limit value (TLV) of 0.2 ppm for an 8-hour day as verified by sampling and chemical analysis of the work area atmosphere. However, due to problems in obtaining satisfactory "real time" analytical data on the MMH levels in work areas, a test was conducted at WSTF to determine if personnel could reliably detect the odor of MMH at the 0.2 ppm level. Knowledge of personnel's ability to detect MMH at the TLV level would be a useful contribution to operational safety.

An MMH odor sensitivity test was performed using the standardized odor test procedure as outlined in NHB 8060.1A[1]. The standardized procedure has been used at WSTF to evaluate odor characteristics of the offgassing of materials used in the Apollo, Skylab, Apollo-Soyuz and Shuttle Programs. This report presents the odor test procedure used and the results obtained.

2.0 Objective

The principle objective of the test was to determine if 0.2 ppm MMH could be detected by the olfactory senses.

In addition, a secondary objective was to determine if personnel routinely exposed to low levels of MMH have developed any insensitivity to the odor of MMH.

3.0 Test Procedure

3.1 Test Outline

The WSTF odor test utilizes a panel of volunteer personnel. A single 30cc sample of the test gas is administered to each panel member by the test conductor and the members then evaluate the odor as:

Undetectable
Barely detectable
Easily detectable
Irritating
Objectionable

A numerical score is assigned to each rating. Test protocol requires that published TLV[2] are not exceeded.

[1]NHB 8060.1A, Flammability, Odor, and Offgassing Requirements and Test Procedures for Materials in Environments That Support Combustion, February 1974, pg 4-30.

[2]N. I. Sax, Dangerous Properties of Industrial Materials (New York),

3.2 Certification of the Odor Panel

A panel of 42 volunteer test subjects composed of NASA and contractor personnel was selected from a pool of personnel which met the following qualifications:

a. Each prospective panel member was required to pass a complete physical examination with emphasis on possible allergies and included a chest x-ray, vital capacity and blood chemistry tests. Appendix I describes the requirements for the examination. In addition to this physical, each test subject was also examined for nasal and respiratory condition prior to and after odor testing.

b. After being medically qualified, each test subject was required to pass an odor sensitivity test to verify that he had an acceptable olfactory response. This consisted of being able to detect seven primary odor standards from ten identical bottles, three of which contained only distilled water (see Appendix II for a description of the odor standards).

3.3 Certification of the Test Chamber

An atmosphere of carbon dioxide-free air was prepared in a 105-liter bell jar which would serve as the test chamber (see Photograph No. 1). The circulating fan was turned on for five minutes to simulate the mix time actually used during the MMH odor test. A chemical analysis was performed on the chamber air which indicated a background of 1 ppm by volume carbon monoxide, less than 0.2 ppm (as pentane) total organics, and less than 0.024 ppm MMH (the minimum detectable limit).

Fifteen members of the regular WSTF odor panel participated in certifying the test chamber was free of extraneous odors. Certification consisted of evaluating three 30cc samples as in a regular odor test except that one sample was of the test chamber and two were samples of room air.

Table I shows the odor scores for the "blank" chamber. These scores verify that the test chamber was free of extraneous odors prior to introduction of the MMH.

3.4 Preparation and Verification of the MMH Odor Standard

One (1.0) microliter of 98 percent pure MMH was injected into the evacuated test chamber that had been tested for odors and found to be odor free as previously described. After 20 minutes, the test chamber was backfilled to 11.0 psia with dry, carbon dioxide-free air. The circulation fan was switched on for approximately five minutes. The fan was then switched off for 20 minutes to allow the mixture to attain equilibrium. The contents were then sampled and analyzed. The final concentration was adjusted to 0.67 ppm by volume. Appendix III contains the analytical procedure used and pertinent calculations. The 0.67 ppm

by volume MMH standard was further diluted to 0.22 ppm by volume immediately prior to the odor test as described in Section 3.5.

3.5 Odor Test

After undergoing a nose and throat examination by the WSTF medical personnel, each subject was again tested for odor sensitivity immediately prior to the odor test. Members were required to successfully determine which of three bottles was a blank (containing only distilled water) and which contained odor standards. If the panel member was able to pass the pretest medical examination and the odor sensitivity test, he was allowed to participate in the MMH odor test.

