

United States Department of Agriculture
Agricultural Marketing Service | National Organic Program
Document Cover Sheet

<https://www.ams.usda.gov/rules-regulations/organic/national-list/petitioned>

Document Type:

National List Petition or Petition Update

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

Technical Report

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.



Isagro USA, Inc.
430 Davis Dr., Suite 240
Morrisville, NC 27560

18 July 2018

National Organic Program
Agricultural Marketing Service
United States Department of Agriculture
Attn: Devon Pattillo

Dear Mr. Pattillo,

Please see the attached rebuttal to the NOSB Technical Evaluation Report, Limited Scope (2017). Isagro USA would like to correct information found within the document to be incorrect or misleading.

Best regards,

A handwritten signature in blue ink that reads "Jennifer Lilly". The signature is written in a cursive, flowing style.

Jennifer Lilly
Regulatory Manager

Response to the Updated USDA National Organic Program Technical Report on Allyl
Isothiocyanate dated February 12, 2018

Submitted by

Isagro USA, Inc.
430 Davis Drive, Suite 240
Morrisville, NC 27560
United States

Date

July 17, 2018

Author

Beth E Mileson, Ph.D., DABT
Technology Sciences Group 1150 18th St
Washington, DC 20036

317 ranging from 2-17g/kg (Dai and Lim, 2014), the equivalent application rate of AITC is 4-33 lb / acre. The
318 The available resources indicate that some organic growers, including organic strawberry producers, are
319 adopting mustard seed meal as a natural option for soil pest control.

Response

Application of tons of mustard meal per acre in order to obtain adequate efficacy is not practical. AITC at 0.2 to 1.7% of the cracked mustard meal under experimental conditions (according to Dai & Lim, 2014) is unlikely to produce the efficacy that the more concentrated biofumigant form does.

Page 8 Excerpt

328 This “activated mustard slurry” is allowed to
329 react for a specified period of time at slightly elevated temperatures (e.g., 50 °C) before the AITC generated
330 through enzymatic hydrolysis of sinigrin is separated from the bulk mustard seed residue.

Response

This sentence is indicative of a pattern of judgements that are made in the document about physical characteristics that are peculiar and sometimes misleading. For example, a “slightly elevated temperature” compared to room temperature (20 to 25°C), might be considered to be 35°C or perhaps even 40°C, except for the qualifying 50°C temperature presented. Fifty degrees Celsius is equal to 122° Fahrenheit, and this is considered hot for water temperature, not slightly elevated in temperature. This peculiarity in judgement is not a major issue for temperature because everyone can relate to temperature, but when the same types of judgements are made with respect to vapor pressure later in the document it is more difficult to interpret the implications of differences in vapor pressure.

Page 9 Excerpt, Evaluation question #4 Describe the persistence or concentration of the petitioned substance and/or its by-products in the environment

378 Because AITC is
379 a volatile organic compound and has the potential to cause irritation and systemic toxicity, exposure of and
380 potential adverse effects on non-target receptors (humans and wildlife) is likely considering its proposed
381 use pattern as a pre-plant soil biofumigant at the application rates proposed (85-340 lbs/acre).

Response

AITC is somewhat volatile and has the potential to cause irritation at some concentration, but this does not mean that exposure to non-targets is likely, given the label-specified application methods and use rate. There are specific directions for use detailed on the product labels to ensure that AITC is applied in a manner that is protective of bystanders and wildlife (e.g., EPA Reg. No. 89285-2). The use directions on EPA-approved labels for AITC are enforced under federal law. The US EPA stated in its Scientific Review in support of the registration of the 99.8% and 96.3% AITC pesticide products (2013), that application methods together with appropriate personal protective equipment will mitigate human exposure, such that human exposure is not a concern for use of AITC. Further, the US EPA stated that the approved application methods minimized the potential for exposure to non-target organisms (US EPA, 2013).

Page 10, Excerpt, Evaluation Question #5 Describe the toxicity and mode of action of the substance and of its breakdown products and any contaminants. Describe the persistence and areas of concentration in the environment of the substance and its breakdown products

444 US EPA classifies pure AITC as moderately toxic for acute oral and inhalation exposure (Category II).

Response

Since the initial registration of the concentrated AITC by the USEPA, Isagro has submitted a new acute inhalation toxicity study that the US EPA agrees supports an EPA Toxicity Category III (LC50 >0.5 mg/L) rather than the original Toxicity Category II for inhalation exposures. That said, the acute oral route of exposure remains US EPA Toxicity Category II.

Page 10 Excerpt, Evaluation Question #5

451 Inhalation toxicity data for AITC and its degradates are not available. US EPA waived data requirements
452 for the 90-day subchronic inhalation toxicity study despite the high volatility of AITC and the fact that the
453 label Personal Protective Equipment requirements for registered AITC products indicates concerns about
454 inhalation exposure (Isagro USA, 2013). The structural similarity of AITC to the conventional fumigant
455 methyl isothiocyanate (MITC) derived from metam-based fumigant pesticides raises additional concerns
456 regarding inhalation toxicity, since respiratory irritation from inhalation exposure is the risk driver for
457 MITC.

Response

Isagro has conducted and submitted to the US EPA and the California Department of Pesticide Regulation (CDPR) repeat-dose inhalation study reports, so there is no reason to infer that characteristics of MITC apply to AITC. The AITC exposure concentrations in a 90-day inhalation study in rats were 0, 5, 10 and 25 ppm for 6 hours per day 5 days per week. The only effects noted were portal of entry effects associated with nasal irritation. The No Observed Adverse Effect Concentration for nasal irritation was 5 ppm.

Page 10 Excerpt, Evaluation Question #5

459 The physical properties of AITC are very similar to those of the conventional soil fumigant MITC (vapor
460 pressure = 16 mm Hg at 25 °C, application rate = 40-300 lbs/acre), for which a great deal of environmental
461 fate and air monitoring data are available (CDPR, 2002a; CDPR, 2002b; US EPA, 2009a). Air monitoring
462 studies for MITC conducted near application sites demonstrate high air concentrations of MITC in the first
463 24 hours after the application, tapering off over the course of a week. Indeed, MITC has been responsible
464 or a number of poisoning incidents in which hundreds of people were evacuated from their homes in
465 response to MITC drift from applications up to 0.5 miles distant (CDPR, 2014). Based on the similar
466 physical properties of AITC to MITC, it is thus possible to predict that use of AITC will result in exposure
467 via inhalation for pesticide applicators and residential bystanders due to the proposed use pattern in soil
468 biofumigation. The impact of these exposures is unknown because inhalation toxicology studies are not
469 available; however, products labels for conventional fumigant products containing AITC indicate high
470 inhalation hazards and require applicators to utilize respirators (Isagro USA, 2014).

Response

The vapor pressure of MITC is identified in the first sentence as 16 mmHg at 25°C, which the report notes is considered to be similar to the vapor pressure of AITC, which is identified on page 12 as 3.7 mm Hg, at 25°C. The MITC vapor pressure is more than 4 times higher than the AITC vapor pressure. This difference in vapor pressure does alter the emission characteristics

of AITC compared to MITC. AITC has been used according to label directions in the US for four years since US EPA approval, and there have been no bystander exposure or poisoning incidents and no home evacuations due to these uses. In addition, Isagro has conducted and submitted to the US EPA and the California Department of Pesticide Regulation (CDPR) repeat-dose inhalation study reports that indicate nasal irritation is the endpoint identified. Furthermore, existing data available indicate that a faint AITC odor can be detected at air concentrations well below 1 ppm (e.g., 0.15 or 0.42 ppm), while barely perceptible nasal irritation does not occur until well above 1 ppm (e.g., 7 ppm) (Katz & Talbert, 1930). Thus, AITC has sufficient warning properties before any irritation will occur.

Page 11, Excerpt, Evaluation Question #5

484
485 included on Columbia University's list of carcinogens, mutagens, and reproductive poisons commonly
486 used in research laboratories (Columbia, 2008). Nevertheless, AITC is

Response

The Columbia University list described in the excerpt appears to be attachment IV to the University Laboratory Safety and Chemical Hygiene Plan. "The Plan" is "intended to assure that all laboratory and administrative personnel on the Health Sciences Division campus work in a healthy and safe environment and act responsibly towards our neighbors and towards the physical areas surrounding our campus." According to the document introduction, Implementation of The Plan is intended to ensure compliance with laws, statutes and regulations including the OSHA Laboratory Standard 29 CFR Part 1910.1450: Occupational Exposure to Hazardous Chemicals in the Laboratory, and other New York laws and regulations. The attachment cited is no longer available with the electronic version of the document, but the list as characterized in "The Plan" document is merely a list of substances that laboratory staff need to recognize require special handling, rather than a list that has gone through peer review for "listing" as other national or international authoritative bodies might (e.g., the National Toxicology Program, or the International Agency for Research on Carcinogens).

Page 12, Excerpt, Evaluation Question #6 Describe any environmental contamination that could result from the petitioned substance's manufacture, use, misuse, or disposal

523 Considering its moderately high volatility (3.7 mm Hg at 25°C), high application rates (85-340 lbs/acre)
524 and agricultural use as a soil biofumigant, releases of allyl isothiocyanate (AITC) to the environment are
525 inevitable. AITC is both flammable and potentially toxic to nontarget organisms such as mammals and fish
526 (Sigma Aldrich, 2014a). Aquatic wildlife may be exposed to AITC through spills and/or irrigation runoff.

Response

Isagro has created a solid stewardship plan, available to growers, which addresses any possible misuse or hazards.

Page 12, Excerpt, Evaluation Question #6

542 It must be noted that the application rates and the emission rates of AITC are very different between
543 mustard cover crops or seed meals (effective application rate 4-33 lbs/acre) and >95% pure AITC applied
544 at 85-340 lbs/acre.

Response

Application of 33 lbs of AITC in the form of mustard seed meals involves application of tons of bulk material per acre. This type of application may not be feasible due to logistical problems and the excess material may alter the characteristics of the soil in an undesirable way.

Page 12, Excerpt, Evaluation Question #6

552 (MITC, the active fumigant from application of metam sodium) are strong respiratory sensitizers suggests
553 that AITC may pose similar risks. Because the inhalation toxicity data are not a part of the data package
554 submitted by the registrant, it is difficult to know precisely how toxic AITC is by the inhalation route.

Response

Isagro has conducted and submitted to the US EPA and the California Department of Pesticide Regulation (CDPR) repeat-dose inhalation study reports. The AITC exposure concentrations in a 90-day inhalation study in rats were 0, 5, 10 and 25 ppm for 6 hours per day 5 days per week. The only effects noted were portal of entry effects associated with nasal irritation. The No Observed Adverse Effect Concentration for nasal irritation was 5 ppm.

Page 13, Excerpt, Evaluation Question #8, Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt index and solubility of the soil), crops, and livestock

607 AITC drift would therefore be problematic for both the beneficial soil fungi and
608 associated plants.

Response

AITC injected into the soil tends to remain close to the site of injection, unlike conventional soil fumigants. The application methods used for AITC soil treatment take into account that water restricts travel of AITC movement through the soil and thus drift through the soil away from the site of application does not occur.

Page 15, Excerpt, Evaluation question 9, Discuss and summarize findings on whether the use of the petitioned substance may be harmful to the environment.

671 Data are lacking on inhalation toxicity;
672 however, the structural similarity of AITC to methyl isothiocyanate (MITC; $\text{CH}_3\text{N}=\text{C}=\text{S}$) and known
673 irritant properties of AITC (see Evaluation Question #10 below) would indicate that inhalation toxicity
674 may be a concern.

Response

As noted above, Isagro has conducted a new acute inhalation toxicity study that the US EPA agrees supports an EPA Toxicity Category III. Thus, AITC is categorized as a lower concern for inhalation exposure than MITC, which is an EPA Toxicity Category II for the inhalation route.

Page 15, Excerpt, Evaluation question 10, Describe and summarize any reported effects upon human health from use of the petitioned substance.

701 Acute, sub-chronic and even chronic (long-term) exposure to AITC is likely for humans living and working
702 near AITC application sites.

Response

Estimated exposures to bystanders at from the use of AITC as a soil treatment at maximum label rates are below any concentration expected to cause adverse effects, including eye irritation, the most sensitive endpoint. AITC has an odor detection threshold that is below the concentration that causes eye irritation.

Page 15, Excerpt, Evaluation question 10

716 Inhalation toxicity data for AITC and its degradates are not available. Data requirements for the 90-day
717 subchronic inhalation toxicity study were waived by US EPA, which is unusual, considering the high
718 volatility of AITC and the fact that the label Personal Protective Equipment requirements for registered
719 AITC products indicates concerns about inhalation exposure.

Response

As noted above in response to question, Isagro has conducted and submitted to the US EPA and the California Department of Pesticide Regulation (CDPR) repeat-dose inhalation study reports. The exposure concentrations in a 90-day inhalation study in rats were 0, 5, 10 and 25 ppm for 6 hours per day 5 days per week. The only effects noted were portal of entry effects associated with nasal irritation. The No Observed Adverse Effect Concentration for nasal irritation was 5 ppm.

References

Columbia University, 2008. Laboratory Safety and Chemical Hygiene Plan. Health Sciences Division of Columbia University.

Katz SH & Talbert EJ, 1930. "Intensities of odors and irritating effects of warning agents for inflammable and poisonous gases; Technical Paper 480. US Department of Commerce, Bureau of Mines, Washington, DC.

US EPA Reg. No. 89285-2. Dominus Label, 96.3% AITC.

US EPA, 2013. Science Review in Support of the Registration of the TGAI/MP IR9804 and the EP, IRF 135, Respectively Containing 99.8% and 96.3% Allyl Isothiocyanate (AITC) As Their Active Ingredient. The TGAI/MP is an unregistered source of the active ingredient. Biochemical Pesticides Branch Biopesticides & Pollution Prevention Division, OCSPP, US Environmental Protection Agency, Washington, DC.

Table of Contents

	<u>PAGE</u>
Laboratory Safety & Chemical Hygiene Plan	
A. Introduction	5
B. Responsibilities	6-8
1. Institutional Health and Safety Council	6
2. Environmental Health and Safety Office	6
3. Principal Investigator	7
4. Departmental Safety Officer	7
5. Laboratory Safety Manager	7
6. Laboratory Workers	8
C. Basic Elements of the Laboratory Safety and Chemical Hygiene Plan	9-10
D. General Safety Procedures	10-14
1. General Laboratory Safety	10
2. Engineering Controls	12
3. Work Practices	13
E. Procedures for Hazardous Substances	14-17
1. Ordinary Hazardous Substances	15
2. High Hazardous Substances	15
3. Extremely Hazardous Substances	15
4. Substances for which there is no Health and Safety Information	17
F. Procedures for Hazardous Devices	18-19
1. Compressed Gas Cylinders	18
2. Extremely Low Temperature Devices	18
3. Biohazardous Materials	18
4. Radioactive Materials	18
5. Ionizing Radiation Producing Devices	18
6. Ultraviolet (UV) Light Sources	18
7. Intense Visible Light Sources (including LASERS)	19
8. Intense Invisible Non-ionizing Radiation Sources (including microwave, infrared and low-frequency e.g. 60 Hz)	19

G. Laboratory Waste Disposal Policies	19-22
1. Disposal of Chemicals by a Qualified Contractor	19
2. Disposal of Substances by Drain or Dumpster	21
H. Personal Protective Equipment	22-23
1. Safety Goggles	23
2. Face Shields	23
3. Laboratory Gloves	23
4. Laboratory Aprons & Coats	23
5. Respiratory Protection	23
I. Chemical Spill Response	24-29
1. General Procedures for a Hazardous Spill Response	24
2. Manageable Spills	25
3. Specific Instructions for Certain Substances	26
4. Unmanageable Spills	28
5. Response to chemical spills occurring after hours	29
J. Personal Chemical Contamination Response Guidelines	29-31
1. Chemical Spills Over a Large Area of the Body	29
2. Chemical Spills on the Skin	30
3. Chemical Splashes into the Eye	30
4. Chemicals Inhaled	30
5. Chemicals Ingested	31
K. Fire Safety & Emergency Response to Fires and Explosions	31-33
1. Classification of Fires	32
2. Fire-fighting Procedures for Controllable Fires	32
3. Evacuation Procedures for Uncontrollable Fires	33
L. OSHA Substance-Specific Laboratory Air Quality Standards	33-34
M. Work-related Illness or Injury	35
N. Required Medical Surveillance	35-36
O. Education and Training of Laboratory Personnel	36-37
P. Laboratory Surveys	37
Q. Record Keeping	37-38

Attachments

- I. Individual Laboratory Safety & Chemical Hygiene Plan**
- II. Institutional Health & Safety Council Membership Listing**
- III. Environmental Health & Safety Office Staff Listing**
- IV. High Hazardous Substances**
- V. Extremely High Hazardous Substances**
- VI. Substances Strictly Prohibited from Drain Disposal**
- VII. Drain Disposable Substances**
- VIII. Dumpster Disposal Substances**
- IX. Chemical Waste Disposal List Form and Continuation Sheet**
- X. OSHA Substance-Specific Laboratory Air Standard**
- XI. Response to After Hours Chemical Spill**
- XII. Columbia University Departmental Accident Report**
- XIII. Guidelines for Vacating Research Laboratory Space**
- XIV. Formaldehyde Exposure Control Program**
- XV. Columbia Presbyterian Center Joint Safety Policy**
- XVI. Glossary**
- XVII. Research Laboratory Health & Safety Survey**

Laboratory Safety and Chemical Hygiene Plan

A. Introduction

The Health Sciences Division of Columbia University is committed to providing safe and healthy conditions for work. The University is also committed to working in ways that reflect its deep concern for its neighbors and for the quality of the surrounding environment.

The goals of implementing the Laboratory Safety and Chemical Hygiene Plan include:

- i. Minimizing risk of chemical exposure;
- ii. Minimizing risk of work-related injury and illness;
- iii. Minimizing risk to the environment;
- iv. Comply with applicable regulations and standards;
- v. Attain these goals with a minimum burden on research activities.

Implementation of this Laboratory Safety and Chemical Hygiene Plan (The Plan) is intended to assure that all laboratory and administrative personnel on the Health Sciences Division campus work in a healthy and safe environment and act responsibly towards our neighbors and towards the physical areas surrounding our campus. Implementation of The Plan is intended to ensure compliance with laws, statutes and regulations including the OSHA Laboratory Standard 29 CFR Part 1910.1450: Occupational Exposure to Hazardous Chemicals in the Laboratory; New York City Community Right-to-Know Law [RTK]: Local law 26 of 1980; and New York City Fire Department Title 3 Chapter 10 RCNY.

The Laboratory Safety and Chemical Hygiene Plan deals with conditions present in research laboratories that can adversely affect the health and safety of workers on this campus. General safety procedures are outlined while specific procedures required for individual laboratories are established by the Principal Investigator.

The Principal Investigator has ultimate responsibility for the safe operation of the laboratory assigned to him/her by the University. Each employee is responsible for maintaining common sense safety habits and is responsible for conducting themselves in such a way that risks associated with hazards are as low as possible.

This Plan must be read by ALL laboratory workers, including the Principal Investigator, the Laboratory Safety Manager, Post-doctoral Fellows, students, technicians and others who are exposed to the laboratory environment. Each laboratory worker must certify with their signature (see Attachment I. Individual Plan) that they have read the Plan.

Additional plans and procedures concerned with:

- i. Biological Safety
- ii. Disposal of Regulated Medical Waste
- iii. Bloodborne Pathogen Protection
- iv. Institutional Animal Care and Use (IACUC)
- v. Radiation Safety

are not parts of the Plan. Information concerning these programs can be obtained from the Environmental Health and Safety Office (6-6780) or Radiation Safety (70303).

B. Responsibilities

1. Institutional Health and Safety Council

The Columbia University Health Sciences Institutional Health and Safety Council is chaired by the Senior Associate Dean for Academic Appointments and Regulatory Compliance and is composed of senior faculty, administrators and chairmen of the separate safety committees dealing with chemical safety, biological safety, radiation safety, animal care and occupational health (see Attachment II.).

The Council oversees the activities of all Environmental Health and Safety programs in the Health Sciences Division and the activities of the Environmental Health and Safety Office to ensure continued high quality in these programs and activities. The Council recommends policies to the Dean and Vice President for Health Sciences.

2. Environmental Health and Safety Office

The Environmental Health and Safety Office (EH&S) serves as the health and safety resource and administrator of University policies at the Health Sciences Campus. The Office is staffed by professionals in chemical safety, biological safety, fire safety, industrial hygiene, hazardous materials, waste management, and safety implementation and education (see Attachment III.).

The Environmental Health & Safety Office is responsible for:

- a. Implementing policies approved by the Institutional Health and Safety Council.
- b. Developing and implementing the Laboratory Safety and Chemical Hygiene Plan for the Health Sciences Division. The Office audits the program for compliance with OSHA, NYC Fire Department and Health Department regulations and represents the University to the various city, state, and federal regulatory and environmental agencies.
- c. Developing and staffing various educational programs designed to improve the health

Laboratory Safety & Chemical Hygiene Plan

and safety of the University community and to foster compliance with governmental regulations and professional standards.

d. Conducting regular audits of laboratories in the Health Sciences Division and assisting P.I.s in complying with the Plan.

3. **Principal Investigator**

The Principal Investigator (P.I.) is a faculty member or research scientist appointed by the University to conduct laboratory research. The P.I. has overall responsibility for safety in his/her laboratory and is responsible for developing, updating and submitting the Individual Laboratory Chemical Hygiene Plan. The P.I. is required to maintain a well-defined table of organization and delineate responsibilities. The Individual Plan is required for the operation of each laboratory and must be re-submitted whenever significant changes in the work of the laboratory take place.

4. **Departmental Safety Officer**

The Departmental Safety Officer is a **senior** faculty member (preferably tenured) appointed by the departmental chair, or chair of an Institute or Center who is responsible for the development, coordination, implementation and maintenance of the Individual Laboratory Chemical Hygiene Plan in all laboratories of the Department in all of the University's buildings.

The Departmental Safety Officer investigates accidents, reviews the Individual Laboratory Chemical Hygiene Plan of each laboratory in the Department, and conducts periodic inspections of each laboratory along with the Environmental Health and Safety representative, local NYC Fire Inspector, and any regulatory inspector. The Departmental Safety Officer also works with the University Administration and the EH&S Office in resolving chemical hygiene and laboratory safety problems within his/her purview.

5. **Laboratory Safety Manager**

The Laboratory Safety Manager is a senior researcher appointed by the Principal Investigator or is the P.I. him/herself, who is responsible for all safety aspects of a laboratory complex under his/her purview. Each laboratory complex must have its own Laboratory Safety Manager. Therefore, if the P.I. has additional laboratory complexes on other floors or in other buildings, a Laboratory Safety Manager must also be appointed at this location.

The Laboratory Safety Manager is responsible for:

- a. Holding a New York City Fire Department Certificate of Fitness (COF) as "in charge of a chemical laboratory". The Certificate of Fitness is obtained by passing a safety test given by the NYC Fire Department, whose regulations require that operation of a chemical laboratory can only be carried out when an individual holding a COF is

present on the floor. Any person working at “off-hours” is strongly recommended to hold a Fire Department COF. The cost of the exam is borne by the University.

- b. Working with the Departmental Safety Officer, the P.I., and the Environmental Health and Safety Office to ensure that laboratory employees are informed of, and follow, the Chemical Hygiene Plan.
- c. Ensuring that all laboratory personnel meet standards for laboratory safety and chemical hygiene and that appropriate chemical hygiene training has been provided. The introduction of a new chemical substance that has an unfamiliar hazard requires all personnel be made aware of safety procedures for the new substance.
- d. Ensuring that appropriate personal protective equipment (PPE), such as safety eyewear, gloves, laboratory coats or aprons; and blast shields are in regular use.
- e. Ensuring that appropriate spill control materials are available and workers are trained in their use.
- f. Ensuring that Material Safety Data Sheets (MSDSs) are maintained for all chemicals used in the laboratory.
- g. Training laboratory workers with new laboratory procedures and equipment.
- h. Ensuring that chemical containers are properly labeled.
- i. Ensuring that chemical inventory is taken and made part of the Plan.
- j. Monitoring regularly the safety procedures used in the laboratory as well as the procurement, use, and disposal of hazardous substances.
- k. Advising and informing facilities operation and maintenance personnel, as well as custodians, of potential hazards that might be encountered in the laboratory.

6. Laboratory Workers

The Laboratory Worker is a term which includes ALL individuals who work in the laboratory including P.I.s, research scientists, post-doctoral fellows, technicians, undergraduate and graduate students, visiting scientists, laboratory volunteers, and support personnel such as secretaries and glassware washers. Each worker:

- a. Must know where the Laboratory Safety & Chemical Hygiene Plan is, review it and make themselves familiar with the Individual Plan.

- b. Must review MSDS procedures, especially for Extremely Hazardous agents used.
- c. Must attend chemical safety training and know how to safely handle and dispose of a hazardous chemical.
- d. Must share responsibility to ensure that all chemical containers are labeled with the identity and hazard.
- e. Must use appropriate PPE when working in the laboratory.