The test was conducted according to the WSTF Odor Test Procedure No. CM-1 and in full compliance with NASA Management Instruction 7100.8, "Human Research Policy and Procedures," February 2, 1972.

Two samples were administered to each panel member; the first was room air and the second was the 0.2 ppm MMH sample, The panel members were not told which sample contained the MMH; they had been informed earlier that either sample, both samples, or neither sample would contain a small quantity of MMH. The test chamber and the sampling operation were hidden from view in accordance with standard procedure.

The MMH sample was administered as follows: a 10cc volume of the 0.6 ppm MMH sample was drawn into a 30cc glass syringe. Then 20cc's of carbon dioxide-free dry air were drawn to make up a 30cc sample of 0.2 ppm MMH. This was then injected into an odorless polyethylene face mask (see Photograph No. 2) which the test subject held over his mouth and nose (see Photograph No. 3).

3.6 Odor Test Evaluation

After sniffing the sample which had been injected into the mask, the test subject then rated it either:

0 - Undetectable
1 - Barely detectable
2 - Easily detectable
3 - Objectionable
4 - Irritating

The numerical scores were then collected and tabulated in Table II.

3.7 Post Test Medical Examination

The nose and throat of each test subject were again examined two hours after the test and those exhibiting any irritations were noted and photographed (see Table II, Appendix V and Appendix VI).

4.0 Test Results and Discussion

The raw data from the test is tabulated in Table II giving the individual scores of the panel members as well as the medical findings of the post test examinations. The significance of the odor detection scores is summarized in Table III.

As indicated in Table II, there were physiological changes as a result of the test. Slight bleeding, cavitation of the mucosa or development of clear blisters was observed in 28.6% (12 out of 42) of those tested (see medical report in Appendix V and photographs in Appendix VI). There seemed to be no correlation between irritations received and past or present routine exposure to MMH, or to the ability to detect the odor of the compound.

It can be noted in the summary of the test results, Table III, that only one of the 42 test subjects (2.4%) was able to detect any odor when the chamber contained only pure air. However, when the air in the chamber contained 0.2 ppm MMH, 28 of the 42 subjects (66.7%) were able to detect the odor of the chemical. The probability that these results are due to chance distribution (see Appendix IV) is less than one percent.

Of those 17 test subjects who had been recently and routinely exposed to MMH fumes at low levels, eight in seventeen (47.1%) were able to detect the odor of MMH at the 0.2 ppm level. Of the 25 test subjects who had never been exposed, or who were less recently or only occasionally exposed to MMH fumes, 20 (80%) were able to detect MMH at the 0.2 ppm level. The probability that the second group detected the odor of the MMH more readily than the first group by chance alone is only two percent.

5.0 Conclusions

From the test results, three conclusions can be deduced.

a. The odor of MMH in pure air at 0.2 ppm can be detected by approximately two-thirds of the test subjects.

b. Frequent exposure to MMH fumes apparently decreased the ability of test subjects to detect the odor of low concentrations of MMH, at least temporarily.

c. A single 30cc inhalation of 0.2 ppm MMH can cause irritation to the nasal mucosa in humans.

6.0 Distribution

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Table I

Verification of Test Chamber

(Odor Scores)

Odor Panel Member No.	Test Chamber Atmosphere (air)	Room Air	Room Air
1	0	0	0
2	0	0	0
3	0	0	0
4	0	0	0
5	0	0	0
6	0	0	0
7	0	0	0
8	1	0	0
9	0	0	0
10	0	0	0
11	0	0	0
12	0	0	0
13	0	0	0
14	0	0	0
15	0	0	0

A score of zero indicates no odor was detected and a score of one indicates an odor was barely detectable.