C. Basic Elements of the Laboratory Safety and Chemical Hygiene Plan

1. Department Chairs must appoint a Departmental Safety Officer in their respective Departments.
2. Principal Investigators must file an **Individual Laboratory Chemical Hygiene Plan** with the Environmental Health and Safety Office. A copy of this plan must be sent to the Departmental Safety Officer. When there are significant changes in the work performed by the laboratory, revisions must be submitted to the EH&S Office and the Departmental Safety Officer.
3. The P.I. must ensure completion of the **List of Laboratory Personnel** including part-time students, their degree and date of completion of the required safety courses.
4. The P.I. must ensure that laboratory personnel have read and have signed the Laboratory Safety and Chemical Hygiene Plan.
5. The P.I. must ensure that new laboratory personnel attend the **Laboratory Safety and Chemical Hygiene Orientation** Lecture within one (1) month of employment.
6. The P.I. must ensure that all current and new laboratory workers receive adequate safety training.
7. The P.I. must identify the location of the nearest safety equipment and must post the list in a conspicuous place in the laboratory. Safety Equipment includes:
 - i. Safety shower
 - ii. Eye wash station
 - iii. Fire blanket
 - iv. Fire extinguisher
 - v. Spill clean-up kits, equipment and supplies.
 - vi. Material Safety Data Sheets (MSDSs)
 - vii. Personal Protective Equipment (PPE- such as safety goggles, gloves, aprons/laboratory coats, face shields)
 - viii. Masks/Respirators,

8. The P.I. must identify laboratory hazards (see Attachment I. Individual Plan) and maintain a current inventory of chemicals, hazardous substances and devices in the laboratory.
9. The P.I. will make available Material Safety Data Sheets (MSDSs) for those High Hazardous and Extremely High Hazardous substances (Appendices D & E) stored in their laboratory. All containers must be labeled so that any laboratory worker can determine the identity of the contents. Each container should be inspected periodically for label and container integrity.
10. The P.I. will develop special operating procedures to accommodate the particular hazards found in each laboratory. Monitoring of the lab environment and/or personal exposure may be required if any substances are used in substantial quantities or are on the list of OSHA (regulated) Substance-Specific Laboratory Air Standards (see Attachment X.).
11. The P.I. must identify the location of other Hazardous Materials and Devices including:
 - A. Compressed Gases
 - B. Extremely Low Temperature Devices
 - C. Biohazardous Materials
 - D. Radioactive Materials
 - E. Ionizing Radiation Producing Devices
 - F. Ultraviolet (UV) Light Sources
 - G. Intense Visible Light Sources (including LASERS)
 - H. Intense Invisible Non-ionizing Radiation Sources (including microwave, infrared and low-frequency e.g. 60 Hz)
12. The P.I. is responsible for ensuring that their Laboratory has proper safety signage including signage at the laboratory entrance as well as signage inside the laboratory where hazards and safety equipment may exist.

D. General Safety Procedures

The following procedures are applicable to all laboratories on the Health Sciences Campus. These procedures are based on the National Research Council Report, "Prudent Practices for Handling Hazardous Chemicals in Laboratories", (National Academy Press, Washington, D.C., 1995). The procedures were adopted as a standard of safe practice by laboratory professionals and are based upon the OSHA Standard. They meet the requirements of the New York City Community Right-To-Know Law, Local Law 26 of 1980, and the New York City Fire Department, Title 3 RCNY Chapter 10.

1. General Laboratory Safety:

1. Minimize all chemical exposures. Avoid unnecessary or routine exposure to chemicals by any

Laboratory Safety & Chemical Hygiene Plan

route (inhalation, skin, eyes and ingestion). General precautionary procedures should be adopted for handling all chemicals.

2. Select the least hazardous substance that presents the least risk.
 - a. Use those substances for which adequate information is available
 - b. Selections should be based on information available in the literature including MSDSs.
 - c. Purchase hazardous substances in the smallest quantity sufficient for your work.
3. Use chemicals only in the laboratory and use the laboratory only for work with chemicals. Use of chemicals in a non-laboratory area such as an office, study, reading or meeting area, should not be permitted.
4. Do not attempt to identify chemicals by smell or taste. When it is necessary to smell a chemical, carefully fan vapors from the open vessel toward the nose that is held to one side of the container. **Never pipette by mouth.** Use aspirator bulbs or automatic pipetting devices.
5. Do not eat, drink, chew gum, smoke or apply cosmetics or hand lotions in laboratories. Wash your hands and face before conducting these activities. Always wash your hands immediately after finishing work with chemicals. Do not store food or beverages in laboratory refrigerators or other chemical storage areas.
6. Use personal protective equipment (PPE) as necessary to augment protection provided by engineering controls, experimental design, standard operating procedures and good work practices.
 - a. Always wear appropriate eye protection where chemicals are stored or handled. **Safety glasses or goggles** are always to be worn when working in a laboratory in which chemicals are used.
 - b. Appropriate gloves must be worn when there is a potential for skin contact. Gloves should be chosen according to the dermal toxicity and the required task. Latex gloves are not suitable for ALL laboratory procedures, specialized gloves are required for use with many compounds. Chemical permeation glove selection charts are available from manufacturers or the EH&S Office.
 - i. Inspect gloves and test glove boxes carefully for leakage.
 - ii. Replace any glove that is damaged or discolored.
 - iii. Always wash hands thoroughly and dry completely before donning a new glove.
 - iv. Never reuse disposable gloves.
 - v. Remove gloves when leaving the lab. Do not wear gloves in other non-lab areas (rest rooms, elevators, offices, etc.).
 - c. Aprons and/or coats should be worn when working in the laboratory.
 - i. They must be removed immediately upon contamination.
 - ii. They are to be removed when leaving the laboratory for breaks, meetings...

7. Contact lenses should not be worn in the laboratory as the lens material absorbs and thus concentrates many chemicals. In the event of a chemical splash to the eye, contact lenses may also impede a thorough flushing of the eye(s).
8. Obey the "Two Person" Rule. A second person should be aware that you are working in the laboratory. According to NYC Fire Department regulations, an individual with a NYC Fire Department **COF** (Certificate of Fitness) must be present on the floor if any laboratory is occupied. For this reason, it is advisable that laboratory workers obtain a COF.
9. Keep appropriate safety equipment readily available and properly maintained to prevent or respond to such laboratory emergencies as personal contamination, fires, spills or splashes.
 - a. Safety equipment must be inspected regularly using the proper instruments to ensure proper function. This must be done regularly according to a prearranged schedule.
 - b. Five types of safety equipment should be regularly checked:
 - i. Fume Hoods
 - ii. Safety Showers
 - iii. Fire Extinguishers
 - iv. Eyewash Fountains
 - v. Spill Control Kits
 - c. EH&S staff is responsible for monitoring fume hoods and the Facilities Department is responsible for adjusting fume hoods, checking safety showers and the maintenance of fire extinguishers.
 - d. If there are presently no eyewash stations installed in the laboratory, a faucet mounted eyewash fixture should be purchased.
 - e. Spill control kits can be purchased through the chemical supplier. An adequate number should be kept on hand including those types necessary to neutralize or absorb any hazardous spill, which has the potential to occur in your laboratory.

2. Engineering Controls

Engineering controls such as the laboratory fume hood are primary means of controlling or minimizing hazardous chemical exposures.

1. Use a fume hood, glove box, glove bag or other specially ventilated or enclosed space, for work in which airborne, toxic or flammable substances may be released either from the materials in use or as products of a reaction.
 - a. Use only fume hoods for which an average face velocity of 100 FPM at a sash height of 12 inches has been confirmed and noted on the fume hood by EH&S. Do not use fume hoods that are posted as "Out of Service- Do not Use". Minimize materials stored in hoods and do not allow materials or apparatus to block vents or airflow.
 - b. Substances that are listed as **Extremely Hazardous** and can become airborne must only be used in a fume hood or glove box.

- c. Vent any device that may discharge hazardous gases, vapors, or fine dusts, e.g., vacuum pumps, distillation columns; by using in a fume hood or by ducting the exhaust into a fume hood, rather than allowing it to discharge directly into the laboratory.
2. Appropriate safety shields should be used whenever splashes or exothermic reactions are possible or evacuated glassware is present. Pulled-down fume hood sashes are also effective for this purpose. Tip-resistant bench-top safety shields stop splashed substances as well as flying glass shards and other debris produced by an uncontrolled reaction or by an implosion resulting from a defect in the glass in an evacuated system.
3. Do not allow the release of hazardous substances into sealed “cold” or “warm” rooms since the air in these facilities is re-circulated and therefore there is little ventilation. Hence, the concentrations of these substances in the air can increase to dangerously high levels.
4. Sewer drain traps, especially in cup sink drains, must be kept filled with water to prevent noxious fumes from entering the laboratory from the sewer drain.

3. Work Practices

1. Aisles and doorways must be free of obstruction. Equipment may not be placed in the corridor at any time. With special approval of the EH&S Office, non-volatile objects may be stored in a fire proof cabinet in the corridor if there is sufficient clearance (44 inches) for pedestrian traffic.
2. Work with flammable substances only after removing any source of ignition near enough to cause a fire or explosion. Sources of ignition include flames, hot surfaces, sparks or electrical switches and motors.
3. Store incompatible substances apart from one another.
 - a. Grouping chemicals into classes according to their chemical compatibility most effectively does this.
 - b. Store acids apart from bases; oxidizing agents apart from reducing agents; water reactive compounds apart from water and aqueous solutions; and acids apart from metals that are higher than hydrogen in the electromotive series, such as aluminum, zinc and iron. Halogenated alkanes must be kept apart from aluminum; air-reactive compounds should be protected from the action of the atmosphere, etc.
4. There is a NYC Fire Department limit on the amount of flammable solvents that may be stored in any laboratory.
 - a. Most laboratories have a limit of fifteen (15) gallons, while some laboratories, depending on the “fire rating” may have a limit of thirty (30) gallons.
 - b. Flammable solvents must be stored in cabinets and kept off the floor to prevent accidental spillage.

- c. Refrigerated flammables must be kept only in explosion-proof refrigerators.
5. Securely clamp or wire all flexible tubing in place on fittings. This prevents leakage of water, coolant fluids, etc., caused when the tubing slips loose from the fittings. Spills of this kind can lead to serious flooding with consequent extensive property damage as well as overheating of equipment or other undesirable effects on experimental activities.
 6. Handle and store laboratory glassware with care to avoid damage. Never use glassware that is nicked or cracked; dispose of it immediately in an appropriate container. Glassware used in vacuum systems should be carefully inspected before each use.
 7. Use extra care with Dewar flasks, vacuum desiccators, and other evacuated glass apparatus. Wrap Dewar flasks with tape; put vacuum desiccators in special protective containers, and place safety shields between evacuated systems and laboratory personnel. These measures will contain glass fragments should an implosion occur.
 8. Always transport chemicals in a safe manner.
 - a. Carry large bottles only in rubber transport buckets.
 - b. Move compressed gas cylinders with a handcart designed for this purpose and only after they have been capped and secured by strap or chain.
 - c. Never carry jugs, jars, or bottles by their caps or by the molded glass rings, always use both hands, one under the vessel, the other around the neck.
 9. Secure all compressed gas cylinders either by chaining to a secure support or by securing them to a laboratory bench with a benchclamp.
 10. Check gas handling systems routinely. Systems containing or generating poisonous, flammable, explosive, or malodorous gases, should always be used in fume hoods or other areas of adequate containment or ventilation. Joints and other connections should be periodically checked for leaks.
 11. Have familiarity with **biological hazards** present in the laboratory, especially if there are materials that must be handled at Biological Safety Level 2 or higher.
 12. The following items and hazardous substances are to be transported via the freight elevator. A proper container for transporting is to be utilized and gloves are to be removed before leaving the laboratory.
 - a. Animals and animal bedding;
 - b. Hazardous chemicals;
 - c. Materials containing radioactivity;
 - d. Chemicals in open containers;
 - e. Biological agents;
 - f. Compressed gas cylinders;

- g. Items requiring the use of a hand truck.

E. Procedures for Hazardous Substances

Chemicals are grouped into the following four groups (see Attachment IV. & V.).

1. Ordinary Hazardous Substances
2. High Hazardous Substances
3. Extremely Hazardous Substances
4. Substances for which there is no Health & Safety Information

1. Ordinary Hazardous Substances

These substances have easily controlled hazards and so present no unusual risk. This includes the bulk of the chemicals used in the laboratory, including those having no currently known hazards.

2. High Hazardous Substances

These are substances that present significantly greater hazards. They require unique or special handling and, under special circumstances, monitoring. The storage and handling of substances in this group involves either high fire or explosion hazards or severe health risks. Examples include chemicals that form explosively unstable substances such as hydroperoxides on standing; substances that show either particularly high toxicity or an insidious toxicity of a special kind such as carcinogens, mutagens; and chemicals that show reproductive toxicity or a high acute toxicity.

Some high hazardous substances may be hazardous only under certain specific conditions. Examples of this type of substance include diethyl ether and secondary alcohols, in which significant quantities of explosive organic peroxides are formed on long-term contact with air. Most of these substances may be safely stored for 12 months or less after breaking the seal on a new container. A few may be kept only for 3 months after the seal is broken. To inhibit the formation of peroxides in ethers, ethers should be kept in tightly sealed cans or amber glass bottles (since light promotes peroxide formation). Any ether container that has an expiration date on the label should be disposed of before the expiration date. New York City Fire Department inspectors routinely visit laboratories and will find a laboratory in violation of the City Fire Department Code if a container is found with an expiration date prior to the date of inspection.

A short list of some of these high hazardous substances is found in Attachment IV. along with a list of common carcinogens, mutagens, and reproductive poisons.

High hazardous substances must be stored in a specially designated storage area that is appropriately posted with signs, e.g. WARNING! HIGH CHRONIC TOXICITY or CANCER SUSPECT AGENTS. Access to this area must be limited to personnel specially trained in the safe

handling and use of these materials. This area should be as small as possible and away from busy areas of the laboratory. Appropriate secondary containment and adequate ventilation must also be used.

3. **Extremely Hazardous Substances**

These substances are orders of magnitude more hazardous than those classified as high hazardous. Severe harm or disastrous situations can occur from their misuse. A list of these substances is included in Attachment V.

Examples of such substances are dimethyl mercury, silver azide (an impact-sensitive compound that can give rise to violent explosions) and nickel tetracarbonyl (a volatile, extremely poisonous liquid, the vapors of which have been fatal at concentrations as low as 1 ppm). The Environmental Health & Safety Office must evaluate the proposed use of any of these substances prior to its use to assure that the appropriate precautions are observed and that the necessary equipment and facilities are available.

Before these substances are used, any researcher using them must be fully aware of the risks involved and must have the necessary safety equipment available. They must be fully trained in the appropriate storage, handling, and disposal procedures prior to the introduction of the material into the laboratory. The Principal Investigator must file a completed copy of the NOTIFICATION OF USE OF EXTREMELY HAZARDOUS MATERIALS FORM (see Individual Plan) with the Environmental Health & Safety Office.

The procedures for proper use of these materials must be reviewed and approved by the Environmental Health & Safety Office prior to their actual use. Their use and storage must be confined to certain designated areas. The EH&S Office, in consultation with the Principal Investigator, will evaluate the proposed procedures, prescribe special limitations, necessary equipment and facilities or operating conditions, personal protective equipment, and additional personnel training requirements. A site visit and evaluation will be made. No work can begin until written approval is obtained. In development of the experimental procedures, the following items should be addressed or prepared:

- a. The appropriate **Material Safety Data Sheet** (MSDS) must be on hand before using a particular substance.
- b. Access to the substance and the work area must be limited to personnel who are aware of the hazards involved and are adequately trained to handle the substance safely.
- c. Special sign and label requirements for fume hoods, glove boxes, containers in which the substance is used, and for the laboratory itself.

- d. Appropriate personal protective measures such as respiratory protection (call EH&S if using a respirator) and protection against skin contamination must be taken in advance of using the substance.
- e. Initiation and maintenance of medical surveillance.
- f. A running written inventory of the stock material quantity, dates of use, names of users and, in cases of overexposure, dates, descriptions of the incidents, and names of the personnel who were overexposed.
- g. Introduction of traps, such as cold traps and soda lime traps, into experimental systems to prevent contamination of such equipment as vacuum pumps.
- h. Special monitoring and decontamination procedures are needed for persons leaving the restricted area.
- i. Special animal-handling procedures. The use of the substance in animals must be approved by the appropriate animal care committee (IACUC), and required forms filed.
- j. Special storage requirements and procedures.
- k. Special ventilation and containment requirements.
- l. Special waste-disposal procedures.
- m. Special spill control procedures and precautions.
- n. Special housekeeping procedures are required and special decontamination procedures are necessary before the work area that had been utilized, can be declared unrestricted again.

4. Substances for which there is No Health and Safety Information

Special attention must be given to the handling, storage and use of compounds that have been synthesized for the very first time, and those for which the chemical properties, stability, flammability characteristics and health hazards are not described in the literature. Exercise prudence and caution when designing the procedures for their handling, storage and use. Since harm occurs only through exposure, eliminating exposure or keeping it to a minimum is clearly indicated.

The precautions to be observed may often be suggested by the experimental data already available. e.g., boiling point and solubility in water or in a solvent of low polarity. The guidelines can be obtained from knowledge of the chemical behavior, flammability, and toxicity characteristics of substances that are in the same homologous series or are closely related chemically in some other way.

General principles that apply to all chemicals of the same type can be used to advantage in predicting properties. For example, volatility of a compound decreases with increasing molecular weight, solubility in non-polar solvents increases with increasing length of an alkyl chain, solubility in such polar solvents as water is increased as the number of functional groups such as -OH, -NH₂, -CHO, and -COOH are increased in a molecule. The weight ratio of polar functional groups to that of the non-polar part of the molecule is a good indication of whether the compound will be soluble in water or in a non-polar solvent.

If a reliable judgment on the anticipated flammability, reactivity, or toxicity characteristics of a substance in question cannot be made, it should be handled as though it were a High Hazard Substance.

F. Procedures for Hazardous Materials and Devices

If using any of the following hazardous devices, the applicable forms in the Individual Plan must be completed.

1. Compressed Gas Cylinders
 2. Extremely Low Temperature Devices
 3. Biohazardous Materials
 4. Radioactive Materials
 5. Ionizing Radiation Producing Devices
 6. Ultraviolet (UV) Light Sources
 7. Intense Visible Light Sources (including LASERS)
 8. Intense Invisible Non-ionizing Radiation Sources (including microwave, infrared and low-frequency e.g. 60 Hz)
-
1. Compressed Gas Cylinders- cylinders must:
 - a. be labeled and hydrostatically tested within the last ten years;
 - b. be stored and secured at all times;
 - c. have the protective cap or regulator in place when not in use;
 - d. be away from heat, flame or spark;
 - e. transported with the aid of a hand truck.
 2. Extremely Low Temperature Devices
 - a. In the event of a power failure, ensure that there is emergency back-up power.
 - b. Follow all manufacturers' operating instructions.
 - c. Instructions should be made available to workers in the laboratory.
 3. Biohazardous Materials
 - a. Biohazardous materials used must be listed.
 - b. Procedures using these agents must be conducted according to those described in CDC Publication N.93-8395 4th edition, *Biosafety in Microbiological Biomedical Laboratories*.

- c. The EH&S Office must be notified prior to their use.
4. Radioactive Materials
 - a. Radioactive Material use is controlled by the Radiation Safety Officer (Extension 7-0303).
 5. Ionizing Radiation Producing Devices
 - a. The design, maintenance and use of these devices are controlled by Radiation Safety.
 6. Ultraviolet (UV) Light Sources
 - a. The design, use and maintenance of these devices must meet ACGIH (American Conference of Government Industrial Hygienist) standards.
 - b. When feasible, proper administrative and engineering controls are to be used to prevent exposure to UV light.
 - c. Proper safety eyewear must be worn at all times.
 7. Intense Visible Light Sources (including lasers)
 - a. The design and use of these devices must meet current ACGIH standards.
 - b. The use of laser must meet the current ANSI (American National Standards Institute) Z135.1 Standard.
 - c. EH&S Office must be notified when Class III or IV lasers are being used.
 8. Intense Invisible Non-ionizing Radiation Sources
 - a. The design and use of these devices must meet current ANSI, ACGIH and IRPA (International Radiation Protection Association) Standards.
 - b. The EH&S Office must be notified prior to their use.

G. Laboratory Waste Disposal Policies

These policies and procedures cover the disposal of laboratory waste. Included are those substances that must be disposed of by qualified contractors (hazardous chemicals, radioactive waste and regulated medical waste) and those that can be disposed as normal trash. Prudence dictates that laboratory waste be considered hazardous and/or regulated unless it has been demonstrated that it can be safely disposed as normal waste.

Substances Strictly Prohibited from Drain Disposal (see Attachment VI.) lists substances that **may not be drain-disposed** under any circumstances.

Drain Disposable Substances (see Attachment VII.) lists the only substances that can be discarded by the sink drain without prior approval. Only aqueous solutions of these substances can be so discarded. Disposal of hazardous substances by drain is not permitted

Dumpster Disposable Substances (see Attachment XIII.) lists typical substances, which must be both essentially harmless and water-insoluble. Disposal of hazardous substances by dumpster is not permitted.

1. Disposal of Chemicals by a Qualified Contractor

All laboratory chemical waste must be discarded by transfer to a qualified contractor unless the EH&S Office explicitly approves otherwise. These procedures do not apply to radioactive waste, biohazard waste, or Regulated Medical Waste (RMW) disposal, each of which is covered by a separate policy. Recycling usable chemicals is encouraged with others on the Health Sciences Division campus.

The Environmental Health & Safety Office coordinates the collection of all unwanted chemicals by the waste contractor upon request from the laboratory supervisor. Laboratory personnel must complete the Chemical Waste Disposal List (Attachment IX.) and facsimile (795-5847) the list to the EH&S Office. In the meantime, chemicals must be labeled properly and safely stored until they are collected by the vendor. There is no direct charge to research laboratories for the disposal of this waste.

a. Chemicals must be collected in individual, leakproof, sealed containers. Chemicals must be compatible with the container material (e.g., acids must not be placed in steel containers, alkalis must not be stored in aluminum containers). Glass containers may be safely used for virtually anything, except hydrofluoric acid, acidic fluoride salts, and strong alkalis.

b. Select the smallest container available that will hold the material, allowing sufficient headspace above the surface of the liquid for thermal expansion. This is both economical and efficient. Five-gallon pails and fifty-five gallon drums are available from the contractor. Do not use your own pails or drums without prior approval as they may not meet US Department of Transportation (DOT) specifications.

c. All containers must be identified and labeled with the complete chemical name of the substance. Trade names, acronyms, abbreviations, IUPAC codes, or formulas are not acceptable. Labels may be obtained through the EH&S Office. Keep the original label on a reagent container only if it describes the contents of the container. Otherwise, cover it with a HAZARDOUS WASTE LABEL that describes the actual contents.

d. If the waste is a mixture of chemicals, identify each component on its label, along with its corresponding concentration. The label of the container must contain both the magnitude and the units of the concentration of each substance contained within. When the solute is either a liquid or a gas, concentrations may not be expressed simply as 'percent' but must be given as either a 'weight percent' or a 'volume percent'. When the solute is a solid, its concentration must be expressed as 'weight percent'.

e. The waste contractor cannot accept substances that are unidentified (unknowns) for regulatory reasons. Responsibility for establishing the identity of an 'unknown' rests with the P.I. wishing to dispose of it. In many cases the waste contractor can, for a fee directly charged to the

laboratory, analyze unknowns for shipping purposes. The EH&S Office will, on request, furnish the names of state-certified analytical laboratories for analysis of these substances.

f. ALL containers of 'spent' chemical waste (waste that cannot be recycled because it is an unusable mixture of substances or a substance that has been contaminated) must have a HAZARDOUS WASTE label affixed prior to removal for disposal. Such labels must not be put on bottles containing pure chemicals.

g. When the 'spent' chemical waste container becomes full, enter the 'accumulation start date' on the label. The U.S. Environmental Protection Agency requires that full containers of 'spent' waste be removed to an approved Storage and Disposal Facility within 90 days after this date. The date upon which each period of accumulation for storage (as defined above) begins must be clearly marked and the container positioned such that the label is easily visible for inspection.

h. Unwanted chemicals must be stored safely in the laboratory while awaiting a waste contractor collection.

2. Disposal of Substances by Drain or Dumpster

There are many laboratory chemicals that will present no hazard when released to the environment. Research and instruction in laboratories continually produce small amounts of water solution wastes. In such cases, laboratory workers must decide whether to pour these solutions down the drain or keep them for pick-up by a waste contractor. This guide will help them make such decisions.

a. Procedure for Drain-Disposable Substances (see Attachment VII.)

Disposal of hazardous substances by drain is not permitted. A few biodegradable, water-miscible solvents, some solutions, aqueous rinses, and innocuous materials such as soapy or detergent water solutions, amino acids, vitamins sodium potassium tartrate, and sodium bicarbonate may be safely drain-disposed.

Wear protective gear (safety glasses, gloves and laboratory apron). Flush tap water down the drain for at least one minute prior to drain disposal of substance in question. Allow the tap water to run for at least one minute after emptying the container. This ensures that the drain and plumbing will be flushed clear.

b. Procedure for Dumpster Disposable Substances (See Attachment VIII.)

Disposal of hazardous substances by dumpster is not permitted. Dumpster disposable substances must meet two criteria; they must be both essentially harmless and water-insoluble. All foodstuffs that are insoluble in water and many minerals meet those two criteria. Minerals which contain such toxic elements as: antimony, arsenic, barium, cadmium,

chromium in the +6 oxidation state, cobalt, gold, lead, mercury, nickel, platinum, selenium, silver, and thallium are excluded from this category. Also excluded from the dumpster are pesticides, rodenticides, fungicides, miticides, insecticides, and herbicides.

Discard the permissible substances by placing in a strong paper or plastic bag, sealing the bag and placing it in the normal trash.

c. Disposal of Empty Containers and Other Equipment

Rinse empty bottles or cans that have contained hazardous substances **three times** with a suitable solvent or appropriate detergent solution (call EH&S for guidance if necessary) before discarding. Remove or deface the container label to make it illegible and discard the cap separately to prevent its re-use. Place in a specially marked rigid container such as a corrugated box for disposal. Containers that previously held hazardous substances are not to be recycled.

Syringes, and other sharp or hazardous objects, such as Pasteur or serological pipettes, is **Regulated Medical Waste (RMW)** and must be placed in specially marked, rigid, puncture-proof 'sharps' containers, available from the Facilities Maintenance Control Center (7-7353).

Waste paper baskets and plastic trash bag inserts are used only for normal office trash.

d. Disposal of Intact or Broken Laboratory Glass

All laboratory glassware must be discarded such that it cannot injure anyone who handles it or is exposed to it. This includes not only laboratory workers but also custodial staff members and members of the general public. This policy applies to all glass, intact as well as broken, except for radioisotope-contaminated glass and registered medical waste-contaminated glass, each of which are discussed separately elsewhere.

Place all laboratory glassware, intact as well as broken, (except for clean chemical source containers) into a specially marked rigid container designed for this purpose. A properly labeled thick-walled, rigid cardboard container may be substituted. The container must be able to withstand penetration by any sharps it contains, and must be lined with a leak-resistant liner (e.g. a polyethylene or polypropylene bag). Seal the container and clearly mark it 'BROKEN GLASS' to describe its contents. Examples of appropriate laboratory glassware disposal containers are listed below. Equivalent containers can be obtained from most large laboratory equipment supply houses.

Table Model 8" x 10", with cover. Fisher Catalogue No. 12-009-7B

Floor Model 12" x 27", with cover. Fisher Catalogue No. 12-009-7A

H. Personal Protective Equipment

Laboratory Safety & Chemical Hygiene Plan

The use of personal protective equipment (PPE) in the laboratory is needed for certain procedures to prevent exposure of laboratory personnel to toxic or corrosive materials. The equipment that will be discussed here serves to prevent contact of toxic or corrosive materials with eyes and skin.

1. Safety Glasses

Safety glasses must always be worn when working with chemicals. For those who wear eyeglasses, a safety goggle should be worn over the glasses.

2. Face Shields

A face shield must be worn whenever there is a possibility that corrosives or toxic substances may be splashed into the face or when there is exposure to UV Light. It also protects the face from skin lacerations resulting from flying debris produced by implosions and small explosions. It does not afford adequate protection against moderate or large explosions.

3. Laboratory Gloves

Since hands are usually directly involved in laboratory manipulations, they, as well as wrists and forearms, are quite vulnerable to exposure by contact with toxic or corrosive materials, irritants and sensitizers. Gloves of the appropriate material and length provide protection from liquids and solids as well as from dusts, mists and particulate.

The selection of the proper glove includes consideration of the glove material as well as the proper length and size. The glove material must be resistant to chemical attack, solvent swelling and to permeation by the substances to be used. No single material is suitable for all chemicals. Therefore, the glove material must be chosen based on an evaluation of its resistance to particular substances. Contact the EH&S Office (ext. 6-6780) if you need information or assistance in selecting the appropriate glove for the task.

Laboratory gloves must be regarded from two points of view

- i. affording personal protection to the wearer and
- ii. as a source of contamination.

Gloves must be removed immediately after work is completed to eliminate the possibility for contamination both of the wearer and before touching such surfaces in the laboratory and neighboring areas as door knobs, telephones, books and lab notebooks.

Even when gloves are worn only to protect biological systems from natural human contaminants such as oils and metabolic products on the hands of the laboratory worker, they must be removed before touching door knobs, telephones etc., to minimize contamination. Always remove gloves and other protective equipment when leaving the laboratory. **Never wear**

gloves when travelling in elevators.

4. Laboratory Aprons and Coats

Consideration about appropriate apron material is the same as those for glove materials. However, since the frequencies of contact with chemicals is usually less and the mechanical stress placed on the apron is considerably less, the choice is usually less critical. Rubber or vinyl is quite often an acceptable choice. However, when large quantities of solvents, or corrosives or materials with strong permeability characteristics are used, or where splashes may be more frequent or the consequences more severe, the material choice is more critical. Cloth laboratory coats are adequate only when small volumes of innocuous aqueous solutions are used.

5. Respiratory Protection

Respiratory protection in the laboratory should be used only if engineering controls such as fume hoods are not adequate. A respirator should be worn only in case of an emergency and only after medical clearance and proper fit testing. Should a condition arise in which a respirator may be needed in the laboratory, contact the Environmental Health & Safety Office (ext. 6-6780) to make arrangements for medical clearance, selection, training and fit testing of the respirator.

I. Chemical Spill Response

In general, chemical spills in the laboratory should be cleaned up immediately, regardless of whether the substance spilled is innocuous or hazardous. A prompt clean up is simply a matter of good housekeeping and common sense that prevents slips, falls and unnecessary personal exposure, as well as a fire or explosion. The only considerations that may prevent an immediate clean up by laboratory workers are:

- i. A determination that the volume of the material spilled is too large to be handled with the equipment at hand.
- ii. The toxicity of the substance spilled is great enough to present a significant hazard to the laboratory workers.
- iii. The lack of appropriate personal protective equipment.

When any of these considerations may be significant, contact the Environmental Health & Safety Office IMMEDIATELY for assistance (see list of Emergency Phone Numbers). For all but very minor spills, inform the EH&S Office (6-6780) as soon as possible so that they can assess the adequacy of the clean up and the potential for unnecessary chemical exposure to lab workers and others in the area.

In order to clean any spill adequately and with a minimum of risk to those nearby and to the environment, the lab worker must understand the nature of the hazards, if any, presented by the chemical used, and know the proper clean-up and disposal procedures. The particular

procedure chosen will depend on the particular spill situation. Factors such as the flammability, volatility and toxicity of the substance, the amount spilled, the location and capacity of the local ventilation systems, the presence of other people in the laboratory, and perhaps the presence of sparks, flames, or other nearby ignition sources must be considered. For these reasons, spill response and clean-up procedures must be developed especially for each hazard class and for each laboratory. There are even certain special cases where procedures must be designed for a particular substance. Each laboratory worker must be familiar with these special procedures and trained in carrying them out.

Each laboratory worker should have on hand the items needed for the clean up and disposal of all of the substances used in the laboratory, appropriate personal protection and other safety equipment. It is the responsibility of the Laboratory Safety Manager to ascertain that these items are available and personnel working in the area are familiar with their presence and use.

1. General Procedures for Response to a Hazardous Substance Spill

a. Move away from the area of the spill. Immediately alert other persons working nearby and advise them to stay away from the contaminated area.

b. Avoid tracking or spreading the material unnecessarily. If you can do so with no risk, contain the spilled material by diking with absorbent or sand.

c. If the spilled material is very hazardous, volatile, or has a large volume, isolate the area by closing, but not locking, all doors leading to the area and by posting clearly visible, hand-printed DANGER, KEEP OUT signs on the closed doors. If it is not possible to do this, delineate the spill area with rope, tape or makeshift barricades, and warning signs, or station a person at an appropriate place to keep people from entering.

d. Avoid breathing the vapors of spilled chemicals. If a respirator is necessary, leave the area immediately, restrict access by other persons, and call Security (Ext. 7-7979) and the Environmental Health & Safety Office (Ext. 6-6780).

e. Prevent the spilled material from entering floor drains, storm or sanitary sewers by diking either the spill or the drains with absorbent.

f. Use an appropriate spill kit or appropriate material to neutralize or absorb the spill. Use only a kit designed for the material spilled. See additional instructions for specific substances below.

g. If there has been any contamination of personnel or clothing, follow procedures for Personal Chemical Decontamination given below. If the contamination is significant, report to the CPC Occupational Health Service (New York Presbyterian Hospital, Extension 6-7580) located on

Harkness pavilion First Floor south. If contamination appears to be life threatening, report immediately to Emergency services.

h. Promptly notify the Environmental Health & Safety Office (Ext. 6-6780) in the event of any significant chemical spill or if a spill results in personal injury or environmental contamination. In addition to mitigating the effects of an exposure or contamination, the Environmental Health & Safety Office may need to notify appropriate federal, state and local environmental regulatory agencies to avoid regulatory violations with the attendant penalties and fines.

2. Manageable Spills.

Spills are either manageable or unmanageable by laboratory workers. A manageable chemical spill is one that meets all these conditions:

- a. the quantity of material spilled is small and can easily be handled,
- b. the substance is not highly toxic or flammable, and
- c. the risk of personal contamination is not too great.

Laboratory personnel can easily clean up these spills. It is University policy that each laboratory worker takes responsibility for the clean up of any manageable spill the worker causes. Handle manageable spills according to procedures described in the following paragraphs.

The clean-up procedure for a spill depends on the location and nature of the spill. Different chemicals require different responses based on the nature of the hazard. For example, procedures for cleaning up a fine powder differ from those for a liquid spill and those for a corrosive liquid acid spill differ greatly from those for a flammable liquid. In addition, the type and amount of equipment required depends on the chemical spilled. Such considerations should be part of a well thought-out spill response plan prepared well in advance. The procedure below should be used as a general guideline. Some specific precautions for chemicals with certain characteristics are also given.

- 1) The following items should be obtained before beginning the clean up.
 - a. Personal protective equipment such as protective eyewear, skin protection, contamination prevention, and respiratory protection. The precise equipment required will depend on the material and size of the spill.
 - b. An appropriate spill kit, neutralizing materials, absorbent materials and the equipment to apply and remove them.
 - c. Containers such as thick (2 mil) plastic bags or drums for disposal
- 2) Don the personal protective equipment before proceeding.
- 3) If a neutralizer is required, apply in adequate quantities and allow any visible reaction to go completion.

- 4) If an absorbent is necessary, apply enough to completely absorb all the liquid.
- 5) Sweep up the absorbed material carefully to avoid airborne dusts and particulates and place it in a plastic bag.
- 6) Decontaminate the area, including any other surfaces or objects that may have been contaminated by the spill. Use a water-detergent mixture unless a special cleaning agent is needed and place the used, contaminated, cleaning materials together with the absorbed spill material for disposal.
- 7) The absorbed spill materials must be discarded as hazardous waste. Call the Environmental Health & Safety Office for disposal instructions.

3. Specific Instructions for Certain Substances

a. Finely Divided Solids

- i. Low toxicity solids e.g. dusts, fibers, powder, etc., are not extremely toxic and can normally be carefully swept into a dustpan with a broom and placed into a suitable waste container for further disposal as specified below.
- ii. Oxidizing solids e.g. nitrates, permanganates, perchlorates, chromium trioxide, etc., should never be discarded into a container in which combustible materials might also be placed. Furthermore they must NOT come into contact with such combustible materials as wood, paper, or reducing agents e.g., glycerol, cane sugar, and powdered zinc.
- iii. Decontaminate any spill area with an appropriate cleaning agent.

b. Liquid Spills

- i. Volatile flammable liquids of low toxicity e.g. acetone, ethanol, toluene, pentane and diethyl ether. Brief exposures to low concentrations of the vapors of one of these substances does not constitute a health risk *per se* to workers in the area, but within a range of concentrations bounded by the upper and lower explosive limits, its presence can easily lead to fires or explosions. The flammability is the main hazard that must be dealt with in such spills. Turn off near-by burners, electric stirrers, refrigerators, other appliances and any other motors or ignition sources. Turn on near-by fume hoods and open windows, as appropriate, in order to increase the ventilation rate in the area.
- ii. If the spilled liquid is water-miscible, quickly pour sufficient water on the spill to make it non-flammable. Then the resulting diluted liquid, if biodegradable and not contaminated by such toxic substances as insecticides, carcinogens or heavy metals, often may simply be flushed down the drain. The most common examples of such

substances are methanol, ethanol, n-propanol, isopropanol, acetone, and methyl ethyl ketone. They are all biodegradable.

c. **Small Spills of Mercury**

- i. Promptly clean up even small mercury spills, such as those from a broken thermometer. Small spills of mercury that result in only droplets or small pools are not an immediate danger to life or health since the concentration of mercury vapor released is extremely low. They can be cleaned with inexpensive kits available from local laboratory supply houses. Exposure to significant concentrations of the vapor over appreciable periods of time - weeks, months, and years - can have irreversible and disastrous health consequences. Therefore, even small spills must not be ignored.
- ii. Restrict access to the area to prevent the spread of mercury droplets. Use a mercury spill kit or a specially designed vacuum cleaner (which will not allow the release of mercury vapors in its exhaust) to pick up the mercury. The mercury vacuum cleaner is available from EH&S.
- iii. Take whatever steps may be necessary to ensure all mercury is removed, even from relatively inaccessible spots such as cracks in the flooring.
- iv. Keep all mercury and mercury contaminated materials separate. Do not discard into the normal trash or other hazardous waste containers.
- v. Call the Environmental Health & Safety Office to arrange disposal of these materials.

4. Unmanageable Spills

Laboratory workers should call Security and the Environmental Health & Safety Office IMMEDIATELY for assistance when:

- the quantity of material spilled is too large to be handled,
- the degree of flammability or toxicity of the substance is too great to be handled, or
- the risk of personal contamination is too high.

Isolate the spill area by closing access doors, barricading with appropriate caution tape or rope, stationing other people at the access points or some combination of these options. Post warning signs where they can be effective. Some spills may require special precautions:

- a. Finely divided highly poisonous solids (dusts, fibers, powders, etc.) such as those from
Laboratory Safety & Chemical Hygiene Plan

elemental beryllium, cadmium, arsenic and their compounds, and barium, thallium and mercury compounds are not manageable and can only be properly handled by specially trained personnel. Call Security and the Environmental Health & Safety Office and report what has been spilled, the quantity, and location of the spill.

- b. Spills of volatile, non-flammable toxic liquids are not manageable when the degree of toxicity and/or the quantity spilled is too large to be absorbed or contained by the absorbent available. The area should be isolated or, if there is a possible hazard to personnel, the area or building should be evacuated by activating the fire alarm paging system where available or by Security personnel in buildings without paging systems. If additional personnel are endangered on floors other than the 'spill floor' and the floor directly above it, they must also be notified and evacuated. Only the 'spill floor' and the one above it are immediately evacuated. This notification and evacuation must be done IMMEDIATELY. Call Security and the Environmental Health & Safety Office and report what has been spilled, the quantity, and location of the spill. Facilities personnel must shut down air handling units serving floors involved to prevent contamination of other floors served by the unit.
- c. The urgency of the response to spills of volatile, non-flammable, low-toxicity irritants is usually not as great as in the case of toxic liquids. The decision to evacuate depends on how severe the problem is. The release of a strong non-toxic lachrimator, for example, might require evacuation, whereas the spill of a somewhat dilute solution of ammonia would not.
- i. Large mercury spills are unmanageable and EH&S should be notified immediately for help in clean up. Mercury spills which result in the deposition of droplets or pools of mercury in the laboratory are not an immediate danger to life or health when they occur as the concentration of mercury vapor released is extremely low. Over appreciable time, the cumulative effect of small amounts of mercury vapor can have an irreversible effect. Spilled mercury must be picked up promptly.
- ii. Accidental release of toxic gases in a volume too large to be handled by local ventilation systems are not manageable and almost always require evacuation of both the affected and adjacent areas until the concentration of the gas is reduced to an acceptable level. Examples of toxic gases include arsine, phosgene, ethylene oxide, hydrogen sulfide, and hydrogen cyanide. Promptly notify any personnel in the area and call Security and the Environmental Health & Safety Office to report the problem and the need for swift action. Facilities must also be notified to shut down air handlers supplying the affected floor(s).

5. Chemical Spills occurring after hours

See Attachment XI. for response to after hours Chemical Spills.

J. Personal Chemical Contamination Response Guidelines

Spills of hazardous chemicals that involve personal contamination generally constitute a greater hazard than other spills, since the probability of the chemical entering the body is increased. For this reason, it is important to act swiftly to remove the contamination from the skin before the skin is damaged or before a significant amount is absorbed into the body. Special medical procedures to counteract the effect of the contaminant on the body tissues may also be necessary. An example of the last kind of contamination is hydrofluoric acid spilled on the skin and absorbed through it. In this case, immediately apply calcium gluconate ointment. Medical examination and surveillance afterward may also be required as subcutaneous injections of calcium gluconate may be necessary. A source of these special medical procedures is the **Poison Control Center (212-764-7667)**.

1. Chemicals spilled over a large area on the body:

All contaminated clothing must be removed as quickly as possible while using the safety shower. Do not waste time deferring to modesty. The only consideration in this type of emergency is acting quickly enough to protect life and health. Immediately wash the affected area with water, apply mild soap and flush with water for at least 15 minutes; repeat these procedures until clean or if pain returns. **DO NOT** use any neutralizing agents, other chemicals or solvents. Medical consultation is clearly necessary when large body areas have been exposed to highly toxic chemicals, take the employee to the New York Presbyterian Hospital Emergency Room.

2. Chemicals spilled on the skin:

Immediately flush the area with water and wash with mild soap and water. Remove any jewelry. If there is no visible burn, gently rub the affected area with warm water and soap (taking care not to abrade the skin surface). Keep the employee quiet and wait for medical assistance. If a delayed action is anticipated or observed (the toxicological effects of some chemicals, e.g., methyl bromide or ethyl bromide, may be delayed for as much as 48 hours), obtain medical consultation promptly and explain carefully and exactly what chemicals were involved. Take a copy of the **MSDS** (Material Safety Data Sheet) or other pertinent literature on the effects of the chemical to the attending physician. Notify the Environmental Health & Safety Office (ext. 6-6780) or Security (ext. 7-7979).

Be alert to the possibility of an inadvertent injection or unnoticed introduction of chemicals into the body. Many solids, oily liquids or water solutions can enter through cuts in the skin. In addition, many oily liquids and oil-soluble solids are easily absorbed through the skin and pass on to other body tissues and the bloodstream.

3. Chemicals splashed into the eye:

Laboratory Safety & Chemical Hygiene Plan

Immediately use an eyewash fountain. If one is not available, use a gentle stream of cold tap water. The eye must be washed continuously with a gentle flow of water for at least 15 minutes with the eyelids held apart to afford maximum exposure of the eyeball to the water. Remove any contact lenses, if possible. Contact lenses may be removed under a gentle stream of water. DO NOT attempt to remove contact lenses by hand or with any object. NEVER rub the eye or use any neutralizing chemical for eyewash. Consult medical attention as soon as possible. Notify the Environmental Health & Safety Office (ext. 6-6780) or Security (ext. 7-7979).

4. Chemicals inhaled:

In case of poisoning by chemical inhalation, immediately call the Environmental Health & Safety Office (ext. 6-6780) or Security (ext. 7-7979). If the employee is conscious, carry or pull the employee to fresh air. DO NOT let the employee walk unassisted or engage in any unnecessary activity that increases the circulation of poison in the bloodstream. If artificial respiration is necessary, take care not to inhale the chemical from the employee.

If the employee is found unconscious in a confined space or an area where vapors are likely to be trapped, do not enter the area; the employee may have been overcome by toxic gases or asphyxiated by lack of oxygen in the space. Your entry into the same space may lead to your becoming incapacitated as well. Immediately summon trained help who will enter the area with a supplied air respirator to remove the person. Monitor the employee from a safe distance.

5. Chemicals ingested:

Take the employee to the Occupational Health Service (Harkness Pavilion, First Floor South) and call the Environmental Health & Safety Office (ext. 6-6780) or Security (ext. 7-7979). Listen carefully and follow their instructions. Do not give the employee water, milk or anything else unless so directed by a medical professional or Material Safety Data Sheet (MSDS). Also, do not induce vomiting if the employee complains of pain or burning sensation in the mouth or throat, or if the ingested substance is known to be caustic, a cleaning fluid, or a petroleum product. Induce vomiting only if so directed by a medical professional. To induce vomiting, place the employee's head below the hips, mouth down or to the side, and place a gloved finger at the back of the employee's throat.

K. Fire Safety and Emergency Response to Fires and Explosions

Research laboratories differ from other work environments in that they usually contain a variety of fire hazards. In addition to the 'ordinary' (Class A) fires, those fueled by wood, paper, textiles, etc., laboratory hazards include the presence of flammable and, quite often, volatile

solvents such as petroleum distillates which are not miscible with water, reactive metals such as sodium and potassium, flammable metal powders such as magnesium, titanium, and zirconium, metal hydrides such as lithium hydride, lithium aluminum hydride, and sodium borohydride, as well as many kinds of electrical equipment.

Complications arise when fighting these fires because each type of fire must be fought with the extinguishing agent and procedure appropriate for it; the use of the wrong technique or extinguisher can be catastrophic. The EH&S Office has simplified fire-fighting in the laboratories by equipping all laboratories with multi-purpose (A, B, C) dry chemical fire extinguishers, which can be used on all types of fire with the exception of reactive flammable metals which must use extinguishers suitable for the particular metal. Laboratory workers must be trained in the procedures and the proper use of the equipment. Regular drills must be held to reinforce this training. Fire extinguishers are inspected and tested every six months by an outside vendor. However, laboratory personnel are responsible for seeing that extinguishers are promptly recharged after each use. If a fire extinguisher in any laboratory, chemical storeroom, or nearby location requires inspection or recharging, call Facilities Operations (ext. 7-7367). A monthly inspection of the fire extinguisher pressure gage by laboratory personnel is strongly recommended as a further safeguard of the extinguisher being properly charged.

Before acting to cope with a particular fire, the fire must first be judged as being controllable by laboratory personnel. Since this depends on the rapid, yet careful, evaluation of several factors, the judgment of the person making the decision is critical. The size of the fire, its intensity, the nature of the burning substance, how near are other flammable or explosive materials to the fire, whether fighting the fire would place the laboratory worker doing so in substantial risk, availability of escape routes, prospect of the fire spreading and availability of the proper fire-fighting equipment, are factors that must be considered in making this decision.

Should the nature of the fire, its size, etc. make it controllable, use the appropriate available fire extinguisher as described below and proceed with the methods described in the section on controllable fires. On the other hand, should the fire be judged uncontrollable, follow the evacuation and notification procedures for uncontrollable fires.

In all cases, however, call Security (ext. 7-7979) and the Fire Safety Officer (ext. 6-6780).

1. Classification of fires

CLASS A. (Wood, paper, textiles, rubber, coal)

This type of fire can be extinguished by the ABC extinguisher.

CLASS B. (Flammable or combustible liquids, greases, petroleum products, solvents)

Carbon dioxide or dry chemical ABC extinguishers should be used. Carbon dioxide extinguishers do not leave any residue, whereas dry chemical devices do. Pressurized water units should not be used since the immiscibility of most solvents and water would result in the spreading of the fire.

CLASS C. (Live electrical equipment involved in a fire)

If possible, turn off the electrical power to the devices, and then use either the dry chemical extinguisher or a carbon dioxide or halon extinguisher, if available.

CLASS D. (Sodium, potassium, magnesium, titanium, zirconium and other metals)

If sodium, potassium, magnesium, or any of the flammable metal powders are to be used in a laboratory, the appropriate dry powder extinguishing agent must be made available for fire emergency use before work is started.

Use specific "Class D" extinguishing agent or any of the following dry powders: graphite, limestone, sand, or sodium carbonate.

DO NOT USE pressurized water, carbon dioxide, dry chemical or halon (Freon) extinguishers on metal fires. The use of these types of extinguishers introduces substances that are very reactive with the burning metal that either will make the fire grow or will trigger an explosion.

2. Fire-fighting procedures for controllable fires

- a. Clothing fires must be extinguished immediately, before anything else is done, in order to minimize skin burns.
- b. For all fires, the fire alarm must be transmitted to ensure the Fire Department response.
- c. The decision of whether to fight the fire oneself or to wait for fire-fighting help must be made according to the type and size of the fire, its location and the circumstances of the fire. A small fire in a container may be easily snuffed out by the placement of a nonflammable cover across the container opening. A small fire in an area free of other fuels can be extinguished with appropriate available extinguishers before calling for help. When extinguishing a burning solid, direct the extinguisher discharge at the base of the flame; in the case of burning liquids, direct it at the leading edge. Larger or rapidly growing fires are best left to the Fire Department.
- d. In the case of an occurrence of any fire, the fire must be reported to Security at ext. 7-7979 or ext. 7-8100. There are no exceptions.

3. Evacuation procedures for uncontrollable fires

i. Leave the area of danger. DO NOT stay to fight a large fire. On your way out, if it can be done safely, turn off equipment and move any explosive or flammable materials away from possible contact with hot surfaces or other sources of ignition. Using the laboratory circuit breaker is often the quickest and most effective way to turn off all the laboratory's electrical equipment simultaneously. For this reason, the circuit breaker must always be readily accessible. Your safe exit, however, must be given the highest priority.

ii. Transmit the fire alarm, notify personnel on the floor and call Security (Ext. 7-7979).

iii. Leave by means of one of the predetermined evacuation routes for your laboratory area. If considerations of safety make it necessary to leave the building, evacuate promptly. .

iv. If a person's clothing is on fire, he/she must not be allowed to run, as this will fan the flames and cause a more serious burn. Either put the person under a shower or wrap him/her in a fire blanket, coat, or whatever is available to smother the flames. Roll the person on the floor if necessary. After calling the emergency numbers, place clean, wet, ice-packed cloths on small burned areas wrap the person warmly to avoid shock, and secure medical assistance.

Remember STOP DROP & ROLL

L. OSHA Substance-Specific Laboratory Air Quality Standards

Some chemicals, such as formaldehyde, methylene chloride and ethylene oxide, must be strictly controlled and monitored because they are subject to OSHA Substance-Specific Standards described in 29 CFR 1910.1001 through 1910.1048. Call the EH&S Office to obtain assistance in complying with the regulatory mandates for these chemicals. The Action Levels and the Permissible Exposure Levels (PELs) for some of the substances are listed in Attachment X.