Table II

Odor Panel Tabulations and Medical Findings

Test Subject Panel Member Number	Past History of Exposure to UDMH and MMH	Presently Routinely Exposed to MMH	Odor Scores Blank Sample (Air Only)	Odor Scores Test Sample (0,2 ppm MMH)	Post Test Medical Findings
1	Yes	Yes	0	0	No irritations
2	Yes	No	0	1	No irritations
3	Yes	Yes	0	0	No irritations
4	Yes	No	0	2	No irritations
5	Yes	No	0	0	Blisters, right nostril
6	Yes	Yes	0	0	No irritations
7	Yes	No	0	1	No irritations
8	Yes	Yes	0	0	No irritations
9	Yes	Yes	0	0	Blisters, left nostril
10	Yes	Yes	0	0	Nasal blisters and bleeding
11	Yes	No	0	0	No irritations
12	Yes	Yes	0	1	Nasal hemmorrhage and blisters
13	Yes	Yes	0	2	Nasal bleeding
14	Yes	Yes	0	0	Irritation, right nostril
15	Yes	No	0	2	No irritations

Table II (continued)

Odor Panel Tabulations and Medical Findings

Test Subject Panel Member Number	Past History of Exposure to UDMH and MMH	Presently Routinely Exposed to MMH	Odor Scores Blank Sample (Air Only)	Odor Scores Test Sample (0.2 ppm MMH)	Post Test Medical Findings
16	Yes	Yes	0	1	No irritations
17	Yes	Yes	0	1	No irritations
18	Yes	No	0	2	No irritations
19	No	No	0	0	No irritations
20	Yes	Yes	0	2	No irritations
21	Yes	No	0	1	No irritations
22	No	No	0	2	Bleeding, left nostril
23	Yes	No	0	2	Slight irritation, dry mucosa
24	Yes	Yes	0	1	No irritations
25	Yes	Yes	0	1	No irritations
26	Yes	Yes	0	0	No irritations
27	Yes	Yes	0	0	No irritations
28	Yes	Yes	0	2	No irritations
29	No	No	0	1	No irritations
30	Yes	No	0	1	No irritations

Table II (continued)

Odor Panel Tabulations and Medical Findings

Test Subject Panel Member Number	Past History of Exposure to UDMH and MMH	Presently Routinely Exposed to MMH	Odor Scores Blank Sample (Air Only)	Odor Scores Test Sample (0.2 ppm MMH)	Post Test Medical Findings
31	No	No	0	0	Nasal irritation
32	No	No	0	1	No irritations
33	No	No	0	1	No irritations
34	No	No	0	1	No irritations
35	No	No	0	1	Increased nasal irritations
36	No	No	0	1	Nasal irritation
37	No	No	1	2	No irritations
38	No	No	0	1	No irritations
39	No	No	0	3	Bleeding, right nostril
40	Yes	No	0	0	No irritations
41	Yes	No	0	1	No irritations
42	No	No	0	1	Blisters, left nostril

Table III

Summary of Test Results

Sample	Group Size	Odor Detected	
Air	42	1	(2.4%)
0.2 ppm MMH	42	28	(66.7%)
0.2 ppm MMH*	17	8	(47.1%)
0.2 ppm MMH**	25	20	(80.0%)

* These test subjects had been exposed to MMH fumes at least once a month within six months prior to the test.

** These test subjects had been exposed to MMH fumes less frequently than once a month, or were exposed more than six months prior to the test, or who had never been exposed before.

Appendix I

Screening Examination Procedure

for

Type 3B Propellant Handlers Physical

This physical will be administered to all contractor personnel who are propellant handlers. A yearly repeat will be performed as long as the individual's job functions require that he be a propellant handler. In addition to the repeat examination, the employee will complete the Propellant Handler's Questionnaire, MSC Form 2084.

Height
Weight
Blood pressure
Pulse
Visual acuity
Audiogram
ECG (electrocardiogram)
Vital capacity (if vital capacity is less than 70%, a timed vital capacity is required. If the first second is less than 60% or the third second is less than 85%, the individual shall not be a propellant handler and should be urged to see his own physician)
Skin test for tuberculosis and coccidiomycoses every two years
Urine - dipstick
CBC (complete blood count)
SGOT (serum glutanic oxaloacetic transaminase)
BUN (blood urea nitrogen), if history of kidney disease
Bilirubin, if history of liver disease
Glucose tolerance - 4-hour if family history of diabetes
Chest x-ray
Examination by physician

NOTE: This physical is also given to all odor panel members annually.