Laboratories using any OSHA regulated specific substances must contact the EH&S Office (6-6780) for exposure assessment and personal exposure monitoring.

If the personal exposures are greater than their respective Action Level (AL) or Permissible Exposure Level (PEL) and/or Short Term Exposure Limit (STEL), then the Laboratory Safety Manager must:

i. Comply with the OSHA exposure-monitoring provisions for that chemical as stated in OSHA regulations specific for that chemical. Call the EH&S Office to get information on this exposure monitoring. Air monitoring must be done by the University Occupational Hygienist in accordance with the exposure monitoring provisions of the relevant standard.

ii. Keep records of the measurements made to monitor the level of employee exposure.

iii. Develop and enforce special written procedures as required by the **OSHA** specific standard when asbestos, benzene, ethylene oxide, formaldehyde, lead, methylene chloride or other such regulated substances be handled.

Special precautions must be taken for work that involves the possibility of either continual, frequent, or repeated exposures to asbestos, benzene, ethylene oxide, formaldehyde (in the form of a dust, mist, solution or gas), or lead (in the form of metallic lead as a dust or vapor, including all inorganic and organic lead compounds and lead soaps). These precautions are spelled out in 29 CFR 1910.1001 for asbestos, 29 CFR.1047 for ethylene oxide, 29 CFR 1910.1048 for

formaldehyde (see Attachment XIV. Formaldehyde Exposure Control Plan), 29 CFR 1910.1025 for the lead, and 29 CFR 1910.1028 for benzene. They include:

- a. Providing pertinent MSDSs to workplace personnel before they begin work with the materials. Keeping copies of these MSDSs available for consultation while the work is being done.
- b. Confining use of the substances to regulated areas and restricting access to these areas.
- c. Posting appropriate signs and cautionary labels in and around these regulated areas.
- d. Monitoring exposure levels at the outset when work has been started.
- e. Notifying employees of the results of the monitoring tests within 15 days of the receipt of the results.
- f. Developing and enforcing a written program to reduce the concentration of an airborne hazardous material to a safe level, when permissible levels of these substances have been exceeded.
- g. Providing adequate training about handling and disposal to those working with the substance.
- h. Providing adequate personal protective equipment.
- i. Including a schedule of leak detection surveys in the program, in those cases where the hazardous substance involved is gaseous.

M. Work-related Illness, Injury and Incident Reporting

For any life-threatening emergency, report to the New York Presbyterian Hospital Emergency Services (West 168th and Broadway).

Employee's suffering from a work-related illness or injury must report this to their supervisor, complete an Incident Form (see Attachment XII.) and get medical attention. Occupational medical care for work-related incidents is provided at no cost to employees. Occupational medical care is provided at the Columbia Presbyterian Center (New York Presbyterian Hospital) **Occupational Health Service (OHS)**, located on Harkness Pavilion, First Floor south (Extension 6-7580) during normal business hours (8:30 a.m. to 4:00 p.m. M-F). Alternatively, an employee may seek medical care by a personal physician of his/her choice with a summary of the findings reported to the EH&S Office. Students suffering from a work-related illness or injury must report

Laboratory Safety & Chemical Hygiene Plan

to **Student Health Services** on 60 Haven Avenue (telephone 795-4181).

Work-related injury or illness should also be reported to the EH&S Office so that a recurrence to you or to others is avoided.

Certain situations or exposure conditions may warrant medical consultation or medical monitoring of laboratory employees that will be provided in the OHS at no cost. Examples include:

- a. Medical evaluation for employees exposed to concentrations of a hazardous substance routinely above the OSHA action level, the PEL or the STEL.
- b. Employee's who have direct skin or eye contact with a hazardous agent should immediately flush with water and seek medical attention.

N. Required Medical Surveillance

A laboratory worker shall be required to obtain medical consultation and examination under the following circumstances. Examinations are provided at no cost to employees at the Occupational Health Service. Alternatively, the employee may seek medical care through a personal physician of his/her choice with a summary of the findings reported to the EH&S Office.

- a. If it is likely that the worker will be or has been exposed to a substance at a level in excess of either the OSHA recommended Action Levels, or Permissible Exposure Limits (PELs) or STEL. The EH&S Office should be consulted for assistance in assessing the exposure or potential for exposure.
- b. If a laboratory worker develops signs or symptoms associated with an over exposure to a chemical being used.
- c. In case of an overexposure to chemicals through a spill, explosion, or other accident.

Medical consultations are provided at no cost through the CPC Occupational Health Services. The Attending physician will decide if the employee needs to be referred for further treatment. If there is a medical emergency, go to the E.R. immediately, and call the Security Office (Ext. 7-7979 or Ext. 7-8100) if assistance is needed. If the Occupational Health Service is closed or not easily accessible, he/she should be sent to the Emergency Room of the New York Presbyterian Hospital, located in the Vanderbilt Clinic Building on 168th Street.

The lab supervisor shall collect as much information as possible about the person, the chemicals involved, MSDSs, symptoms, and any other relevant data, to provide to the attending physician.

The physician in charge will inform the employee about the medical examination results, related conditions, tests required, and whether any follow-up is required.

The Environmental Health & Safety Office will be advised of the results of relevant tests conducted by the Attending physician.

The Occupational Health Service shall keep written records of all such medical examinations and must maintain these records for the duration of employment plus 30 years. Such records must contain, but are not limited to, physicians' opinions, recommendations, results of any tests performed, and any follow-ups. Upon written request, the employee or an authorized representative shall make such records available for review.

O. Education and Training of Laboratory Personnel

The purpose of education and training in Laboratory Safety includes:

- a. To instruct laboratory workers to recognize known hazards and to use available methods of protection;
- b. To provide each laboratory worker with background information about the nature, estimation and mechanism of hazards in research areas;
- c. To provide technical information about appropriate precautions including hazard elimination, personal hygiene methods and the use of PPE necessary in the specific work area. ;
- d. To reduce work related injury and illness by instruction in proper use and maintenance of tools, equipment and materials;
- e. To provide instruction on the need for medical monitoring;
- f. To provide instruction and knowledge of emergency procedures including spill procedures;
- g. To explain the importance and use of MSDSs and labeling.

Education and training sessions offered to laboratory personnel include:

- a. New employees attend a general orientation lecture provided by the EH&S Office including Fire Safety training;
- b. New laboratory workers attend the Laboratory Safety and Chemical Hygiene Orientation within one month of employment. This orientation provides an introduction and overview of laboratory safety;
- c. After attending the initial session, every laboratory worker is encouraged to attend periodic problem-solving sessions;
- d. Laboratory workers working with formaldehyde must attend a special training session offered by EH&S;
- e. Laboratory workers working with bloodborne pathogens must attend a special training session offered by EH&S.

Sessions are designed not only to meet the OSHA Laboratory Standard (29 CFR 1910.1450) but also to incorporate the requirements of the New York City Community Right-to-Know Law (Local Law 26, 1980) and the New York City Fire Department Title 3 RCNY, Chapter 10, May 31, 1995.

Laboratory Safety & Chemical Hygiene Plan

P. Laboratory Surveys

The environmental Health & Safety Office will enhance its laboratory safety program through regular and periodic visits to each Columbia University Health Sciences Division Laboratory.

The enclosed survey tool, Research Laboratory Health & Safety Survey (see Attachment XVII.), is meant to be a guide or checklist to help laboratory personnel evaluate the laboratory for essential items concerning health & safety.

Q. Record Keeping

The following records shall be maintained.

1. Personnel exposure monitoring.
 - a. EH&S will keep and maintain the following records for the duration of employment plus 30 years:
 - b. Results of routine and special personal and/or area monitoring
 - c. Evaluations of worker exposures to chemicals as a result of an accident spill explosion, etc.
 - d. Chemical exposure records that are made available to the worker by EH&S
2. Medical Consultation Records.

All records concerning medical consultations related to chemical exposure shall be maintained by the CPC Occupational Health Services, Harkness Pavilion, First Floor South; (305-7590) for the duration of employment plus 30 years as required under OSHA standard 29 CFR 1910.20. Records of medical consultations shall be made available to the exposed worker in accordance with the OSHA standard 29 CFR 1910.20.

3. Chemical inventories

A list of all chemicals present in the laboratory must be prepared, maintained and updated by the laboratory supervisor and maintained in the laboratory. The list should include, for each container, the chemical name(s) of its contents, the CAS Number (Chemical Abstracts Service Number), the quantity and the container type. This list provides great assistance in the acquisition of the MSDSs needed and to carry out work both safely and in compliance with applicable regulatory standards. A complete inventory of all chemicals in the laboratory is required by the NYC Community Right-To-Know Act.

Laboratory Safety & Chemical Hygiene Plan

4. Container labels

Containers must be labeled so that any laboratory worker can determine the identity of the contents. The OSHA Laboratory Standard, 29 CFR Part 1910.1450 and 1910-1200, and New York City Community Right-To-Know Law (Local Law 26 of 1980) require that the label on a mixture which is a hazardous substance list the chemical name of each of the hazardous ingredients present in descending order of the concentrations. This is not required on a vessel containing 2 ounces (56 grams or 56 ml) or less of the substance. Each label must have both the chemical name (IUPAC name) and the CAS Number on each label for purposes of identification of the chemical. Each container should be inspected annually for label and container integrity.

5. Safety information sheets and references, e.g. Material Safety Data Sheets (MSDSs).

Information sheets for each chemical present in the laboratory must be available to any laboratory worker within 72 hours of a written request.

6. The Laboratory Safety and Chemical Hygiene Plan and Checklist.

These documents must be kept current, kept in the laboratory, and made readily available to all laboratory workers. Copies of these documents must be sent to EH&S for review.

R. Compliance

The Principal Investigator is responsible for ensuring compliance with the Laboratory Safety and Chemical Hygiene Plan on the Health Sciences campus. The following procedure will be followed if there is a violation.

In the event that the Environmental Health and Safety Office (EH&S) determines that a significant health or safety hazard exists, EH&S in conjunction with the Laboratory Safety Manager will immediately take measures to eliminate or reduce the hazard. The EH&S will issue a written report, including recommendations about remedial action to the Laboratory Safety Manager, Principal Investigator and Departmental Safety Officer specifying a time period in which the violations must be corrected. If the violation is not corrected within the time period specified, a formal written warning will be sent to the Department Chair.

If the matter is still unresolved within the stated time period, the matter will be referred to the Dean's Office and the Institutional Health and Safety Council for action. If EH&S determines that a safety hazard remains uncorrected, EH&S can recommend closing the laboratory until the hazard has been corrected. The Dean and the Safety Council may require the P.I. and/or Chair to appear before the Safety Council as well as shut the laboratory down.

U. S. DEPARTMENT OF COMMERCE

R. P. LAMONT, Secretary

BUREAU OF MINES

SCOTT TURNER, Director

Technical Paper 480

**INTENSITIES OF ODORS AND IRRITATING EFFECTS
OF WARNING AGENTS FOR INFLAMMABLE
AND POISONOUS GASES**

BY

S. H. KATZ and E. J. TALBERT

**This report represents work done under a cooperative agreement
between the Bureau of Mines, Department of Commerce,
the American Gas Association, and the Carnegie
Institute of Technology**



**UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1930**

For sale by the Superintendent of Documents, Washington, D. C. - - - Price 10 cents

UNIVERSITY OF MICHIGAN

Digitized by Google



UNIVERSITY OF MICHIGAN
3 9015 07755 9717

CONTENTS

	Page
Purpose of investigation.....	1
Acknowledgments.....	1
Previous investigations.....	1
Scales for measuring odors and irritations.....	2
Odorimeter.....	2
Vaporizers.....	5
Apparatus for measuring gaseous substances into odorimeter.....	6
Sense-affecting properties of air-borne chemicals.....	6
Use of scales for measuring intensities of odors and irritations.....	7
Procedure in testing.....	8
Preliminary trials.....	8
Number of observers.....	8
Records.....	8
Operations.....	8
Calculations.....	9
Materials tested.....	12
Source and character of materials tested.....	12
Results of measurements.....	13
Intensities of odors versus concentrations in parts per million.....	14
Intensities of nasal irritation versus concentrations in parts per million.....	16
Intensities of eye irritation versus concentrations in parts per million.....	18
Intensities of odors versus concentrations in milligrams per liter.....	20
Intensities of nasal irritation versus concentrations in milligrams per liter.....	22
Intensities of eye irritation versus concentrations in milligrams per liter.....	24
Character of odors and their physiological effects.....	26
Discussion.....	28
Concentrations for definite intensities of odor.....	28
Precision and interpretation of the measurements.....	29
Test of ethyl mercaptan extending three days.....	29
Odor intensities presented irregularly in test of isoamyl isovalerate.....	30
Entire face presented to atmosphere of chloracetophenone in a box.....	30
Duplicate tests.....	33
Agreement with other investigators.....	35
Homologous series.....	36
Summary and conclusions.....	37

ILLUSTRATIONS

Figure	Page
1. Diagram of odorimeter.....	3
2. Vaporizers.....	4
3. Intensities of odors, nasal and eye irritations of benzyl mercaptan.....	11
4. Odor intensities of ethyl mercaptan at various concentrations in air.....	29
5. Average of odor intensities of isoamyl isovalerate versus concentrations in air, test 66; the odors were presented in irregular order of intensity.....	30
6. Sensory effects caused by chloracetophenone from a glass orifice, also by exposing the entire face in a box.....	31
7. Duplicate tests with crotonaldehyde.....	32
8. Triplicate tests with ethyl mercaptan.....	33
9. Duplicate tests with allyl mercaptan.....	33
10. Duplicate tests with crotyl mercaptan.....	34
11. Duplicate tests with trinitrotertiarybutylxylene.....	34
12. Intensities of the odors of the alkyl mercaptans in homologous series.....	36
13. Intensities of the odors of the alkyl thioethers in homologous series.....	36

II

INTENSITIES OF ODORS AND IRRITATING EFFECTS OF WARNING AGENTS FOR INFLAMMABLE AND POISONOUS GASES ¹

By S. H. KATZ ² AND E. J. TALBERT ³

PURPOSE OF INVESTIGATION

Measuring the intensities of odors and irritating effects of chemicals constituted one phase of an investigation of warning agents for fuel gas which was conducted by the Bureau of Mines at the suggestion of and with the financial assistance of the American Gas Association. In this work persons were subjected to various known concentrations of substances in air and their sense perception or reaction noted. The data obtained for a large number of odorous or irritating substances afforded a basis for selecting the most promising warning-giving substances, for estimating practical concentrations to use in gas, and for estimating the economic feasibility of their use.

ACKNOWLEDGMENTS

The investigation described in this report was made in the Pittsburgh Experiment Station of the United States Bureau of Mines. The American Gas Association assisted through support of the fellowship of the mining advisory board to the bureau and Carnegie Institute of Technology. The work was directed by A. C. Fieldner, chief engineer, experiment stations division, of the bureau, and by W. P. Yant, supervising chemist, health laboratory section. Many of the materials used in the tests were synthesized or purified by J. B. Shohan, chemist, and E. R. Perry, research fellow, who conducted another phase of the warning-agent study.

PREVIOUS INVESTIGATIONS

Previous investigators have measured the minimum concentrations of gases or vapors at which their odors were perceptible; these are "threshold concentrations." The principal threshold concentrations are compiled in the International Critical Tables.⁴ This work lists 97 threshold concentrations of odors determined for a somewhat smaller number of substances by 11 authorities; these concentrations range from a minimum of 16×10^7 molecules per cubic centimeter for ionone to a maximum of 17×10^{17} for apiol. Expressed

¹ Work on manuscript completed March, 1930.

² Until July 31, 1929, chemist in charge, gas masks and respirators laboratory, health laboratory section, Pittsburgh Experiment Station; subsequently principal chemist, Edgewood Arsenal, Md., Chemical Warfare Service.

³ Research fellow (1926-27), Carnegie Institute of Technology.

⁴ Zwaardemaker, H., *Odoriferous Materials: International Critical Tables*, vol. 1, 1926, pp. 358-362.

2 INTENSITIES OF ODORS AND EFFECTS OF WARNING AGENTS

in parts per million the figures are: Ionone, 0.0000059; and apiol, 63,000. Threshold concentrations determined by the authors lie within this range.

In general, the earlier investigators employed methods based on disseminating a weighed or measured volume of vapor in a flask or in a box of known volume; then the nose was inserted through a temporary opening to smell. Zwaardemaker⁵ used a cubical box of glass and metal of 64 liters capacity. Residual odors were dispelled after a test by removing a side to air out the box and scour the inside surfaces with chalk.

In 1920 an odor scale of five degrees of increasing intensities was devised and used by Katz and Allison.⁶ They also developed an apparatus or odorimeter for determining weights of vapors volatilized at uniform rates and diluting the vapors to various concentrations by means of measured streams of air. These methods were followed in the present investigation.

In 1898, Gamble⁷ proved that Weber's law applies to the sense of smell; this law⁸ states that the sense reaction is proportional to the logarithm of the stimulus. These relations have been found to hold for the sense of smell, also for nasal irritation and eye irritation throughout the investigations reported herein.

SCALES FOR MEASURING ODORS AND IRRITATIONS

The scale of odor intensities used in this investigation consists of zero and five degrees of intensity, thus:

0 = No odor.	3 = Easily noticeable.
1 = Very faint.	4 = Strong.
2 = Faint.	5 = Very strong.

The scale of irritation of nose and eyes devised for present purposes has four degrees above zero, as follows:

0 = No irritation.	3 = Strong.
1 = Faint.	4 = Intolerable.
2 = Moderate.	

The numerals indicate uniform increments in odor or irritation; the words corresponding aim to describe the subjective effects. Qualities of odors, as pleasant or repulsive, are not considered; the degrees are conceived equal, regardless of the qualities of various odors or those of irritations. The odor scale has more divisions over its range than the irritation scale, as the sense of smell can doubtless perceive small differences more readily than can the sense of irritation.

ODORIMETER

Figure 1 shows the essential parts of the odorimeter diagrammatically. The arrows point the flow of the air, which is rendered originally odorless with activated charcoal. Dry air from the pri-

⁵ Zwaardemaker, H., Geruch und Geschmack; Chapter in Tigerstedt, R., Handbuch der physiologischen Methodik: Vol. 3, Leipzig, 1910, pp. 46-108.

⁶ Katz, S. H., and Allison, V. C., Stenches for Detecting Leakage of Blue Water-Gas and Natural Gas: Tech. Paper 267, Bureau of Mines, 1920, 22 pp.

⁷ Gamble, Eleanor A. M., The applicability of Weber's Law to Smell: Am. Jour. of Psychology, vol. 10, 1898, pp. 82-142.

⁸ James, Wm., The Principles of Psychology: H. Holt & Co., New York City, 1890, 2 vols. (Weber's law is considered in vol. 1, pp. 537-49.) Weber's Law, New International Encyclopedia: Vol. 23, 1925, pp. 428-429.

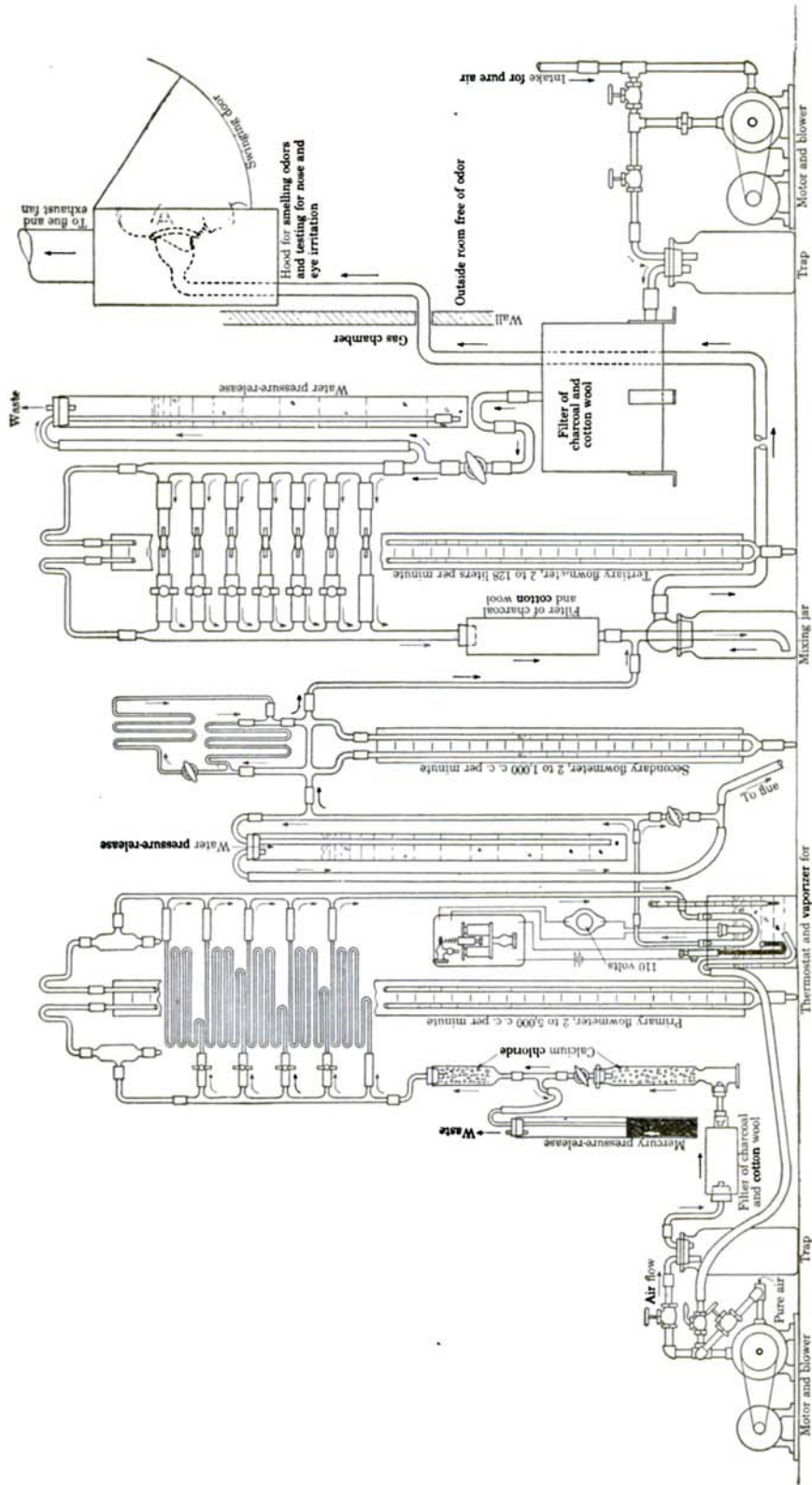


FIGURE 1.—Diagram of odorimeter

4 INTENSITIES OF ODORS AND EFFECTS OF WARNING AGENTS

mary flow meter passes over or through the chemical held in a vaporizing tube in the small thermostat, at a temperature of $25^{\circ}\text{C.} \pm 0.1^{\circ}$ for most chemicals but at 0°C. for some very volatile liquids. The rate of vaporization of a chemical is governed when in contact with the air stream by the rate of air flow, the kind of vaporizer used, and the temperature in the thermostat. Five types of vaporizers were used in the water bath; they are shown in Figure 2 and are described in detail later.

The odoriferous air stream from the vaporizer may be passed to the secondary flow meter or direct to the mixing jar (by changing tube connections) according to the concentrations desired. To obtain very low concentrations the odoriferous air is passed to the secondary flow meter, as in Figure 1, where a portion of the air from the vaporizer is wasted to a flue and another portion is measured through the secondary flow meter to the mixing jar. Large volumes of pure air are also measured into the mixing jar through the tertiary flow meter toward the right of Figure 1. The tertiary flow meter

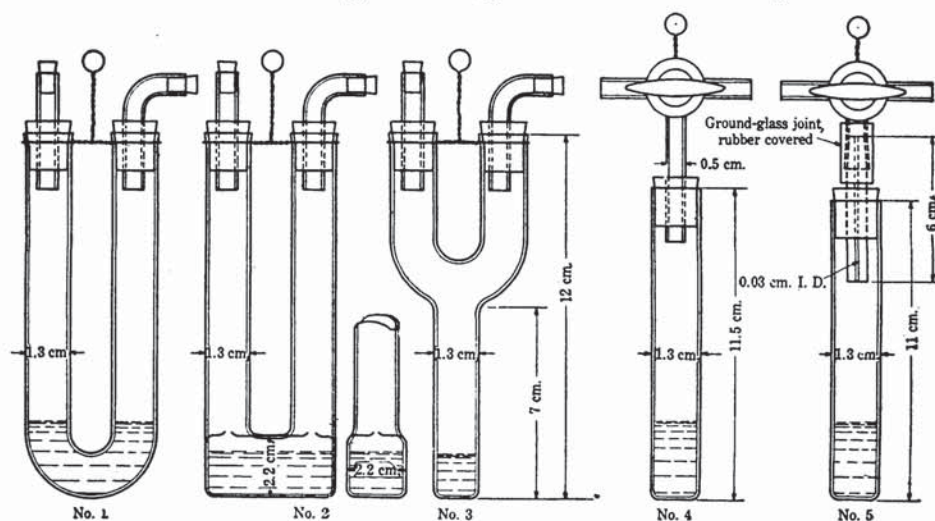


FIGURE 2.—Vaporizers for adding odoriferous materials of different volatilities to air streams at uniform rates

gives 2 to 128 liters of air per minute, but it was found best to use not less than 8 liters per minute because of dilution at lower rates of the test air with outside air before smelling at the outlet.

A small hood strongly ventilated by an exhaust fan is built around the nose piece at the outlet. The odorimeter is inside and the outlet outside of a continuously and thoroughly ventilated gas chamber within another large room. Any odors in the gas chamber are quickly withdrawn and do not pass to the outer room; this room also is ventilated continuously by a powerful fan.

The observers or subjects, except the operator of the odorimeter, who also acted as an observer, remained in the outer room where they breathed air free of odor except for the few seconds of testing. They were thus free from any effects of fatigue or cumulative effects from extended exposure to odors. The operator of the odorimeter was protected as far as practicable from odors when not making observations. As a rule there was some odor inside the gas chamber in spite of thorough and continuous ventilation, but it was faint and apparently did not affect the observations of the operator.

The conduits were of glass with rubber nipples at connections; the rubber was eliminated as far as practicable, and glass tubes conveying vapors were set end to end within the nipples to expose a minimum of rubber. After a test, the odorimeter was aired out with pure air flowing usually for hours to remove residual odors. In a few tests the tubes were removed to clean them with chemicals. To minimize the effects of adsorption and evolution of odors the tests were in general run in order of increasing concentration; and time was allowed for adsorption equilibrium in the conduits, as judged by the operator smelling the odors, before observations were made for record.

VAPORIZERS

The five vaporizers (fig. 2) for delivering odors to the primary air stream were necessary because of the differences in volatilities of various materials as well as their different sense affecting properties. The vaporizers are: (1) A simple U tube for nearly saturating air with vapors of granular solids or of liquids by passing or bubbling the primary air through the material. The U tube is submerged in the thermostat to the rubber stoppers which are always kept dry. (2) A tube made to expose a rectangular surface of liquid to air passed over it and to maintain constant surface area as liquid evaporates. (3) A Y tube holding liquid in the stem of the Y and passing air through the top arms; the vapor passes from the liquid to the air stream by diffusion and some convection caused by the passing air stream. (4) A 3-way stopcock with plug bored T which constitutes a tube similar to No. 3 but with small internal passages; the vapors pass to the primary air stream entirely by diffusion; the cock is well ground and is used without lubrication. (5) A T constructed of a 3-way cock similar to No. 4, but used to reduce diffusion with addition of capillary tubing in sizes down to thermometer tubing and of different lengths. The capillary tubes are inserted between the liquid and the primary air stream; the vapors pass through the capillary entirely by diffusion. It is always necessary to allow sufficient time for the concentration gradient of vapor in air through the capillary to become fixed before concentrations may be determined accurately. The capillary diffusion tubes were not immersed in the thermostat but were just above it; the temperature of the air in the gas chamber was constant during the period of the testing; 2° C. was the greatest deviation of the temperature of the air from 25° C.

The vaporizers are weighed before and after a series of odor measurements, and the loss in weight divided by the volume of air passed through a vaporizer (plus volume of vapor in a few tests for precision) gives the concentration of vapor as milligrams per liter in the primary air stream. From this and the subsequent dilutions the concentrations of the vapors in the air as finally smelled are computed. If the rate of flow of the primary air stream is varied, it is necessary to weigh the vaporizer before and after each change of rate. When some of the more powerful and less volatile materials, such as trinitro-tertiarybutylxylene (artificial musk) were measured, the apparatus was operated as long as 36 hours to vaporize a few milligrams of material for accurate determinations of weight of vaporized substance.

APPARATUS FOR MEASURING GASEOUS SUBSTANCES INTO ODORIMETER

The apparatus just described is adapted only to the measurement of odors of substances that are liquid or solid at ordinary temperatures. To measure the odors of substances that are gases at normal temperatures, such as hydrogen sulphide and butylene, the vaporizer tubes are replaced by a special flow meter for each gas (not shown on figs. 1 and 2) and designed to introduce the gas at suitable measured rates into the primary air stream. The gases are generated or stored under pressure and are delivered through a valve or cock to control the supply. The special flow meters are calibrated for rates of flow of the respective gases against the heads of water in the flow-meter manometer by measuring the volumes of gas delivered per minute at various heads into a calibrated gas burette, or by chemical methods of determination such as the iodine method for hydrogen sulphide.

A small gas-mixing chamber is put in place of the ordinary vaporizer; the primary air is passed through it, and the measured stream of odorous gas is thoroughly mixed with the primary air therein. This odoriferous air stream is passed to the secondary flow meter or direct to the mixing jar and the tertiary air stream.

SENSE-AFFECTING PROPERTIES OF AIR-BORNE CHEMICALS

As a rule, when a person encounters a foreign gas or vapor in air its presence becomes known through the sense of smell, the taste, and irritation of the nose and respiratory passages or the eyes; even the skin is irritated by exposure to sufficient concentrations of certain gases. As a rule, the olfactory nerves are affected first but not necessarily so; chloracetophenone, for example, can cause eye irritation when odor is not perceived, and the odor of some irritants in higher concentrations is lost entirely in the pain of irritation in the nose. Throughout the observations reported herein effort was made to distinguish between odor and nasal irritation when both were perceived simultaneously. This is easily done when irritation is slight, but when it becomes strong the irritation sometimes masks the odor greatly.

A few gases and vapors produce no effects on the senses, but most of them have odors even if they cause no other effects. Although man's sense of smell may not be as acute as that of some animals, it is still extraordinarily acute; a person can discern 1 part of musk in 20 billion parts of air; some persons can perceive it at even greater dilutions. Chemical analysis has not been developed to such a fine point. No other effects of gases on the senses were perceptible at the low concentrations which in some instances affected the sense of smell.

Fatigue of the olfactory nerves when exposed to an odoriferous atmosphere through a period has been experienced by everybody. During a visit to stockyards the odor, at first strong and offensive, becomes less perceptible until it is almost unnoticeable after sufficient exposure. Regarding fatigue, Parry⁹ says:

The well-known phenomenon of smell fatigue is explained by the theory that actual chemical action takes place between the odoriferous body and some react-

⁹ Parry, E. J., *The Chemistry of Essential Oils and Artificial Perfumes*, 4th ed., vol. 2, 1922, p. 28.

ing material in the nose; thus it can easily be conceived that some sort of additional reaction takes place and that directly the osmoceptor in the nose becomes saturated no further reaction is possible and no further odor can be appreciated until fresh osmoceptor is formed. Ruzicka suggested two such osmoceptors are involved since substances inspired in a concentrated state have odors different to those perceived in a dilute condition.

For these reasons the observers testing the odors and other effects were exposed to the substances only during the limited time of observation—an inhalation for odor and nasal irritation, and 10 seconds exposure for eyes. Irritants affect the nose and eyes variously. Some irritate almost immediately on short exposure, and the irritation quickly disappears after exposure. The effects of others is delayed; for example, the irritation by allyl alcohol is not apparent until several seconds after exposure. Some substances cause slowly increasing irritation after exposure until a maximum is perceived; the intensity then decreases. Crotonaldehyde is an example.

In general, it was found that irritants did not give strong odors. Unpleasant odors or stenches may be very faint or very strong; pleasant odors are not very strong, and if they increase to very strong they become repulsive.

USE OF SCALES FOR MEASURING INTENSITIES OF ODORS AND IRRITATIONS

The arbitrary scales adopted for measuring the odors, nasal irritations, and eye irritations afford a means of comparing the effects of different chemicals at any concentration in air. It would be convenient to measure odors by some physical method apart from the senses of persons, but that is now unattained. The degrees of the odor scale were explained to the subjects in terms of the sense of smell thus: 0, Or no odor, requires no amplification; No. 1 is the threshold odor, just perceptible. Consider now the opposite end of the scale. No. 5, or very strong, is the most intense odor without regard to quality and perceived aside from any other physiological effects such as irritation or nausea. No. 3, or easily noticeable, is the median odor midway between Nos. 1 and 5. No. 2, or faint, is conceived as midway between Nos. 1 and 3; similarly No. 4, or strong, is conceived as midway between Nos. 3 and 5.

With this scale the observers recorded their impressions of odor intensities. They might not agree closely, but it is found that with a number of observers and taking averages of results of observations satisfactory measurements can be made.

In explanation of the scale of nasal irritations No. 1, or slight, is the threshold irritation, just perceptible, not painful; No. 3, or strong, is painful, exceedingly discomforting, yet it may be endured voluntarily by the observer; No. 2, or moderate, is midway between Nos. 1 and 3 and is very unpleasant; and No. 4, or intolerable, is exceedingly painful, so painful that it can not be voluntarily endured.

The scale of eye irritation is explained as above, but whereas a single inhalation sufficed to determine odor or nasal irritation, eye irritation was determined by exposing the eye for 10 seconds (estimated by counting) to an air stream bearing the chemical. It was permissible for an observer to wink involuntarily, provided that the eye was opened again. When the eye was closed involuntarily and could

not be opened in a few seconds, owing to painful irritation, the irritation was considered as degree No. 4.

It was necessary in all tests to distinguish between any mild sense of irritation due to the air current on the eye and the irritation due to effects of the chemical. This was readily done.

PROCEDURE IN TESTING

PRELIMINARY TRIALS

Before observations were made for record the operator of the odorimeter tested each material to determine how to adapt the odorimeter through the range of intensities represented by the scales of odors and irritations. These preliminary trials determined the kind of vaporizers to be used and the adjustments of air flow needed in the odorimeter, but no quantitative determinations of concentrations were made.

NUMBER OF OBSERVERS

As a rule, six observers, including the operator of the odorimeter, were employed to test the intensities of odors and irritants. The minimum number was four, throughout 1 test only with nitrobenzene, the first test made; in a few tests 5 observers were used, and in a few others 7 or more were employed. The maximum number was 14 on a test with butyl mercaptan, which, however, extended through three days; some subjects did not observe on more than one day. The operator of the odorimeter took part as an observer in 73 of the 74 tests. Another observer took part in 43 tests. Following this the numbers decreased, down to one test. Altogether, 55 persons acted as observers; 24 were members of the Bureau of Mines, and 31 were students of chemistry, medicine, or engineering.

A number of observers was found advisable because of considerable variations in the reactions of the individual observers to odors and irritants. The mean of impressions recorded by a large number gave a value representative of the average individual.

RECORDS

Each subject was given a blank form on which to record his observations. The paper was folded to conceal notations, and all results were secret till completion of a test. The observers noted any special effects or qualities observed from time to time. At the conclusion of the experiment, statements of the character of the odors and of physiological effects caused by the exposure were recorded. Records of time, rates of air flow in the odorimeter, and weights of the vaporizers were kept by the operator.

OPERATIONS

When the requisite vaporizer had been charged, weighed, and fixed to the apparatus the air flow was adjusted for the lowest concentration desired, the time recorded, and the operation continued eight minutes or longer to assure equilibrium in the apparatus, as judged by the operator before observations were made. Similar periods for equilibrium were allowed after each subsequent adjustment. Records of time and weight were again made at the conclusion of

any one rate of primary air flow. Sometimes, when vaporization was slow, the odorimeter was operated for hours before starting observations so as to increase the evaporation for precision in determining weight of vapor.

Usually, tests were started at concentrations at which no odor or irritation was observed. Each observer in turn lifted the cover on the small hood, placed his nose well into the glass nose piece and smelled with one inhalation; he then decided the intensity of the nasal irritation. A second inhalation at a later time was permissible, if desired, but seldom taken. To determine eye irritation, one eye was held open to the charged air stream at the glass nose piece for 10 seconds; the observer then recorded his determinations.

After a round of observations by the subjects and any repetitions desired the concentration was increased as deemed best by the operator, and observations were continued thus through the entire scale of intensities or to the limit permitted by the vapor pressure of the material.

CALCULATIONS

The concentrations of the odorous materials in the air were calculated as milligrams per liter of air-vapor mixture and as parts per million by volume, considering vapors as perfect gases.

The purest chemicals obtainable were mostly used. Sometimes pure chemicals were not available, or commercial materials were tried to compare their effects. When the impurities consisted of volatile materials which vaporized together with the chemical in question, errors resulted according to the amount of impurity vaporized. In some instances when mixtures of volatile materials were tried, the milligrams of vapor per liter were calculated, but parts per million were not determined. The data on the sensory effects of the chemicals in air were correlated graphically with the concentrations to derive the concentrations corresponding most nearly to each degree of the scales of odor or of irritation.

An example will show the method most readily. Test 2, with ethyl mercaptan, may be chosen because the greatest number of observations was made during this test. There were no irritations. All observations of the odor intensities are recorded in Table 1, and the average intensity at each concentration is indicated. These averages are plotted in Figure 4 (p. 29) against the corresponding concentrations on a logarithmic scale. A straight line along which the points fall closest as judged by eye is drawn on the chart. The intersections of this line with the respective lines of the unit intensities give the accepted concentrations for each degree. Discussion of further data in Table 1 follows later (p. 11).

Concentrations for the respective degrees of nasal and of eye irritation were determined likewise. Figure 3 shows the averages yielded by benzyl mercaptan in test 36 as an example of a material yielding nasal and eye irritations as well as odor.

TABLE 1.—Observations on intensities of the odors of ethyl mercaptan at various concentrations in test 2 (no irritations were reported)

Order of observation.....	1	2	3	4	5	6	7	8	9	10	18	19	11	20	12	21	13	22	14
Concentration of ethyl mercaptan, parts per million.....	0.000060	0.00012	0.00024	0.00048	0.00072	0.00096	0.0012	0.0039	0.012	0.035	0.052	0.095	0.13	0.19	0.27	0.37	0.56	0.75	1.2

ODOR INTENSITY

Observers:	0	0	0	0	0	1	1	2	2	3	2	2	3	2	3	3	3	3	3
A.....	0	1	1	1	1	1	1	2	2	3	2	2	3	2	3	3	3	3	3
B.....	0	0	0	0	0	0	0	1	2	3	1	2	3	3	2	2	4	3	4
C.....	1	1	1	1	1	1	1	0	2	0	2	2	2	3	2	2	2	4	2
D.....	0	1	1	1	1	1	1	2	0	0	2	2	1	2	1	2	3	3	3
E.....	0	2	2	2	2	0	2	2	2	2	2	2	2	2	2	2	2	2	2
Average.....	0.2	0.8	0.8	0.8	0.7	0.7	1.0	1.5	1.7	2.0	1.7	2.0	2.2	2.1	2.3	2.5	2.7	3.3	2.7

Order of observation.....	23	15	24	16	17	25	26	27	32	28	33	29	34	35	30	36	31	37	38
Concentration of ethyl mercaptan, parts per million.....	1.5	2.2	3.0	4.3	8.6	17	35	73	79	140	150	280	300	510	540	840	1,100	1,200	1,600
Observers:	3	3	3	3	3	4	5	4	5	5	4	5	4	4	4	4	5	4	5
A.....	3	4	3	4	4	3	3	4	4	4	4	4	5	5	5	5	5	5	5
B.....	4	3	3	3	3	4	4	4	5	4	4	3	4	5	3	4	3	4	4
C.....	3	2	4	2	2	3	3	3	4	3	4	4	4	5	4	5	4	5	5
D.....	3	2	4	2	2	3	3	3	4	4	4	4	4	5	4	4	4	5	5
E.....	3	3	4	3	4	4	4	4	4	4	4	4	4	4	4	4	5	5	5
F.....	2	2	2	2	3	4	4	4	4	4	4	4	4	4	4	4	5	5	5
Average.....	3.3	2.8	3.3	2.8	3.2	3.6	3.8	3.8	4.4	4.0	4.0	4.0	4.2	4.6	4.0	4.4	4.4	4.6	4.8

- Only two significant figures for concentration at the respective degrees of intensity are recorded, because precision in the sense of smell or irritation does not justify more or even such precision. However, for purposes of calculation it is desirable to record each two significant figures so that they conform with the other terms of their

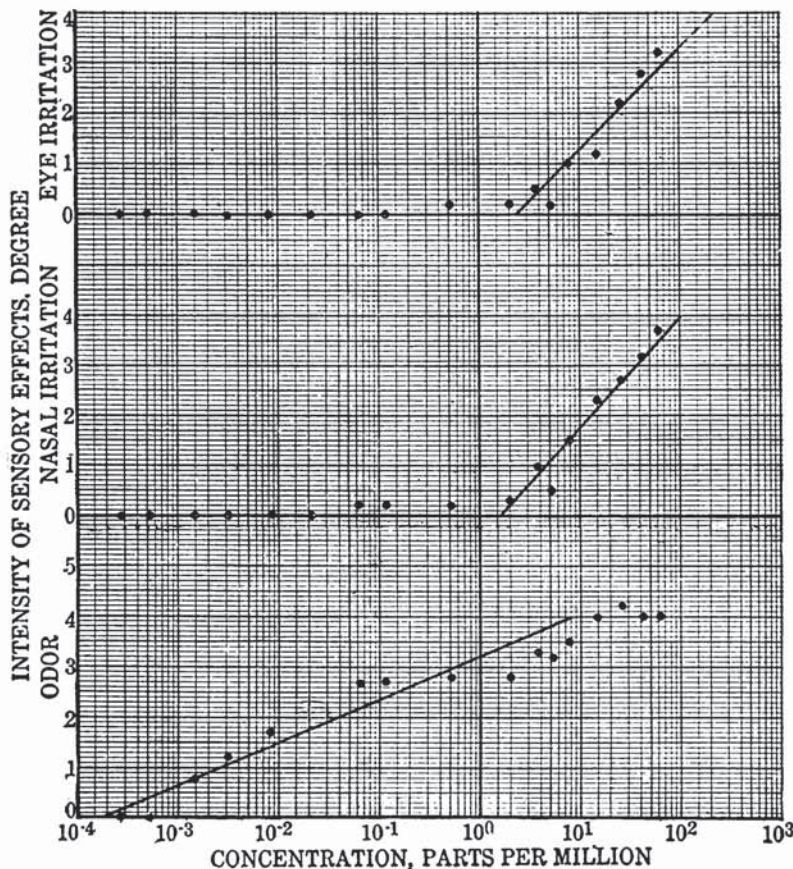


FIGURE 3.—Intensities of odors, nasal and eye irritations of benzyl mercaptan in test 36, showing averages of individual determinations

series. Two significant figures may not be read accurately from the small chart, but they may be computed according to the formula:

$$C_n = C_o f^n, \tag{1}$$

where

C_n = concentration giving degree of intensity n as 0, 1, 2, 3, 4, 5,

and

f = a factor called "concentration factor" and defined as the ratio between concentrations at any successive degrees of the scale; f is computed from

$$f = \left(\frac{C_5}{C_o} \right)^{1/5} \tag{2}$$

or in general

$$f = \left(\frac{C_n}{C_m} \right)^{\frac{1}{n-m}} \tag{3}$$

12 INTENSITIES OF ODORS AND EFFECTS OF WARNING AGENTS

C_n and C_m are read from the graph, and the intermediate terms are computed.

MATERIALS TESTED

Measurements with the odorimeter were made on 55 different materials obtained from commercial sources as far as possible. Some were prepared by J. B. Shohan and E. H. Perry of the Pittsburgh Experiment Station of the Bureau of Mines. The materials are listed in Table 2 in order of test. Their source and purity or properties are also indicated. Some crude materials were included for comparison with pure materials—phenyl isocyanide, for example.

SOURCE AND CHARACTER OF MATERIALS TESTED

TABLE 2.—Source and character of materials tested

Test No.	Material	Material No.	Source	Grade
1	Nitrobenzene	32	Fisher Scientific Co.	C. P.
2	Ethyl mercaptan	14-2	Mallinckrodt Chemical Co.	Pure.
3	N-Butyl mercaptan	33	Edgewood Arsenal	War gas.
4	Methyl sulphide	34-1	Champion Fiber Co.	Commercial.
5	Crotonaldehyde	35-1	Niacet Chemical Co.	Do.
6	Acrolein	36-1	Bureau of Mines	C. P.
7	Allyl amine	38	Eastman Kodak Co.	B. P. 52½°-53½° C.
8	Allyl alcohol	37	do.	B. P. 95½°-97° C.
9	Oxidized oils	39	J. H. James	Commercial.
10	Skatole	40	Van Dyk & Co.	Pure.
11	Thiophenol	41	Eastman Kodak Co.	B. P. 70° 71° C./15 mm.
12	Allyl isothiocyanate	42-1	Organo Chemical Co.	U. S. P.
13	Ethyl isothiocyanate	43	Eastman Kodak Co.	B. P. 129°-131° C.
14	Phenyl isothiocyanate	44	do.	B. P. 85°-86° C./12 mm.
15	Chloracetophenone	45-1	do.	M. P. 57° C.
16	Allyl isocyanide	19	Bureau of Mines	Crude.
17	Propargyl aldehyde	46	do.	B. P. 59°-67° C.
18	Chloracetophenone	45-1	See test 15.	
19	Allyl mercaptan	21-1	Bureau of Mines	B. P. 80°-100° C.
20	Crotyl mercaptan	20	do.	B. P. 90°-105° C.
21	Methyl thiocyanate	47	Eastman Kodak Co.	B. P. 130°-131° C.
22	Pyridine	48	J. T. Baker Co.	B. P. 113° C.
23	Phenyl isocyanide	2-2	Bureau of Mines	B. P. 60°-61° C./5 mm.
24	do.	2-3	do.	Crude.
25	Crotonaldehyde	35-2	Niacet Chemical Co.	"98°-99°"
26	Ethyl selenide	49	General Motors Corporation.	B. P. 103°-108° C.
27	Allyl sulphide	50	Eastman Kodak Co.	B. P. 140°-142° C.
28	Isoamyl mercaptan	51	do.	B. P. 116°-118° C.
29	Ethyl mercaptan	14-2	See test 2.	
30	P-Thio cresol	52	Eastman Kodak Co.	M. P. 41°-43° C.
31	Allyl mercaptan	21-2	Bureau of Mines	B. P. 80°-100° C.
32	N-Propyl mercaptan	53	Eastman Kodak Co.	B. P. 65.5°-67° C.
33	Chloracetophenone	45	See test 15.	
34	Ethyl sulphide	54	Eastman Kodak Co.	B. P. 92°-93° C.
35	Amyl acetate	55	Kahlbaum	C. P.
36	Benzyl mercaptan	56	Eastman Kodak Co.	B. P. 72°-75° C./9 mm.
37	N-Butyl sulphide	57	do.	B. P. 184°-187° C.
38	Isoamyl sulphide	58	do.	B. P. 97°-101° C./10 mm.
39	Bromacetophenone	59	do.	M. P. 49°-50° C.
40	Benzaldehyde	60	Fritzsche Bros.	"Pure."
41	Akrol	61	Pensacola Tar & Turpentine Co.	Commercial.
42	N-Butyl mercaptan	33	American University	War gas, redistilled.
43	Dithio ethylene glycol	43	Bureau of Mines	B. P. 141°-146° C.
44	Acetaldehyde	65	Niacet Chemical Co.	B. P. 20°-21° C.
45	Bisalpha dichlor diethyl sulphide.	45	Bureau of Mines	B. P. 64°-69° C./27 mm.
46	Methyl mercaptan	66	Eastman Kodak Co.	No specification obtained.
47	Benzyl sulphide	68	do.	M. P. 49°-50° C.
48	Ethyl seleno mercaptan	31	Bureau of Mines	B. P. 50°-54° C.
49	Ethyl mercaptan	14-2	See test 2.	
50	Chloracetophenone	45	See test 15.	
51	Ethyl mercaptan	14-2	See test 2.	
52	Chloracetophenone	45	See test 15.	
53	Pyridine	69	Barrett Co.	Crude.

TABLE 2.—Source and character of materials tested—Continued

Test No.	Material	Material No.	Source	Grade
54.....	Crotonaldehyde.....	35-2	See test 25.....	
55.....	do.....	35-2	do.....	
56.....	Hydrogen sulphide.....	70	Bureau of Mines.....	Crude.
57.....	Dimethyl trithio carbonate.....	10	do.....	Do.
58.....	Benzyl chloride.....	72	Van Dyk & Co.....	B. P. 174°-180° C./745 mm.
59.....	N-Propyl sulphide.....	73	Eastman Kodak Co.....	B. P. 142.5°-144° C.
60.....	Diphenyl ether.....	74	do.....	M. P. 26°-27° C.
61.....	Methyl anthranilate.....	86	do.....	M. P. 23°-24° C.
62.....	2:4:6 trinitrotertiarybutylxylene.	77	Unknown.....	M. P. 103°-105° C.
63.....	O-Chlorophenol.....	75	Eastman Kodak Co.....	B. P. 66°-67° C./10 mm.
64.....	Crotyl mercaptan.....	22-26	Bureau of Mines.....	B. P. 80° C.
65.....	2:4:6 trinitrotertiarybutylxylene.	77	See test 62.....	
66.....	Isoamyl isovalerate.....	76	Bureau of Mines.....	B. P. 68°-70° C./10 mm.
67.....	Diallyl disulphide.....	20	do.....	B. P. 95°-105° C./40 mm.
68.....	Diphenyl sulphide.....	79	Eastman Kodak Co.....	B. P. 151°-153° C./15 mm.
69.....	Coumarin.....	80	Merck & Co.....	M. P. 68°-70° C.
70.....	Methyl sulphide.....	34-2	Eastman Kodak Co.....	B. P. 38°-39° C.
71.....	Amylene.....	81	Bureau of Mines.....	Mixed isomers.
72.....	Beta butylene.....	78	do.....	99.7 per cent unsaturated hydrocarbon.
73.....	Gama butylene.....	82	do.....	97.1 per cent unsaturated hydrocarbon.
74.....	Alpha butylene.....	84	do.....	91.1 per cent unsaturated hydrocarbon.