Appendix II

Primary Odor Standards Used for

Certifying the Odor Panel

Primary Odor	Standard Compound	Amount Dilution in Water
Ethereal	1,2-Dichloroethane	0.4 ml in 500 ml
Camphoraceous	1,8-Cineole	5 µl in 500 ml
Musky	15-Hydroxpentadecanoic acid lactone	1 mg in 1,000 ml
Floral	1-Methyl-1-ethyl-2-phenyl propanol-1	0.075 ml in 500 ml
Minty	Methone (dl)	2 µl in 333 ml
Pungent	Formic acid	25 ml of 90% solution in 500 ml
Putrid	Methyl disulfide (methyl dithiomethane)	1 µl in 10,000 ml

Appendix III

1.0 Analytical Method

The analytical method used is a modification of a procedure published in Analytical Chemistry, Volume 26, No. 21, 1954.

A 500 ppm by weight (ppmw) stock solution of MMH was prepared by dissolving 0.1275 grams of 98.15% pure MMH in 250 ml 0.36N H_2SO_4. A 1:1000 dilution of this stock solution with 0.05N H_2SO_4 gives a 0.50 ppmw MMH standard. This 0.50 ppm standard was further diluted 1:20 and 1:10 with 0.05N H_2SO_4 to give standards of 0.025 and 0.050 ppmw MMH. After applying the calibration factor for the pipets used, the actual calibration standards were 0.44, 0.04 and 0.02 ppmw MMH. Fifty (50.0) ml of 0.05N H_2SO_4 were used as a blank.

Five (5.0) ml of paradimethylaminobenzaldehyde solution (2g PDAB per 50 ml 2N H_2SO_4) was added to the blank and 2.5 ml PDAB solution was added to 25.0 ml of each standard, 20 minutes was allowed for color development and the absorbance was determined at 458 nm using the blank to zero the instrument (Bausch and Lomb Spectronic 600) and as the reference solution.

Work at WSTF has shown that the resulting calibration curve is linear (using 5 cm path length cells) over the concentration range of 0 to 5.0 ppmw MMH).

A 50.8 liter sample of the test chamber atmosphere (containing the MMH) was bubbled through a solution made up of 100 ml of 0.05N H_2SO_4; 10 ml of PDAB was then added and 20 minutes was allowed for color development. The concentration of the MMH was read from the calibration curve. The absorbance reading of the sample was too high for use of the curve and it was subsequently diluted by 2:5 and the absorbance was slightly higher than the highest standard. Extrapolation of the calibration curve was considered valid as the linear range of the curve is known to extend to a concentration of at least ten times higher than our highest standard.

PPMW was then converted to ppm by volume as detailed below.

2.0 Calculations

a. Sample Volume

The fractional pressure drop between the initial pressure and final pressure can be directly related to the initial volume.

$$\frac{P_i - P_f}{P_i} \quad (V_i) = V \text{ sample}$$

$$\frac{11.0 - 5.68}{11.0} \quad (105 \text{ liter}) = V \text{ sample}$$

50.8 liters (5.08×10^{-2} M^3) = V sample at 11.0 psia

b. Conversion of PPMW to PPMV

The weight of MMH present in the scrubbing solution may be determined as follows:

$$PPMW = \frac{\text{weight in milligrams}}{\text{liters of solution}}$$

$$1.32 = \frac{\text{weight}}{0.1 \text{ liter}}$$

weight = 0.132 mg

Converting this mass to a volume of gas at 22°C and 11.0 psia using the Ideal Gas Law:

$$PV = nRT$$

$$V = \frac{wt \times R \times T}{MW \times P}$$

$$V = \frac{1.32 \times 10^{-4} \times 8.21 \times 10^{-2} \times 2.95 \times 10^{2}}{4.6 \times 10^{1} \times \frac{11.0}{14.7}}$$

$$V = 9.28 \times 10^{-5} \text{ liters}$$

PPMV may be expressed as $\frac{ml}{M^3}$

$$PPMV = \frac{9.28 \times 10^{-2} \text{ ml}}{5.08 \times 10^{-2} \text{ } M^3}$$

PPMV = 1.83

c. Dilution of Test Chamber Concentration

The concentration of MMH in the test chamber can be diluted by lowering the pressure in the test chamber to a pressure that when backfilled to 12.4 (WSTF ambient pressure) will yield the desired concentration.

$$P_1 C_1 = P_2 C_2$$

$$P_1 1.83 = 12.4 \times 0.66$$

$$P_1 = \frac{12.4 \times 0.66}{1.83}$$

$$P_1 = 4.47 \text{ psia}$$

Thus, the test chamber pressure was reduced to 4.47 psia and then back-filled with air to 12.4 psia to yield a final value of 0.66 ppm by volume MMH.