NOTE.—C. P. = commercially pure; B. P. = boiling point; M. P. = melting point.

RESULTS OF MEASUREMENTS

Table 3 lists the concentrations of the materials in parts per million producing the several degrees of odor. The chemicals are grouped according to their classes; concentration factors are given in column 6. Similarly, Table 4 presents the nasal irritations and Table 5 the eye irritations. Tables 6, 7, and 8, expressed in milligrams per liter, correspond otherwise to Tables 3, 4, and 5.

The results of all tests performed are given without omission in Tables 6 to 8. No data were discarded. Tests 9, 24, 41, and 53, respectively, for oxidized oils, crude phenyl isocyanide, akrol, and crude pyridine appear only in Tables 6 to 8, with concentrations expressed as milligrams per liter, for the reason that these materials were mixtures of chemicals or were crude and impure preparations. The oxidized oils were obtained by the James¹⁰ process of catalytic oxidation of kerosene. The akrol was a commercial, light, mobile oil with acrid, empyumatic odor obtained in pine distillation.

The crude pyridine and phenyl isocyanide were contaminated with considerable portions of other volatile substances. The average concentrations of these materials expressed as milligrams per liter are accurate, but the compositions of the vapors were not necessarily the same as those of the liquid materials.

¹⁰ James, J. H., Some New Petroleum Products: Chem. and Met. Eng. vol 26 1922, pp. 209-212.

14 INTENSITIES OF ODORS AND EFFECTS OF WARNING AGENTS

INTENSITIES OF ODORS VERSUS CONCENTRATIONS IN PARTS PER MILLION

TABLE 3.—Intensities of odors versus concentrations, parts per million

Test No.	Material	Intensity of odor, degree						Dilution factor
		0	1	2	3	4	5	
<i>Hydrocarbons</i>								
74	Alpha butylene	0.060	0.92	14	210	3,300	² 50,000	15
72	Beta butylene	.17	2.1	26	330	4,000	² 50,000	12
73	Gamma butylene	.080	1.3	22	360	6,000	² 100,000	17
71	Amylene (mixed isomers)	.015	.19	2.3	29	360	² 4,500	12
<i>Alcohol</i>								
8	Allyl alcohol	.29	1.4	7.2	36	180-1,400	-----	5.0
<i>Esters</i>								
35	Isoamyl acetate	.000095	.0033	.11	3.8	130	4,500	34
66	Isoamyl isovalerate	.00040	.0066	.11	1.8	30	-----	17
61	Methyl anthranilate	.0015	.0094	.059	.37	² 2.3	-----	6.3
<i>Aldehydes</i>								
44	Acetaldehyde	.0020	.066	2.2	73	2,400	² 80,000	33
40	Benzaldehyde	.0025	.042	.71	12	200	-----	17
6	Acrolein	.19	1.8	17	160	² 1,500	-----	9.4
5	Crotonaldehyde (commercial)	.63	3.5	20	110	² 630	-----	5.6
54	Crotonaldehyde	.010	.062	.39	2.4	15	-----	6.2
25	do.	.018	.20	2.3	26	² 290	-----	11
55	do. ¹	-----	-----	-----	50	-----	-----	-----
17	Propargyl aldehyde	.025	.16	1.0	6.8-450	-----	-----	6.5
<i>Amine</i>								
7	Allyl amine	1.3	6.2	29	140	650	3,100	4.7
<i>Isocyanides</i>								
23	Phenyl isocyanide	.00010	.0010	.010	.11	1.1	11	10
16	Allyl isocyanide	.0020	.018	.16	1.4	12	110	8.9
<i>Nitro compounds</i>								
1	Nitrobenzene	.62	1.9	5.9	18	55	170	3.1
65	2:4:6 Trinitrotertiarybutylxylene (artificial musk)	.0000030	.000051	.00088	.015	-----	-----	17
62	do.	.00000030	.0000065	.00014	.0030	-----	-----	22
<i>Cyclic nitrogen compounds, carbon, hydrogen, and nitrogen</i>								
22	Pyridine	.025	.23	2.0	18	170	1,500	9.0
10	Skatole	.0016	.019	.23	2.8	-----	-----	12
<i>Miscellaneous carbon, hydrogen and oxygen compounds</i>								
60	Diphenyl ether	.00010	.0010	.010	.10	1.0	10	10
69	Coumarin	.00020	.0033	.055	.90	-----	-----	17
<i>Mercaptans</i>								
46	Methyl mercaptan	.0030	.041	.57	7.9	110	1,500	14
2	Ethyl mercaptan	.000021	.00097	.045	2.1	97	4,500	46
29	do.	.0000060	.00026	.011	.49	21	920	43
49	do.	.00010	.0030	.088	2.6	78	2,300	30
51	do. ³	² .00030	² .0070	.16	3.8	90	2,100	23
32	N-Propyl mercaptan	.00011	.0016	.024	.36	5.4	81	15
3	N-Butyl mercaptan (war gas)	.0027	.048	.84	15	260	4,600	18
42	N-Butyl mercaptan	.000045	.0010	.022	.50	11	250	22
28	Isoamyl mercaptan	.000022	.00043	.0083	.16	3.1	60	19
36	Benzyl mercaptan	.00018	.0026	.038	.55	8.0	-----	15
43	Dithio ethylene glycol	.0023	.031	.41	5.6	75	1,000	13
11	Thiophenol	.0000050	.00026	.014	.72	38	2,000	52

¹ Starting with No. 2 or moderate eye irritation.

² Extrapolated value.

³ Starting with No. 2 or faint odor.

TABLE 3.—Intensities of odors versus concentrations, parts per million—Continued

Test No.	Material	Intensity of odor, degree					Dilution factor
		0	1	2	3	4	
<i>Mercaptans—Continued</i>							
30	P-Thiocresol	0.00035	0.0027	0.020	0.16	1.2-280	7.6
19	Allyl mercaptan	.00046	.0015	.0047	.015	3.6	3.2
31	do	.0012	.0059	.029	.14	.70	4.9
20	Crotyl mercaptan	.0000030	.00012	.0048	.19	7.6-120	40
64	do	.000015	.00040	.011	.28	7.6	27
<i>Thioethers, polysulphide, and thioester</i>							
56	Hydrogen sulphide	.022	.13	.77	4.6	27	5.9
4	Methyl sulphide (commercial)	.0010	.027	.73	20	530	14,000
70	Methyl sulphide	.00016	.0037	.084	1.9	44	1,000
34	Ethyl sulphide	.00011	.0028	.069	1.7	44	1,100
59	N-Propyl sulphide	.00070	.011	.17	2.5	39	600
37	N-Butyl sulphide	.0012	.015	.19	2.6	31	400
38	Isoamyl sulphide	.00021	.0030	.044	.63	9.0	130
47	Benzyl sulphide	.00050	.0060	.071	.85		12
68	Diphenyl sulphide	.00018	.00034	.0064	.12	2.3	43
27	Allyl sulphide	.0000020	.00014	.010	.71	50	3,600
67	Allyl disulphide	.000080	.0012	.17	.24	3.5	50
57	Dimethyl trithiocarbonate	.00085	.0058	.40	.28	1.9	13
<i>Thiocyanate and isothiocyanates</i>							
21	Methyl thiocyanate	.019	.25	3.2	42	540	7,000
13	Ethyl isothiocyanate	.27	1.7	11	68	430	6.3
14	Phenyl isothiocyanate	.020	.094	.44	2.1-64		4.7
12	Allyl isothiocyanate	.054	.15	.42	1.2-94		2.8
<i>Halogenated hydrocarbon</i>							
58	Benzyl chloride	.0050	.040	.32	2.6	21	170
<i>Halogenated ketones</i>							
39	Bromacetophenone	.0027	.015	.082	.45		5.5
15	Chloracetophenone	.0045	.016	.059	.21	1.77	3.6
18	do. ⁴	.0020	.11	6.2			56
33	do. ⁵	.010	.051	.26	1.3		5.1
50	do	.0031	.028	.25	2.3		9.1
52	do	.014	.039	.11	.30	1.84	2.8
<i>Halogenated phenol</i>							
63	O-Chlorphenol	.00040	.0036	.033	.30	2.7	25
<i>Halogenated thioether</i>							
45	Bisalpha dichlorethyl sulphide	.00020	.0023	.026	.30	3.5	40
<i>Seleno mercaptan and seleno ether</i>							
48	Ethyl seleno mercaptan	.000023	.00030	.0038	.050	.64	8.3
26	Ethyl selenide	.00012	.0012	.011	.11	1.0	10

¹ Extrapolated value.⁴ 60-second exposure with face in a wooden box.⁵ 10-second exposure with face in a wooden box.

6168°—30—3

INTENSITIES OF NASAL IRRITATION VERSUS CONCENTRATIONS IN PARTS PER MILLION

TABLE 4.—Intensities of nasal irritation versus concentrations, parts per million

Test No.	Material	Intensity of nasal irritation, degree					Concentration factor
		0	1	2	3	4	
<i>Hydrocarbons</i>							
74.....	Alpha butylene.....			None.			
72.....	Beta butylene.....			None.			
73.....	Gamma butylene.....			None.			
71.....	Amylene (mixed isomers).....			None.			
<i>Alcohol</i>							
8.....	Allyl alcohol.....	11	30	82	230	620	2.7
<i>Esters</i>							
35.....	Isoamyl acetate.....			None.			
66.....	Isoamyl isovalerate.....			None.			
61.....	Methyl anthranilate.....			None.			
<i>Aldehydes</i>							
44.....	Acetaldehyde.....	440	2,200	11,000	² 55,000		5.0
40.....	Benzaldehyde.....	1.1	23	480			21
6.....	Acrolein.....	2.8	11	45	180		4.0
5.....	Crotonaldehyde (commercial).....	14	36	93	240		2.6
54.....	Crotonaldehyde.....	5.0	13	33	85	220	2.6
25.....	do.....	2.5	8	25	81	260	3.2
53.....	do. ¹	² 15	² 28	51	93	170	1.8
17.....	Propargyl aldehyde.....	3.1	11	37	130	450	3.5
<i>Amine</i>							
7.....	Allyl amine.....	18	80	360	1,600		4.5
<i>Isocyanides</i>							
23.....	Phenyl isocyanide.....		³ 13				
16.....	Allyl isocyanide.....	0.11	110				
<i>Nitro compounds</i>							
1.....	Nitrobenzene.....		44.9				
65.....	2 : 4 : 6 Trinitrotertiarybutylxylene (artificial musk).....		None.				
62.....	do.....		None.				
<i>Miscellaneous carbon, hydrogen, and oxygen compounds</i>							
60.....	Diphenyl ether.....		None.				
69.....	Coumarin.....		None.				
<i>Cyclic nitrogen compounds, carbon, hydrogen, nitrogen</i>							
22.....	Pyridine.....	17	² 22,000				
10.....	Skatole.....		None.				
<i>Mercaptans</i>							
46.....	Methyl mercaptan.....		None.				
2.....	Ethyl mercaptan.....		None.				
29.....	do.....		None.				
49.....	Ethyl mercaptan.....		³ 3,500				
51.....	do.....		⁵ 2,100				
32.....	N-Propyl mercaptan.....		None.				
3.....	N-Butyl mercaptan (war gas).....		⁴ 576				
42.....	N-Butyl mercaptan.....		None.				
28.....	Isoamyl mercaptan.....		None.				
36.....	Benzyl mercaptan.....	1.6	4.5	13	36	100	2.8
43.....	Dithio ethylene glycol.....		None.				
11.....	Thiophenol.....	0.4	85				

¹ Starting with No. 2 or moderate eye irritation.² Extrapolated value.³ Irritation reported by two observers.⁴ Irritation reported by three observers.⁵ Irritation reported by one observer.

TABLE 4.—*Intensities of nasal irritation versus concentrations, parts per million—Continued*

Test No.	Material	Intensity of nasal irritation, degree					Concentration factor
		0	1	2	3	4	
30.....	P-Thiocresol.....	24	170	² 1, 200			
19.....	Allyl mercaptan.....		⁵ 150				
31.....	do.....	7.8	84				
20.....	Crotyl mercaptan.....		None.				
64.....	do.....	4.0	² 1, 300				
	<i>Thioethers, polysulphide, and thioester</i>						
56.....	Hydrogen sulphide.....		None.				
4.....	Methyl sulphide (commercial).....		³ 6, 200				
70.....	Methyl sulphide.....		None.				
34.....	Ethyl sulphide.....		None.				
59.....	N-Propyl sulphide.....		⁵ 580				
37.....	N-Butyl sulphide.....		None.				
38.....	Isoamyl sulphide.....		None.				
47.....	Benzyl sulphide.....		None.				
68.....	Diphenyl sulphide.....		None.				
27.....	Allyl sulphide.....		⁴ 1, 400				
67.....	Allyl disulphide.....	15	100				
57.....	Dimethyl trithiocarbonate.....		None.				
	<i>Thiocyanate and isothiocyanates</i>						
21.....	Methyl thiocyanate.....	190	990	5, 200			5. 2
13.....	Ethyl isothiocyanate.....	12	36	110	330	990	3. 0
14.....	Phenyl isothiocyanate.....	4. 7	20	87			4. 3
12.....	Allyl isothiocyanate.....	1. 7	7. 0	29	120	² 480	4. 1
	<i>Halogenated hydrocarbon</i>						
58.....	Benzyl chloride.....	6. 0	35	² 200			
	<i>Halogenated ketones</i>						
39.....	Bromacetophenone.....	. 023	. 066	. 19	. 55	1. 6	2. 9
15.....	Chloracetophenone.....	. 0056	. 021	. 082	. 31	² 1. 2	3. 8
18.....	do. ⁶ 0016	. 012	. 084	. 61	4. 4	7. 2
33.....	do. ⁷ 027	. 070	. 18	. 46	1. 2	2. 6
50.....	do.....	. 021	. 044	. 092	. 19	. 40	2. 1
52.....	do. ¹	² . 027	. 056	. 12	. 24	. 51	2. 1
	<i>Halogenated phenol</i>						
63.....	O-Chlorphenol.....	7. 0	² 1, 500				
	<i>Halogenated thioether</i>						
45.....	Bis alpha dichlorethyl sulphide.....	2. 1	14	100			6. 9
	<i>Seleno mercaptan and seleno ether</i>						
48.....	Ethyl seleno mercaptan.....		None.				
26.....	Ethyl selenide.....		None.				

¹ Starting with No. 2 or moderate eye irritation.² Extrapolated value.³ Irritation reported by two observers.⁴ Irritation reported by three observers.⁵ Irritation reported by one observer.⁶ 60-second exposure with face in a wooden box.⁷ 10-second exposure with face in a wooden box.

18 INTENSITIES OF ODORS AND EFFECTS OF WARNING AGENTS

INTENSITIES OF EYE IRRITATION VERSUS CONCENTRATIONS IN PARTS PER MILLION

TABLE 5.—Intensities of eye irritation versus concentrations, parts per million

Test No.	Material	Intensity of eye irritation, degree					Concentration factor ^a
		0	1	2	3	4	
<i>Hydrocarbons</i>							
74	Alpha butylene		None.				
72	Beta butylene		None.				
73	Gamma butylene		None.				
71	Amylene (mixed isomers)		None.				
<i>Alcohol</i>							
8	Allyl alcohol	21	59	170	460	1,300	2.8
<i>Esters</i>							
35	Isoamyl acetate		720				
66	Isoamyl isovalerate		None.				
61	Methyl anthranilate		None.				
<i>Aldehydes</i>							
44	Acetaldehyde	2,200	11,000	² 58,000			5.1
40	Benzaldehyde	0.45	3.8	33	280		8.5
6	Acrolein	3.9	12	38	120		3.1
5	Crotonaldehyde (commercial)	5.9	22	79	290		3.7
54	Crotonaldehyde	6.0	16	41	110	280	2.6
25	do.	4.9	13	35	94	250	2.7
55	do. ¹	² 20	34	58	100	170	1.7
17	Propargyl aldehyde	4.5	11	28	72	180	2.5
<i>Amine</i>							
7	Allyl amine	40	140	490	1,700		3.5
<i>Isocyanides</i>							
23	Phenyl isocyanide		³ 3.4				
16	Allyl isocyanide	.010	6.3	4,000			630
<i>Nitro compounds</i>							
1	Nitrobenzene		None.				
65	2:4:6 Trinitrotertiarybutylxylene (artificial musk)		None.				
62	do.		None.				
<i>Cyclic nitrogen compounds, carbon, hydrogen, and nitrogen</i>							
22	Pyridine	190	490	1,300	3,300	⁴ 8,400	2.6
10	Skatole		None.				
<i>Miscellaneous carbon, hydrogen, and oxygen compounds</i>							
60	Diphenyl ether		None.				
69	Coumarin		None.				
<i>Mercaptans</i>							
46	Methyl mercaptan		None.				
2	Ethyl mercaptan		None.				
29	do.		None.				
49	do.		⁶ 13,000				
51	do.		None.				
32	N-Propyl mercaptan		None.				
3	N-Butyl mercaptan (war gas)		None.				
42	N-Butyl mercaptan		None.				
28	Isoamyl mercaptan		None.				
36	Benzyl mercaptan	2.4	7.5	24	74	230	3.1
43	Dithio ethylene glycol		840				
11	Thiophenol	18	45	110	250	580	2.4

¹ Starting with No. 2 or moderate eye irritation.

² Extrapolated value.

³ Irritation reported by two observers.

⁶ Irritation reported by three observers.

TABLE 5.—Intensities of eye irritation versus concentrations, parts per million—Con.

Test No.	Material	Intensity of eye irritation, degree					Concentration factor
		0	1	2	3	4	
<i>Mercaptans—Continued</i>							
30	P-Thiocresol	54	93	160	280	480	1.7
19	Allyl mercaptan		⁵ 150				
31	do	32	140				
20	Crotyl mercaptan		None.				
64	do		⁶ 350				
<i>Thioethers, polysulphide, and thioester</i>							
56	Hydrogen sulphide		None.				
4	Methyl sulphide (commercial)		⁴ 6,200	³ 24,000			
70	Methyl sulphide		⁵ 8,800				
34	Ethyl sulphide		None.				
59	N-Propyl sulphide		None.				
37	N-Butyl sulphide		None.				
38	Isoamyl sulphide		None.				
47	Benzyl sulphide		None.				
68	Diphenyl sulphide		None.				
27	Allyl sulphide		⁴ 1,400				
67	Allyl disulphide	1.2	6.4	34	180		5.3
57	Dimethyl trithio carbonate		None.				
<i>Thiocyanate and isothiocyanates</i>							
21	Methyl thiocyanate	59	160	430	1,200	3,100	2.7
13	Ethyl isothiocyanate	8.3	19	43	97	220	2.3
14	Phenyl isothiocyanate	1.6	10	62			6.2
12	Allyl isothiocyanate	.95	4.2	19	83	² 370	4.4
<i>Halogenated hydrocarbon</i>							
58	Benzyl chloride	3.7	8.0	17.0	37	80	2.2
<i>Halogenated ketones</i>							
39	Bromacetophenone	.016	.038	.090	.21	.51	2.4
15	Chloracetophenone	.0041	.0083	.017	.034	.068	2.0
18	do. ⁷	.0051	.020	.078	.31	1.2	3.9
33	do. ⁸	.017	.043	.11	.28	.70	2.5
50	do	.0090	.018	.038	.078	.16	2.1
52	do. ¹	¹ .025	¹ .036	.052	.076	.11	1.4
<i>Halogenated phenol</i>							
63	O-Chlorphenol	6.0	130				
<i>Halogenated thioether</i>							
45	Bis alpha dichloro ethyl sulphide.	2.0	4.6	11	24	56	2.3
<i>Seleno mercaptan and seleno ether</i>							
48	Ethyl seleno mercaptan		None.				
26	Ethyl selenide		None.				

¹ Starting with No. 2 or moderate eye irritation.² Extrapolated value⁴ Irritation reported by four observers.⁵ Irritation reported by one observer.⁶ Irritation reported by three observers.⁷ 60-second exposure with face in a wooden box.⁸ 10-second exposure with face in a wooden box.

INTENSITIES OF ODORS VERSUS CONCENTRATIONS IN MILLIGRAMS PER LITER

TABLE 6.—Intensities of odors versus concentrations, milligrams per liter

Test No.	Material	Intensity of odors, degree					
		0	1	2	3	4	5
<i>Hydrocarbons</i>							
74	Alpha butylene	0.0014	0.0021	0.032	0.48	7.6	² 110
72	Beta butylene	.00039	.0048	.060	.76	9.2	² 110
73	Gamma butylene	.00018	.0030	.050	.83	14	² 230
71	Amylene (mixed isomers)	.000043	.00054	.0066	.083	1.0	² 13
<i>Alcohol</i>							
8	Allyl alcohol	.00069	.0033	.017	.085	.43-3.3	-----
<i>Esters</i>							
35	Isoamyl acetate	.0000051	.000018	.00059	.020	.69	24
66	Isoamyl isovalerate	.0000028	.000046	.00077	.013	.21	-----
61	Methyl anthranilate	.0000093	.000058	.00036	.0023	² .014	-----
<i>Aldehydes</i>							
44	Acetaldehyde	.0000036	.00012	.0040	.13	4.3	² 140
40	Benzaldehyde	.000011	.00018	.0031	.052	.87	-----
6	Acrolein	.00044	.0041	.039	.37	² 3.4	-----
5	Crotonaldehyde (commercial)	.0018	.010	.057	.31	² 1.8	-----
54	Crotonaldehyde	.000029	.00018	.0011	.0069	.043	-----
25	do.	.000051	.00057	.0066	.074	-----	-----
55	do. ¹	-----	-----	-----	14	-----	-----
17	Propargyl aldehyde	.000055	.00035	.0022	.015-.99	-----	-----
<i>Amine</i>							
7	Allyl amine	.0030	.014	.068	.33	1.5	7.2
<i>Isocyanides</i>							
23	Phenyl isocyanide	.0000042	.0000042	.000042	.00046	.0046	.046
24	Phenyl isocyanide (crude)	.0000013	.000014	.00016	.0018	.0020	.022
16	Allyl isocyanide	.0000055	.000049	.00044	.0038	.033	.30
<i>Nitro compounds</i>							
1	Nitrobenzene	.0031	.0096	.030	.091	.28	.86
65	2:4:6 trinitrotertiarybutyl- xylene (artificial musk)	.000000035	.00000059	.000010	.00017	-----	-----
62	do.	.000000035	.00000075	.000016	.000035	-----	-----
<i>Cyclic nitrogen compounds, carbon, hydrogen, and nitrogen</i>							
22	Pyridine	.000081	.00074	.0065	.058	.55	4.8
53	Pyridine (crude)	.0000090	.00010	.0011	.012	.14	1.5
10	Skatole	.0000086	.00010	.0012	.014	-----	-----
<i>Miscellaneous carbon, hydrogen, and oxygen compounds</i>							
60	Diphenyl ether	.0000070	.000070	.00070	.00070	.0070	.070
69	Coumarin	.0000012	.000020	.00033	.0054	-----	-----
9	Oxidized oils	.0000072	.000088	.0011	.013	.16	-----
41	Akrol	.0000050	.00013	.0033	.085	2.2	-----
<i>Mercaptans</i>							
46	Methyl mercaptan	.0000059	.000081	.0011	.016	.22	3.0
2	Ethyl mercaptan	.00000053	.000025	.00011	.0053	.25	11
29	do.	.00000015	.0000066	.000028	.0012	.053	2.3
49	do.	.0000025	.000076	.00022	.0066	.20	5.8
51	do. ³	² .0000076	² .000018	.00041	.0097	.23	5.3

¹ Starting with No. 2 or moderate eye irritation.² Extrapolated value.³ Starting with No. 2 or faint odor.

TABLE 6.—*Intensities of odors versus concentrations, milligrams per liter—Continued*

Test No.	Material	Intensity of odors, degree					
		0	1	2	3	4	5
<i>Mercaptans—Continued</i>							
32	N-Propyl mercaptan	0.0000034	0.0000050	0.000075	0.0011	0.017	0.25
3	N-Butyl mercaptan (war gas)	.0000099	.00018	.0031	.055	.96	17
42	N-Butyl mercaptan	.0000017	.0000037	.000081	.0018	.040	.92
28	Isoamyl mercaptan	.00000094	.0000018	.000035	.00068	.013	.26
36	Benzyl mercaptan	.00000090	.000013	.00019	.0028	.041	-----
43	Dithio ethylene glycol	.0000089	.00012	.0016	.022	.29	3.9
11	Thiophenol	.00000023	.0000012	.000063	.0032	.17	9.0
30	P-Thiocresol	.0000018	.000014	.00010	.00081	.0061-1.4	-----
19	Allyl mercaptan	.0000014	.0000045	.000014	.000045	.011	-----
31	do	.0000036	.000018	.000088	.00042	.0021	² 1.8
20	Crotlyl mercaptan	.00000011	.00000043	.000017	.00069	.027-4.3	-----
64	do	.00000054	.0000014	.000040	.0010	.027	.72
<i>Thioethers, polysulphide, and thioester</i>							
56	Hydrogen sulphide	.000031	.00018	.0011	.0064	.038	-----
4	Methyl sulphide (commercial)	.0000025	.000069	.0019	.051	1.3	36
70	Methyl sulphide	.0000041	.0000094	.00021	.0048	.11	2.5
34	Ethyl sulphide	.00000041	.000010	.00025	.0063	.16	4.1
59	N-Propyl sulphide	.0000034	.000053	.00082	.012	.19	2.9
37	N-Butyl sulphide	.0000072	.000090	.0011	.016	.19	2.4
38	Isoamyl sulphide	.0000015	.000021	.00031	.0045	.064	.93
47	Benzyl sulphide	.0000044	.000053	.00062	.0074	-----	-----
68	Diphenyl sulphide	.0000014	.000026	.000049	.00091	.018	² .33
27	Allyl sulphide	.000000093	.00000065	.000047	.0033	.23	17
67	Allyl disulphide	.00000048	.0000072	.00010	.0014	.021	.30
57	Dimethyl trithiocarbonate	.0000048	.000033	.00023	.0016	.011	² .073
<i>Thiocyanate and isothiocyanates</i>							
21	Methyl thiocyanate	.000057	.00075	.0096	.13	1.6	21
13	Ethyl isothiocyanate	.00096	.0061	.039	.24	1.5	-----
14	Phenyl isothiocyanate	.00011	.00052	.0024	.012-35	-----	-----
12	Allyl isothiocyanate	.00022	.00061	.0017	.0049-38	-----	-----
<i>Halogenated hydrocarbon</i>							
58	Benzyl chloride	.000026	.00021	.0017	.013	.11	² .88
<i>Halogenated ketones</i>							
39	Bromacetophenone	.000022	.00012	.00067	.0037	-----	-----
15	Chloracetophenone	.000028	.00010	.00037	.0013	² .0049	-----
18	do. ⁴	.000013	.00070	.039	-----	-----	-----
33	do. ⁵	.000063	.00032	.0016	.0082	-----	-----
50	do	.000020	.00018	.0016	² .015	-----	-----
52	do. ¹	² .000088	.00025	.00070	.0019	² .0053	-----
<i>Halogenated phenol</i>							
63	O-Chlorphenol	.0000021	.000019	.00017	.0016	.014	.13
<i>Halogenated thioether</i>							
45	Bis alpha dichloro ethyl sulphide	.0000013	.000015	.00017	.0020	.023	.26
<i>Seleno mercaptan and seleno ether</i>							
48	Ethyl seleno mercaptan	.000000010	.00000013	.0000017	.000022	.00029	.0037
26	Ethyl selenide	.00000067	.0000067	.000062	.00062	.0056	.056

¹ Starting with No. 2 or moderate eye irritation.² Extrapolated value.⁴ 60-second exposure with face in a wooden box.⁵ 10-second exposure with face in a wooden box.

INTENSITIES OF NASAL IRRITATION VERSUS CONCENTRATIONS IN MILLIGRAMS PER LITER

TABLE 7.—Intensities of nasal irritation versus concentrations, milligrams per liter

Test No.	Material	Intensity of nasal irritation, degree				
		0	1	2	3	4
<i>Hydrocarbons</i>						
74	Alpha butylene		None.			
72	Beta butylene		None.			
73	Gamma butylene		None.			
71	Amylene (mixed isomers)		None.			
<i>Alcohol</i>						
8	Allyl alcohol	0.026	0.071	0.19	0.55	1.5
<i>Esters</i>						
35	Isoamyl acetate		None.			
66	Isoamyl isovalerate		None.			
61	Methyl anthranilate		None.			
<i>Aldehydes</i>						
44	Acetaldehyde	.79	4.0	20	² 99	
40	Benzaldehyde	.0048	.10	2.1		
6	Acrolein	.0064	.025	.10	.41	
5	Crotonaldehyde (commercial)	.040	.10	.27	.69	
54	Crotonaldehyde	.014	.037	.094	.24	.63
25	do	.0072	.023	.072	.23	.74
55	do. ¹	² .043	² .080	.15	.27	.49
17	Propargyl aldehyde	.0068	.024	.082	.29	.99
<i>Amine</i>						
7	Allyl amine	.042	.19	.84	3.7	
<i>Isocyanides</i>						
23	Phenyl isocyanide		³ .055			
24	Phenyl isocyanide (crude)		None.			
16	Allyl isocyanide	.00030	.30			
<i>Nitro compounds</i>						
1	Nitrobenzene		.23			
65	2:4:6 Trinitrotertiarybutylxylene		None.			
62	do		None.			
<i>Cyclic nitrogen compounds, carbon, hydrogen, and nitrogen</i>						
22	Pyridine	.055	² .71			
53	Pyridine (crude)		None.			
10	Skatole		None.			
<i>Miscellaneous carbon, hydrogen, and oxygen compounds</i>						
60	Diphenyl ether		None.			
69	Coumarin		None.			
9	Oxidized oils		³ .67			
41	Akrol		³ 9.8			
<i>Mercaptans</i>						
46	Methyl mercaptan		None.			
2	Ethyl mercaptan		None.			
29	do		None.			
49	do		³ 8.9			
51	do		⁴ 5.3			
32	N-Propyl mercaptan		None.			
3	N-Butyl mercaptan (war gas)		⁵ 2.1			
42	N-Butyl mercaptan		None.			
28	Isoamyl mercaptan		None.			

¹ Starting with No. 2 or moderate eye irritation.² Extrapolated value.³ Irritation reported by two observers.⁴ Irritation reported by one observer.⁵ Irritation reported by three observers.

TABLE 7.—Intensities of nasal irritation versus concentrations, milligrams per liter—
Continued

Test No.	Material	Intensity of nasal irritation, degree				
		0	1	2	3	4
<i>Mercaptans—Continued</i>						
36	Benzyl mercaptan	.0081	0.023	0.066	0.18	0.51
43	Dithio ethylene glycol		None.			
11	Thiophenol	.0018	.38			
30	P-Thiocresol	.12	.86	² 6.1		
19	Allyl mercaptan		⁴ 4.5			
31	do.	.024	.25			
20	Crotyl mercaptan		None.			
64	do.	.014	² 4.7			
<i>Thioethers, polysulphide, and thioester</i>						
56	Hydrogen sulphide		None.			
4	Methyl sulphide (commercial)		³ 16			
70	Methyl sulphide		None.			
34	Ethyl sulphide		None.			
59	N-Propyl sulphide		⁴ 2.8			
37	N-Butyl sulphide		None.			
38	Isoamyl sulphide			None.		
47	Benzyl sulphide			None.		
68	Diphenyl sulphide			None.		
27	Allyl sulphide		⁵ 6.5			
67	Allyl disulphide	.09	.60			
57	Dimethyl trithiocarbonate			None.		
<i>Thiocyanate and isothiocyanates</i>						
21	Methyl thiocyanate	.57	3.0	16		
13	Ethyl isothiocyanate	.043	.13	.39	1.2	3.2
14	Phenyl isothiocyanate	.026	.11	.48		
12	Allyl isothiocyanate	.0069	.028	.12	.49	1.9
<i>Halogenated hydrocarbon</i>						
58	Benzyl chloride	.031	.18	¹ 1.0		
<i>Halogenated ketones</i>						
39	Bromacetophenone	.00019	.00054	.0015	.0045	.013
15	Chloracetophenone	.000035	.00013	.00052	.0020	² .0076
18	do. ⁶	.000010	.000076	.00053	.0039	.028
33	do. ⁷	.00017	.00044	.0011	.0029	.0076
50	do.	.00013	.00028	.00058	.0012	.0025
52	do. ¹	² .00017	.00035	.00076	.0015	.0032
<i>Halogenated phenol</i>						
63	O-Chlorphenol	.037	¹ 7.9			
<i>Halogenated thioether</i>						
45	Bis alpha dichlorethyl sulphide	.014	.091	.65		
<i>Seleno mercaptan and seleno ether</i>						
48	Ethyl seleno mercaptan			None.		
26	Ethyl selenide			None.		

¹ Starting with No. 2 or moderate eye irritation.² Extrapolated value.³ Irritation reported by two observers.⁴ Irritation reported by one observer.⁵ Irritation reported by three observers.⁶ 60-second exposure with face in a wooden box.⁷ 10-second exposure with face in a wooden box.

24 INTENSITIES OF ODORS AND EFFECTS OF WARNING AGENTS

INTENSITIES OF EYE IRRITATION VERSUS CONCENTRATIONS IN MILLI-GRAMS PER LITER

TABLE 8.—Intensities of eye irritation versus concentrations in milligrams per liter

Test No.	Material	Intensity of eye irritation, degree				
		0	1	2	3	4
<i>Hydrocarbons</i>						
74	Alpha butylene		None.			
72	Beta butylene		None.			
73	Gamma butylene		None.			
71	Amylene (mixed isomers)		None.			
<i>Alcohol</i>						
8	Allyl alcohol	0.050	.14	0.40	1.1	3.1
<i>Esters</i>						
35	Isoamyl acetate		3.9			
66	Isoamyl isovalerate		None.			
61	Methyl anthranilate		None.			
<i>Aldehydes</i>						
44	Acetaldehyde	4.0	20.	¹ 100		
40	Benzaldehyde	.0020	.016	.14	1.2	
6	Acrolein	.0089	.027	.087	.27	
5	Crotonaldehyde (commercial)	.017	.063	.23	.83	
54	Crotonaldehyde	.017	.046	.12	.31	.80
25	do	.014	.037	.10	.27	.72
55	do ¹	² .057	.097	.17	.29	.49
17	Propargyl aldehyde	.0099	.024	.062	.16	.40
<i>Amine</i>						
7	Allyl amine	.093	.33	1.1	4.0	
<i>Isocyanides</i>						
23	Phenyl isocyanide		⁵ .014			
24	Phenyl isocyanide (crude)			None.		
16	Allyl isocyanide	.000027	.017	11		
<i>Nitro compounds</i>						
1	Nitrobenzene			None.		
65	2:4:6 Trinitrotertiarybutylxylene (artificial musk)			None.		
62	do			None.		
<i>Cyclic nitrogen compounds, carbon, hydrogen, and nitrogen</i>						
22	Pyridine	0.61	1.6	4.2	11	² 27
53	Pyridine (crude)			None.		
10	Skatole			None.		
<i>Miscellaneous carbon, hydrogen, and oxygen compounds</i>						
60	Diphenyl ether			None.		
69	Coumarin			None.		
9	Oxidized oils		³ .67			
41	Akrol		9.8			
<i>Mercaptans</i>						
46	Methyl mercaptan			None.		
2	Ethyl mercaptan			None.		
29	do			None.		
49	do		³ 33			
51	do			None.		
32	N-Propyl mercaptan			None.		
3	N-Butyl mercaptan (war gas)			None.		
42	N-Butyl mercaptan			None.		

¹ Starting with No. 2 or moderate eye irritation.
² Extrapolated value.
³ Irritation reported by three observers.
⁵ Irritation reported by two observers.

TABLE 8.—Intensities of eye irritation versus concentrations in milligrams per liter—Continued

Test No.	Material	Intensity of eye irritation, degree				
		0	1	2	3	4
<i>Mercaptans—Continued</i>						
28	Isoamyl mercaptan.....			None.		
36	Benzyl mercaptan.....	.012	.038	.12	.38	1.2
43	Dithio ethylene glycol.....		3.2			
11	Thiophenol.....	.081	.20	.50	1.1	2.6
30	P-Thiocresol.....	.27	.47	.81	1.4	2.4
19	Allyl mercaptan.....		⁴ .45			
31	do.....	.097	.42			
20	Crotyl mercaptan.....			None.		
64	do.....	.029	³ 1.2			
<i>Thioethers, polysulphide, and thioester</i>						
56	Hydrogen sulphide.....			None.		
4	Methyl sulphide (commercial).....		⁶ 16	⁵ 61		
70	Methyl sulphide.....		⁴ 22			
34	Ethyl sulphide.....			None.		
59	N-Propyl sulphide.....			None.		
37	N-Butyl sulphide.....			None.		
38	Isoamyl sulphide.....			None.		
47	Benzyl sulphide.....			None.		
68	Diphenyl sulphide.....			None.		
27	Allyl sulphide.....		⁶ 6.5			
67	Allyl disulphide.....	.0072	.038	.20	1.1	
57	Dimethyl trithiocarbonate.....			None.		
<i>Thiocyanate and isothiocyanates</i>						
21	Methyl thiocyanate.....	.18	.48	1.3	3.6	9.3
13	Ethyl isothiocyanate.....	.030	.068	.15	.35	.78
14	Phenyl isothiocyanate.....	.0088	.55	.34		
12	Allyl isothiocyanate.....	.0038	.017	.077	.34	² 1.5
<i>Halogenated hydrocarbon</i>						
58	Benzyl chloride.....	.019	.041	.088	.19	.41
<i>Halogenated ketones</i>						
39	Bromacetophenone.....	.00013	.00031	.00073	.0017	.0042
15	Chloracetophenone.....	.000026	.000052	.00011	.00021	.00043
18	do. ⁷000032	.00013	.00049	.0020	.0076
33	do. ⁸00011	.00027	.00070	.0018	.0044
50	do.....	.000057	.00011	.00024	.00049	.0010
52	do. ¹	² .00016	² .00023	.00033	.00048	.00070
<i>Halogenated phenol</i>						
63	O-Chlorphenol.....	.032	6.8			
<i>Halogenated thioether</i>						
45	Bis alpha dichloro ethyl sulphide.....	.013	.030	.072	.16	.36
<i>Seleno mercaptan and seleno ether</i>						
48	Ethyl seleno mercaptan.....			None.		
26	Ethyl selenide.....			None.		

¹ Starting with No. 2 or moderate eye irritation.² Extrapolated value.³ Irritation reported by three observers.⁴ Irritation reported by one observer.⁵ Irritation reported by two observers.⁶ Irritation reported by four observers.⁷ 60-second exposure with face in a wooden box.⁸ 10-second exposure with face in a wooden box.

CHARACTER OF ODORS AND THEIR PHYSIOLOGICAL EFFECTS

Table 9 gives the character of the odors and the physiological effects produced in odorimeter tests of the chemicals.

TABLE 9.—Character of odors and physiological effects induced

Material	Character of odor	Physiological effects observed
<i>Hydrocarbons</i>		
Alpha butylene.....	Typical gas-house odor; disagreeable to some observers.	Nauseating in higher concentrations.
Beta butylene.....	do.....	Do.
Gamma butylene.....	do.....	Do.
Amylenes (mixed isomers).....	do.....	Do.
<i>Alcohol</i>		
Allyl alcohol.....	Slightly acrid; alcoholic, not unpleasant.	Irritates eyes and nose, produces effect of temporary cold in the head. Made the eyes sore for some hours after exposure.
<i>Esters</i>		
Isoamyl acetate.....	Banana oil; pleasant to most observers.	Produces tickling in the throat causing coughing in higher concentrations.
Isoamyl isovalerate.....	Dried apricots or bananas; pleasant; in higher concentrations it leaves the disagreeable effects of valeric acid due to hydrolysis.	Produces tickling in the throat with tendency to cough.
Methyl anthranilate.....	Fruity, pleasant.....	None.
<i>Aldehydes</i>		
Acetaldehyde.....	Pungent.....	At high concentrations produces tickling in throat with desire to cough; suffocating. An irritant.
Benzaldehyde.....	Bitter almonds, pleasant.....	Produces slight nasal and eye irritation.
Acrolein.....	Acrid odor of burning fat; unpleasant.	Irritates eyes and nose; leaves the eyes irritated for about 12 hours after exposure.
Crotonaldehyde.....	Acrid.....	Irritates eyes, nose, and throat; irritation cumulative. Produces effect of temporary cold in head; eyes irritated for only short time after exposure.
Propargyl aldehyde.....	do.....	Irritates eyes, nose, and throat; leaves the eyes irritated for an hour or more after exposure.
<i>Amine</i>		
Allyl amine.....	Ammonia.....	Irritates eyes and nose; produces temporary cold in head; coughing and sneezing at higher concentrations.
<i>Isocyanides</i>		
Phenyl isocyanide.....	Exceedingly disagreeable, repulsive.	Nauseating.
Allyl isocyanide.....	Very disagreeable; sweet effect in higher concentrations but repulsive.	Do.
<i>Nitro compounds</i>		
Nitrobenzene.....	Bitter almonds, pleasant.....	One observer reported slight headache after tests.
2:4:6 Trinitrotertiarybutylxylene (artificial musk).	Musk; pleasant.....	None.
<i>Cyclic nitrogen compounds, carbon, hydrogen, and nitrogen</i>		
Pyridine.....	Very disagreeable.....	Nauseating, irritates eyes and nose at high concentrations.
Skatole.....	Decayed flesh; putrid; repulsive.	None.
<i>Miscellaneous carbon, hydrogen, and oxygen compounds</i>		
Diphenyl ether.....	Geraniums, pleasant.....	None.
Coumarin.....	Vanilla, pleasant.....	None.
Oxidized oils.....	Acrid, disagreeable.....	Irritating.
Akrol.....	Acrid, pine tar.....	Do.

TABLE 9.—Character of odors and physiological effects induced

Material	Character of odor	Physiological effects observed
<i>Mercaptans</i>		
Methyl mercaptan.....	Decayed cabbage, onions, garlic.	Nauseating.
Ethyl mercaptan.....	Decayed cabbage; very disagreeable.	Do.
N-Propyl mercaptan.....	Onions; disagreeable.....	Do.
N-Butyl mercaptan.....	Skunk; disagreeable.....	Do.
Isoamyl mercaptan.....	do.....	Do.
Benzyl mercaptan.....	Very disagreeable; repulsive, persistent.	Irritation of the eyes, nose, and throat develops immediately after exposure. Leaves the eyes irritated for hours. Some observers developed headache.
Dithio ethylene glycol.....	Disagreeable, garliclike.....	Irritates the eyes; delayed effects; produces choking sensation in throat; caused jaws to ache.
Thiophenol.....	Putrid, very disagreeable.....	Produces choking sensation in throat; irritates eyes and nose; leaves the eyes with a feeling of soreness some hours after exposure. Some felt headache.
Thiocresol.....	Rancid, putrid, phenolic in higher concentrations, very disagreeable, skunklike.	Nauseating; irritates; leaves soreness in jaws and eyes and a bad taste.
Allyl mercaptan.....	Very disagreeable.....	Nauseating; irritates eyes and nose slightly at higher concentrations.
Crotyl mercaptan.....	Skunklike, very disagreeable.....	Irritates eyes and nose slightly at higher concentrations.
<i>Thioethers, polysulphides, and thioester</i>		
Hydrogen sulphide.....	Rotten eggs, disagreeable.....	Nauseating.
Methyl sulphide.....	Somewhat sweet at low concentrations but foul; suggests decayed vegetables.	Nauseating; leaves bad taste.
Ethyl sulphide.....	Sulphurous, foul, becomes ethereal in higher concentrations, disagreeable.	Nauseating; bad aftertaste in mouth worse than first effects on inhalation.
N-Propyl sulphide.....	Sulphurous, foul; becomes ethereal but disagreeable.	Nauseating; causes feeling of congestion in head and throat; leaves disagreeable taste.
N-Butyl sulphide.....	Sulphurous, foul, disagreeable.....	Nauseating.
Isoamyl sulphide.....	Foul, but ethereal, disagreeable.....	Do.
Benzyl sulphide.....	Ethereal, but unpleasant.....	None.
Diphenyl sulphide.....	do.....	Produces choking sensation in throat.
Allyl sulphide.....	Garlic oil, disagreeable.....	Nauseating, slight irritation of eyes and nose at higher concentrations.
Allyl disulphide.....	Garlic, putrid, disagreeable.....	Nauseating, irritates the eyes and nose at higher concentrations; leaves bad taste.
Dimethyl trithiocarbonate.....	Foul but ethereal, disagreeable.....	Nauseating.
<i>Thiocyanates and isothiocyanates</i>		
Methyl thiocyanate.....	Resembles almonds, sweet, unpleasant.	Irritates the eyes and nose at higher concentrations.
Ethyl isothiocyanate.....	Mustard, unpleasant.....	Irritates the eyes, nose, and throat; irritation augments gradually.
Phenyl isothiocyanate.....	Cinnamonlike, rather pleasant.....	Irritates eyes and nose.
Allyl isothiocyanate.....	Mustard oil, unpleasant.....	Do.
<i>Halogenated hydrocarbon</i>		
Benzyl chloride.....	Aromatic, benzenelike.....	Irritates eyes and nose; produces choking sensation in throat at higher concentrations.
<i>Halogenated ketones</i>		
Bromacetophenone.....	Brominelike, unpleasant.....	Intense irritation of eyes and nose; tears formed; irritates the skin.
Chloracetophenone.....	Somewhat ethereal, not unpleasant except for irritation.	Do.
<i>Halogenated phenol</i>		
O-Chlorphenol.....	Empyumatic, phenolic.....	Slight irritation of eyes and nose at higher concentrations.
<i>Halogenated thioether</i>		
Bis alpha dichlorethyl sulphide.	Like brimstone, matches, pungent, and very disagreeable.	Irritates eyes, nose, and throat; produces coughing at higher concentrations; also choking.
<i>Seleno mercaptan and seleno ether</i>		
Ethyl seleno mercaptan.....	Foul, putrid, sweet at higher concentrations; exceedingly disagreeable.	Nauseating; produces choking and coughing; at higher concentrations material is sensed in lungs; leaves bad taste in mouth.
Ethyl selenide.....	Garliclike, foul, putrid; very disagreeable.	Nauseating; leaves bad taste in mouth; produces slight headache.

These records were made mostly at the conclusion of a series of measurements on each chemical and represent effects after numerous intermittent exposures of short duration to various concentrations, usually in increasing order. Although some substances gave pleasant effects in lower concentrations they were unpleasant at higher concentrations. Only a few substances with vapor pressures insufficient to produce sense effects of higher intensities remained pleasant throughout the concentrations tested; for instance, trinitrotertiarybutylxylene and coumarin. Vapors of all the chemicals in concentrations sufficient to produce odor intensities above degree 3, or easily noticeable, are unpleasant owing to the intense odor or to other effects that arise. This conforms with the observations of perfumers that odors must be of lower intensities to delight the senses. Askinson¹¹ has said:

Perfumes should never be employed other than in very dilute conditions; this necessity arises from a peculiarity of the odorous substances which when concentrated and pure have by no means a pleasant smell and become fragrant only when highly diluted. Oil of roses, or orange flowers, or of jasmine, in fact nearly all aromatic substances have an almost disagreeable odor when concentrated; only in an extremely dilute state they yield those delightful scents which we admire so much in the blossoms from which they are derived.

DISCUSSION

CONCENTRATIONS FOR DEFINITE INTENSITIES OF ODOR

Table 3 shows great differences in the concentrations of various chemicals required to produce a definite intensity of odor. For instance, 6.2 parts per million of allyl amine were required for a No. 1, or very faint odor, whereas trinitrotertiarybutylxylene gave a very faint odor at 1 part in 20 billion parts of air (omitting another test which gave 1 part in 160 billion parts); the ratio is about 1:120,000. For No. 3, or easily noticeable odors, trinitrotertiarybutylxylene with 0.015 parts per million and gamma butylene with 360 parts per million represent the extremes with a ratio of 1:24,000; for No. 5, or very strong odors, the extremes found in actual measurements with pure materials are 8.3 parts per million for ethylseleno mercaptan and 7,000 parts per million for methyl thiocyanate; this ratio is 1:840, but it is hardly representative because numerous substances had insufficient vapor pressure to yield very strong odors with the methods employed, if at all. It appears then that some of the selected agents are many tens of thousand times more effective in imparting odors than others.

Nasal irritations and eye irritations can not be compared by ratios as were the odors, because many substances produced no irritations. No irritations were produced at as low concentrations as were some odors.

Mercaptans, thioethers, selenium compounds, and one member of the nitro compounds (trinitrotertiarybutylxylene) gave very faint odors at lower concentrations than members of other classes of chemicals. Crotyl mercaptan showed among the 11 mercaptans tested a No. 1, or very faint, odor at the lowest concentration of 0.00012 parts per million, whereas isoamyl mercaptan gave a very strong odor at the lowest concentration of 60 parts per million. Allyl sulphide gave, among the nine thioethers, a very faint odor at the lowest concen-

¹¹ Askinson, G. W., *Perfumes and Their Preparation*; translation from 3d German edition by Furst, L.: N. W. Henley & Co., New York City, 1892, 312 pp.

tration of 0.00014 parts per million. Aldehydes, isothiocyanates, and halogenated ketones are, according to Table 3, not as effective in giving odors as are the mercaptans and selenium compounds; but according to Tables 4 and 5, the former classes are the more effective irritants. Of the 11 mercaptans only benzyl mercaptan, p-thiocresol and thiophenol caused appreciable irritation of the nose and eyes; these are all of the aromatic group. None of nine thioethers caused irritation. Chloracetophenone was the most effective as an irritant in low concentrations of all the substances tested; No. 3, or strong nasal irritation and strong eye irritation, was caused at the lowest concentrations of 1 and 0.1 parts per million, respectively. Allyl isothiocyanate and crotonaldehyde appear very effective as nasal irritants with No. 1, or slight irritation, at 7 and 8 parts per million, respectively. Bromacetophenone gave No. 1 eye irritation at 0.038 parts per million, benzaldehyde at 3.8 parts per million and allyl isothiocyanate at 4.2 parts per million. These are with chloracetophenone aforementioned the most effective eye irritants.