Appendix IV

Statistical Procedures

The purpose of this appendix is to explain the statistical method used to test the validity of the Conclusions, Section 5.0.

The statistical method which was used is commonly known as "Student's t Test." The "t" test is used to determine the significance of the difference between two group averages. By applying the "t" test, one can determine the probability that the difference between two averages is caused merely by normal chance variations of individual data points, and is, therefore, not a "real" difference. If there is a high probability that the difference between the averages of two data groups is due solely to chance variations of individual data points, there is a low probability that the difference represents any actually measurable variation between the two groups. On the other hand, a low probability of a chance difference is strongly indicative that the two groups are different.

Values of "t" may be calculated using the equation

$$t = \frac{(\bar{X}_A - \bar{X}_B)^2 \, (N_A N_B) \, (N_A + N_B - 2)}{\left[\sum_{i=1}^{N_A} (X_{A,i} - \bar{X}_A)^2 + \sum_{i=1}^{N_B} (X_{B,i} - \bar{X}_B)^2 \right] (N_A + N_B)}$$

$\bar{X}$ = average value of a group

N = number of data points in a group

X = a data point within a group

Subscripts denote the value of the above variables associated with particular groups; e.g., N_A is the number of data points in group "A", $\bar{X}_B$ is the average value of group "B", etc. The number of "degrees of freedom" is given by

$$\phi = N_A + N_B - 2$$

In general, as "t" becomes larger, the probability that the difference between two averages is due solely to chance becomes smaller. If the "t" value of two averages has a value of two, or larger, the probability is quite small - ten percent or less - that the variation in these values is due solely to chance. Exact probabilities are determined by both the value of "t" and the number of degrees of freedom, and can be obtained from "t" tables published in all statistical textbooks and most general references, such as the "Handbook of Chemistry and Physics."

The test described in this report essentially required that the subjects give a "yes" or "no" response. To analyze the results of the test mathematically required that a "yes" response be assigned a value of "one," while a "no" response was given a value of "zero."

Using the results of the first two tests in which the entire test group compared the odor of pure air to the odor of air containing 0.2 ppm MMH, a "t" value of 8.31 is obtained. This indicates that there is a less than one percent probability that the difference in the results of these two tests is due solely to chance.

If the results of the second test are subdivided according to the frequency of exposure of each test subject to MMH, as they are in Table III, the "t" value associated with these two groups is 2.31, giving a probability of a mere chance difference of two percent.

Clearly, in both cases, the probability that the difference in the test results is due to chance alone is very small. Therefore, it may be concluded with a high degree of confidence, that the Conclusions, Section 5.0, are statistically valid.

Appendix V

Medical Report

Odor Panel Test

December 17, 1975

Forty-nine NASA and LEC employees were medically examined before the special odor test on December 17, 1975. Five were rejected due to areas of bleeding of their nasal mucosa and one was rejected due to a hole in his septum. One person did not odor test because he had been working with oxidizer that day and was disqualified.

Two hours after the odor test the 42 employees who were used were medically examined for any signs of irritation of the nose or throat. Twelve employees showed marked irritation with clear blisters, bleeding or cavitation of the mucosa. Most employees checked showed an increased appearance of dryness, 75% complained of a tingling, irritating sensation of their nose for a period of time after the test. Photographs were taken of the nasal mucosa of the employees with irritations.

The 12 employees who showed signs of irritation, were checked 24 hours post test. All had noticeable irritations, three showed white patches and had sinus congestion, four showed signs of bleeding. The major complaint was a feeling of irritation compared to inhaling something strong.

This was a mixed panel of employees, some were qualified members of the Odor Panel, some were employees who had known allergies, others were employees who had never been used on an Odor Panel. Of the 12 with irritations, six were Odor Panel members, five work at Test Stand 401 and have had previous exposure to MMH, and three of the 12 had a history of allergies (hayfever, sinusitis, etc.).

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