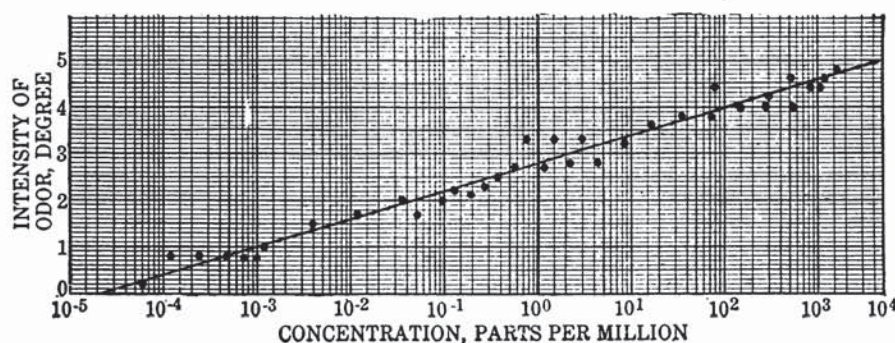


FIGURE 4.—Odor intensities of ethyl mercaptan at various concentrations in air, test 2

PRECISION AND INTERPRETATION OF THE MEASUREMENTS

As a rule, tests with a material were run in order of increasing concentration to avoid interference due to evolution of odor from the apparatus. However, the order of concentrations and some other procedures were varied in some tests with ethyl mercaptan, methyl anthranilate, chloracetophenone, and crotonaldehyde to compare observations on different days, to see if deviations occur due to the order of observing the intensities of odors and to determine whether a series started with some sensory effects proved regular. Other tests were made in duplicate without change in procedure. Special tests employed a box to immerse the entire face in comparatively still air instead of using a stream from an orifice. Except for the box tests the changes produced no special differences; results usually agree in order of magnitude.

TEST OF ETHYL MERCAPTAN EXTENDING THREE DAYS

Test 2, for which the primary data are presented in Table 1 and the averages of intensity observations against concentrations of ethyl mercaptan in air are shown in Figure 4, was conducted during three days. Observations 1 to 17 (Table 1) were made the first day, 18 to 31 the second day, and 32 to 38 the third day. None of the observers knew the actual concentrations, and except for the operator of the

odorimeter none knew what parts of the odor scale might be used each day. The range of concentrations on the second day overlap those of the first day and similarly on the second and third days. Figure 4 shows that the averages of observations on any one day agree with those of other days as well as they agree with those found the same day; a group of observers thus discriminates among odors of different intensities as well on one day as on another day.

ODOR INTENSITIES PRESENTED IRREGULARLY IN TEST OF ISOAMYL ISOVALERATE

Test 66 with isoamyl isovalerate was conducted by presenting the different intensities in irregular order; sufficient time was permitted between observations to eliminate effects of adsorption and evolution of odor from the odorimeter itself. The averages of odor intensities recorded at various concentrations of isoamyl isovalerate in air are presented in Figure 5; the order of observations is shown by the figures

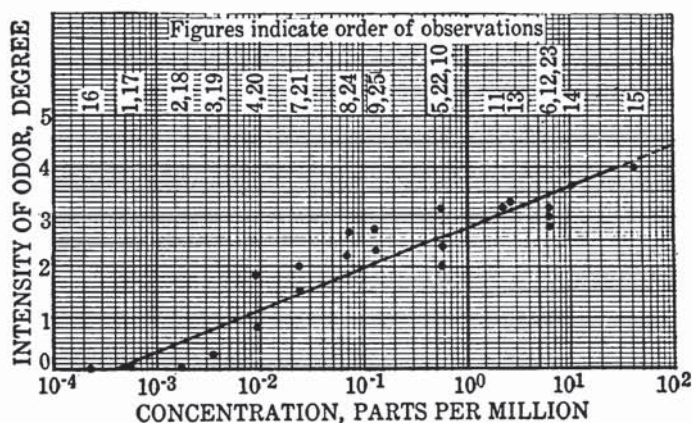


FIGURE 5.—Average of odor intensities of isoamyl isovalerate versus concentrations in air, test 66; the odors were presented in irregular order of intensity

above the graph. All of the averages fall within one degree of intensity from the straight line on the chart corresponding to Weber's law. The agreement is sufficient and shows that the order of presenting the concentrations is not important.

ENTIRE FACE PRESENTED TO ATMOSPHERE OF CHLORACETOPHENONE IN A BOX

Five tests—15, 18, 33, 50, and 52—were made with chloracetophenone. Two—15 and 50—were conducted according to regular procedure with the glass nose piece and beginning with no noticeable sensory effects; another test—52—was made beginning with some eye irritation and then increasing intensities thereafter. Two were made by substituting a wooden box for the glass orifice, large enough to receive the entire face and head; the first of these—18—was made by immersing the head in the box for observations of one minute each; 10-second observations were used in the latter—33. The eyes exposed in the box were in contact with relatively still air, and it was the purpose of the box test to determine whether eye irritation was produced by the quiet atmosphere as readily as by the stream emerging

from the glass orifice. The results of the tests with chloracetophenone are given in Tables 3 to 8; comparison is facilitated by the graphic presentation in Figure 6. The nasal irritations determined by the usual method with the glass orifice and with a single inhalation for observation, and the eye irritations determined by exposing the eye 10 seconds to the effluent stream from the glass (solid lines on fig. 6) agree well enough; the determinations made with the face exposed to the impregnated air in the wooden box do not agree so well either for

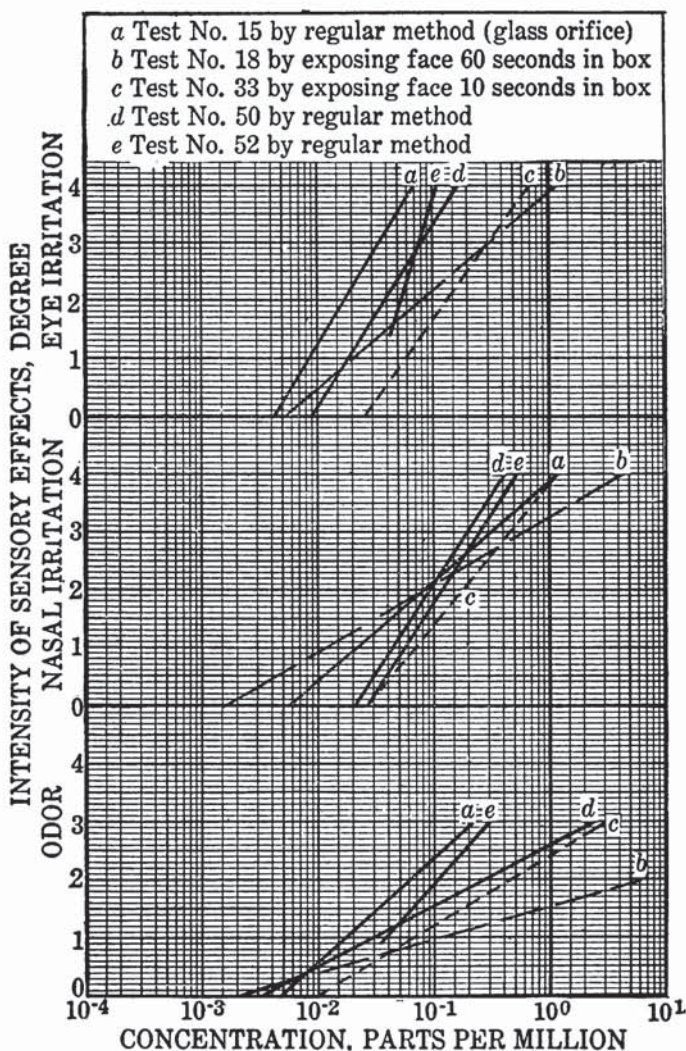


FIGURE 6.—Sensory effects caused by chloracetophenone from a glass orifice, also by exposing the entire face in a box

10 seconds' or 60 seconds' exposure. The determinations of odor do not agree quite as well as the irritations, and in no case did they exceed degree 3, or easily noticeable, in intensity, because the sense of smell was almost obscured by the strong or intolerable nasal irritations. That the irritation impaired the keenness of smell is shown by the test exposing the face 60 seconds in the box; each observer took a number of breaths during the period for a single observation; the resultant continued irritations impaired the sense of smell, and odor intensity No. 2, or faint, was not exceeded at the highest concentrations

employed. Also, the extended exposures seemed to develop a tolerance or insensitivity toward chloracetophenone as regards nasal and eye irritations. Possibly the higher concentrations for a given sensory effect, as calculated from the tests in the box, are caused partly by dilution with pure air entering the box when the face is put into it—the box was kept covered other times to prevent such dilution—or it may be due partly to absorption of chloracetophenone by the box. Also, the higher concentrations required for eye irritations in the box may be due partly to lack therein of rapid air motion to bring the

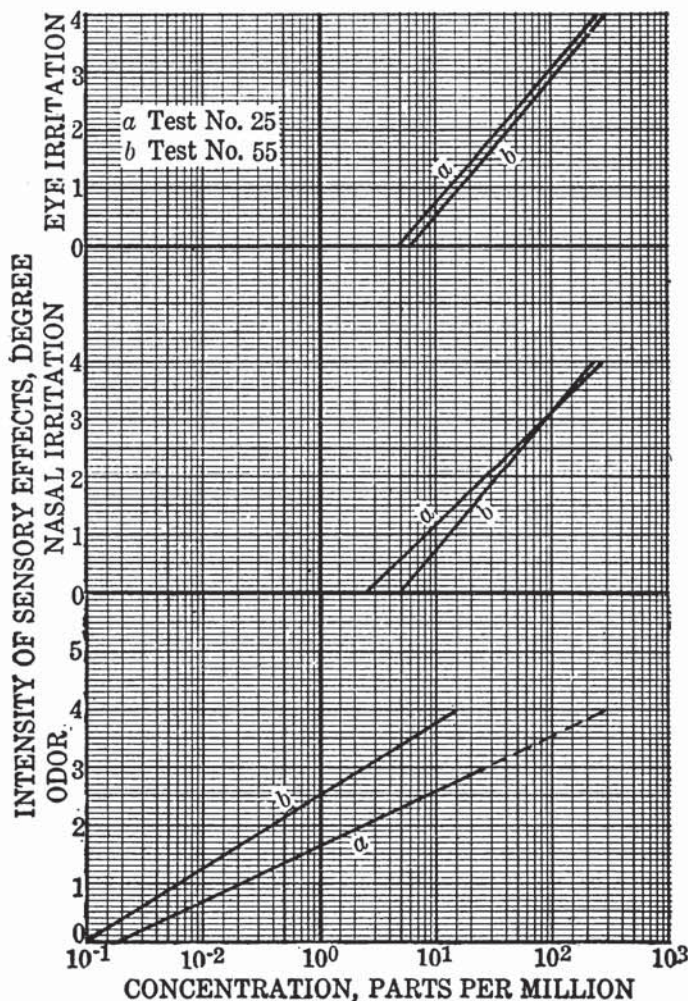


FIGURE 7.—Duplicate tests with crotonaldehyde, "98-99" per cent pure

chloracetophenone to the eyes, but this can not account for the differences in measurements of nasal irritation or of odor.

These tests indicate then that extended exposure to irritants may tend to develop tolerance for the irritant and require higher concentrations of chemical to produce a sense of irritation like that produced on a short, immediate exposure; irritation is enhanced by air motion bringing chemical irritant to the eye; the sense of smell is rendered less keen by continued irritation in the nasal passages. Although these conclusions might have been assumed from general experience, they are supported here by quantitative measurements.

DUPLICATE TESTS

Duplicate or triplicate tests were made with crotonaldehyde, ethyl mercaptan, allyl mercaptan, crotyl mercaptan, and trinitro-tertiarybutylxylene in addition to those shown previously for chloracetophenone. Graphs for these are given in Figures 7 to 11.

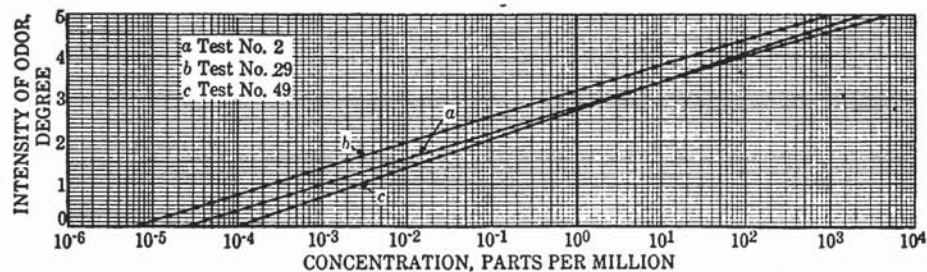


FIGURE 8.—Triplicate tests with ethyl mercaptan

Figure 7 shows excellent agreement in duplicate determinations of nasal irritation and eye irritation made with crotonaldehyde at widely separated times; the odor measurements do not agree as well. The triplicate tests of the odor of ethyl mercaptan in Figure 8 all agree well; the subjects in test 2, except for the operator of the odorimeter, were different from those in tests 29 and 49, and some of the subjects in the latter two tests were different. Both graphs for the tests of

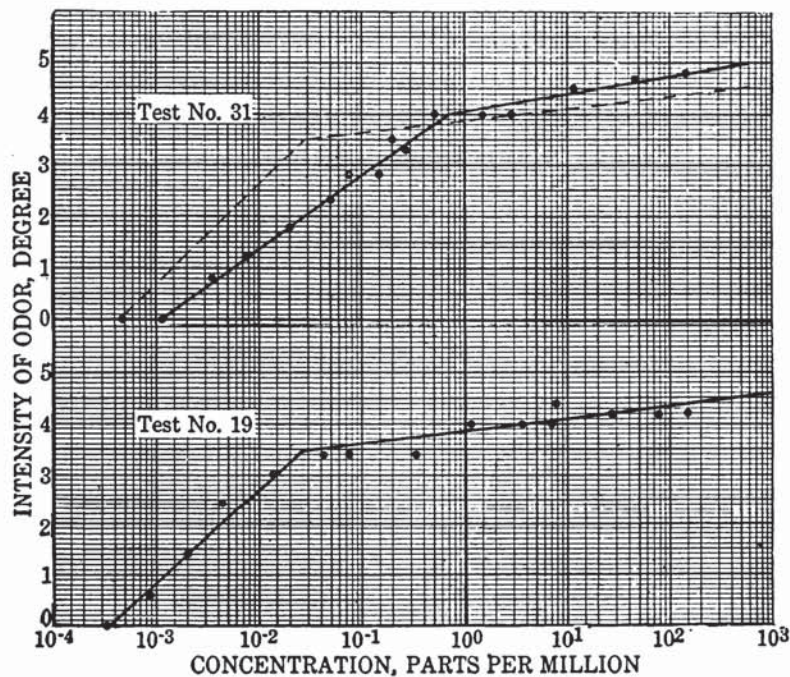


FIGURE 9.—Duplicate tests with allyl mercaptan

allyl mercaptan, Figure 9, show a pronounced change in direction. The separate averages determined are all indicated on Figure 9; they show that the irregularities are more pronounced than those due to lack of precision in measurements. The graphs on both sides of the breaks appeared to follow Weber's law. It would be interesting to

investigate this irregularity further. Some other cases of change of direction of the odor graphs appeared; one with parathiocresol was pronounced. All the instances were associated with chemicals causing nasal irritation. In the case of allyl mercaptan the nasal irritation was observed at concentrations considerably higher than the points at which breaks in the odor graphs appear.

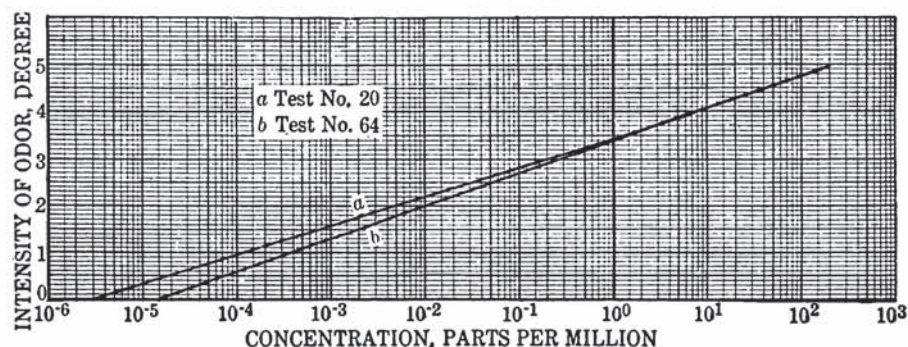


FIGURE 10.—Duplicate tests with crotyl mercaptan

Figure 10 presents duplicate tests with crotyl mercaptan that agree well. (The differences in boiling points of the two preparations of crotyl mercaptan in Table 2 are due to the presence of polymer of crotyl mercaptan in material 20.) There was indication of a break in the graph for test 20 above degree 4, but the data are insufficient for a conclusion; test 64 appeared regular throughout.

Figure 11 gives the results from trinitrotertiarybutylxylene (artificial musk), the most powerful odorant at low concentrations which was measured. The concentration ranges indicated on Figure 11 beginning with 10^{-7} parts per million or 1 part in 10 trillion were the lowest found necessary among all the measurements. Agreement between the two tests in Figure 11 is only fair.

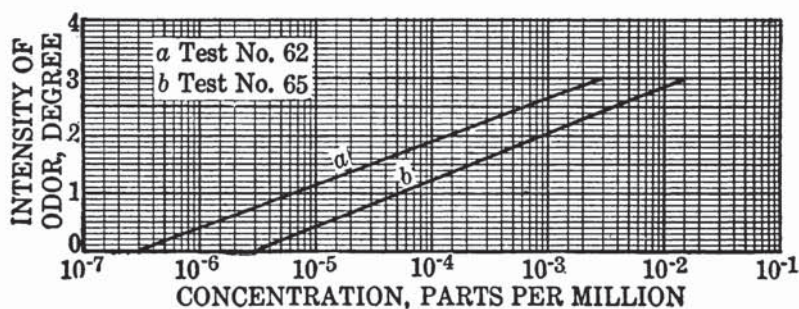


FIGURE 11.—Duplicate tests with trinitrotertiarybutylxylene

In general, the duplicate tests show that the concentrations of chemicals producing a degree of odor intensity or irritation as determined by groups of human subjects may be checked as to order of magnitude. Although the odorimeter may undergo some improvements, elimination of a few small rubber parts may help; it appears that larger groups of observers than those employed for the present work would be more likely to provide good agreement.

AGREEMENT WITH OTHER INVESTIGATORS

Other investigators have determined only the concentrations for threshold odors. Their measurements reported in the International Critical Tables¹² for those chemicals included also in the present work are compared in Table 10 with the authors' measurements for degree No. 1, or very faint. The agreement is generally satisfactory; discrepancies are not as great as some between measurements by two authorities cited in the International Critical Tables; for instance, for pyridine two authorities differ four thousand fold. Error may possibly have crept into the authors' test 1 with nitrobenzene owing to inexperience or experimental error, for the authors' measurement differs from the others more than in the other instances. However, it is reported here, as are in fact all other tests that were performed. Skatole shows the next largest discrepancy; possibly moisture in the material employed by the authors is the cause of the discrepancy between their measurements on skatole and those of others. The remaining measurements in Table 10 agree in order of magnitude.

TABLE 10.—Comparison of concentrations for "very faint" odors, degree No. 1, with threshold concentrations for odors reported in International Critical Tables

Materia.	Concentration for odor degree No. 1, very faint, determined by the authors, parts per million	Concentration for threshold odor reported in International Critical Tables	
		Parts per million	Observer
Acetaldehyde.....	0.066	0.35	Tempelaar.
Isoamylacetate.....	.0033	.016	Do.
Do.....		.016	Hermanides.
Coumarin.....	.0033	.00012	Tempelaar.
Do.....		.0015	Passy.
Do.....		.0078	Do.
Methylanthranilate.....	.0094	.00089	Tempelaar.
Nitrobenzene.....	1.9	.0012	Henning.
Do.....		.0074	Hermanides.
Do.....		.0074	Tempelaar.
Pyridine.....	.23	.011	Do.
Do.....		44	Hermanides.
Skatole.....	.019	.000059	Do.
Do.....		.000067	Tempelaar.
Trinitroisobutyltoluene ¹000078	Do.
Trinitrotertiarybutylxylene.....	.000051		
Do.....	.000065		

¹ Published data on trinitroisobutyltoluene are compared with the measurements by the authors on trinitrotertiarybutylxylene. Any actual difference in odors of these homologs is probably insignificant.

It should be remembered, however, in comparing the concentrations in Table 10, that the authors' figures represent not the concentration at which odor was first perceptible to an observer, but rather an average taken from numbers of observations by a group of persons covering a range of concentrations in which they judged the odor to be of minimum perceptible intensity. Although the authors' figures may be expected to be somewhat higher than those of others, that is not always the case; in fact, the differences are nearly equally divided between positive and negative.

¹² See footnote 4. The data used by the authors have been corrected according to the list of errata for volume 1 of the International Critical Tables.

HOMOLOGOUS SERIES

Odors of the alkyl mercaptans and of the alkyl thioethers in homologous series are compared in Figures 12 and 13. All were normal or straight chain compounds excepting the isoamyl mercaptan and the isoamyl thioether. The ethyl mercaptan line in Figure 12

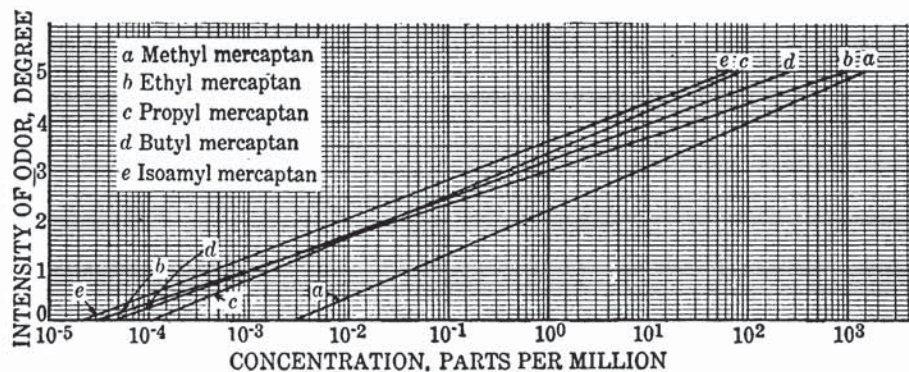


FIGURE 12.—Intensities of odors of the alkyl mercaptans in homologous series versus concentrations in air

represents an average taken from the triplicate tests. The odor intensities determined for the different substances at any concentration differ in most cases hardly more than those in duplicate measurements on a single material, yet there is a general trend with the methyl compounds as least powerful to amyl compounds as most powerful and the other substances between. The others are partly in order of molecular weight, especially at higher odor intensities;

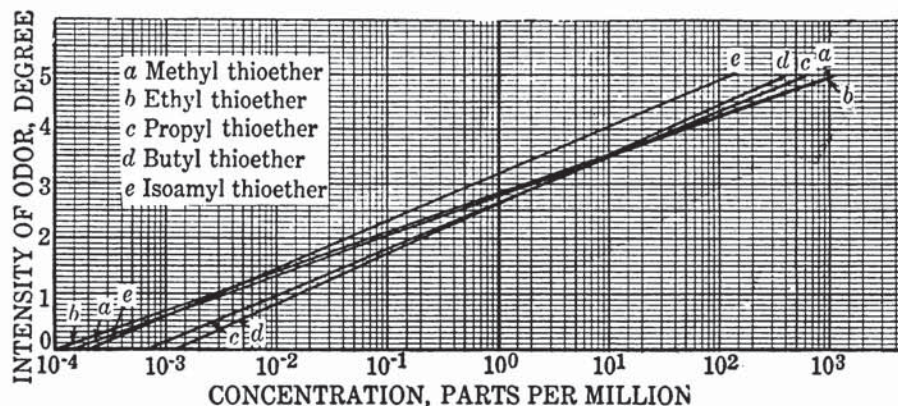


FIGURE 13.—Intensities of the odors of the alkyl thioethers in homologous series versus concentrations in air

their graphs cross in some instances. It may be concluded that the mercaptans and thioethers increase in odor intensity with the molecular weights at least through the first five members of each series. The fatty acid series also increases in odor intensity up to butyric acid, then decreases, possibly owing to lesser volatility.¹³ The three isomeric butylenes were found almost alike in odor intensity, as shown in Table 3.

¹³ Passy, J., Le pouvoir odorant dans la serie grasse: *Compt. Rend.*, vol. 64, 1893, pp. 361-364.

SUMMARY AND CONCLUSIONS

1. An odorimeter is described based on an air-flow system whereby streams of chemical vapors and gases were diluted with air from concentrations ranging from 10 per cent vapor down to 1 part in 10 million million (10^{13}) parts of air.

2. Scales for comparing (a) the intensities of the odors of chemicals at various dilutions, (b) the intensities of nasal irritations, and (c) the intensities of eye irritations were devised and employed. The odor scale is: 0, No odor; 1, very faint; 2, faint; 3, easily noticeable; 4, strong; 5, very strong. The scale for nasal irritation and also for eye irritation is: 0, No irritation; 1, slight; 2, moderate; 3, strong; 4, intolerable.

3. Observations of odor were made with one inhalation from the odorimeter; any nasal irritation was noted at the same time. Eye irritation was determined by exposing an eye 10 seconds to the impregnated stream of air flowing against the eye.

4. The odors and irritations accord with Weber's law that the intensity of the sensory effect is proportional to the logarithm of the stimulus or concentration of the chemical.

5. Groups of about six subjects were employed to determine the intensities of the odors and the irritations caused by chemicals in air. Although considerable differences between observations of intensities noted by individuals may occur, a method for deducing very satisfactory averages based on mathematical and graphic procedures is presented.

6. Intensities of odors, of nasal irritations, and of eye irritations produced by 55 substances at various concentrations in air are presented from 74 series of measurements.

7. The concentration of a chemical substance for a given intensity of odor or irritation can be checked in order of magnitude in duplicate tests with the same subjects or with a different group.

8. Trinitrotertiarybutylxylene was most powerful as an odor at the lowest concentration, a very faint odor was observed at 0.000051 part per million. Chloracetophenone was the most powerful as a nasal irritant, also as an eye irritant; respective concentrations required were 0.021 and 0.0083 parts per million.

