1979

Development of procedures for determining industrial odor thresholds.

Suresh C. Varshney
University of Windsor

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DEVELOPMENT OF PROCEDURES
FOR
DETERMINING INDUSTRIAL ODOR THRESHOLDS

A Thesis
Submitted to the Faculty of Graduate Studies
Through the Department of Chemical Engineering
in Partial Fulfilment of the Requirements for the
Degree of Master of Applied Science at the
University of Windsor

by

Suresh C. Varshney

Windsor, Ontario, Canada

May 1979

ABSTRACT

Establishment of odor control regulations requires fast and practical procedures for the determination of odor levels of industrial emissions. This report presents the results of an investigation aimed at developing reliable methods of odor storage and threshold measurements.

Odor detection techniques, particularly the threshold concept, are discussed with emphasis on complications arising in odor measurements. The different parameters which influence the precision of odor thresholds are reviewed.

The suitability of various commercially available synthetic polymer bags for odor sampling and collection has been studied. Odor losses for several odorants over storage times have been measured. The effect of initial odor concentration on odor loss was also evaluated. An attempt was made to study the adsorption and permeation characteristics of Tedlar bags.

The practicality of odor measurements with a Dynamic Dilution Triangle Olfactometer (IITRI) has been investigated. The threshold values of pure odorants measured by IITRI Olfactometer are compared with the standard ASTM Syringe Method results as well as with the available literature.

The effect of panel size and sensitivity on the reproducibility and reliability of odor threshold data has been examined. An attempt is also made to study the influence of noise and darkness on the panel response.

A general procedure for evaluating thresholds of odorous emissions is proposed. The method is fast and reliable, and was successfully applied to measurement of acetic-acid odor.

ACKNOWLEDGEMENTS

The writer is greatly indebted to Professors G. P. Mathur and A. W. Gnyp for their able guidance and supervision on this research project. Thanks are also due to Professor S. J. W. Price for technical supervision of total hydrocarbon measurement work. Frequent technical discussions with Mr. D. S. Smith are gratefully acknowledged.

The writer wishes to thank Mr. George Ryan for his generous assistance in fabricating and supplying parts during the course of the investigation. Mrs. Elizabeth Sheehan is gratefully acknowledged for typing the manuscript.

Lastly, I would like to thank the Ontario Ministry of the Environment for the financial support of this project.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Odor is perhaps the most complex of the air pollution problems because it is difficult to measure objectively. Although odors are so obvious that they attract immediate public attention, it is fortunate that they are usually non-toxic to humans at the levels normally encountered.

Because psychological factors play an important role in determining a person's reactions to his perception of air quality, both pleasant and unpleasant odors become objectionable if they persist for long periods of time. For example, the odors from a bakery shop are pleasant to the customers, but those who live in the immediate vicinity of the bakery may find it a nuisance. Generally the effect of odors on people is primarily one of nuisance, but secondary effects may also be of importance. Offensive odors can lead to nausea, vomiting, headache, loss of appetite, upset stomach, and interference with breathing and sleeping functions besides destroying the peaceful enjoyment of homes in the neighborhood. They may also cause an interference with proper working conditions and a depreciation of property values [1].

Emissions from industrial stacks constitute the major source of odor pollution. In recent years, with increasing public awareness of "offensive" or "disagreeable" odors, local governments and environmental agencies have received numerous complaints. As a consequence, local and federal governments have tightened legislation on new plants by demanding sufficient evidence of protection of the environment. Even existing plants have been asked to meet specific objectives that satisfy government regulations. As a result, the operating companies now consider the use of control equipment and process modifications to minimize odors.

Odors can cause problems in the vicinity of a source or in a community several miles away, as a result of transport by unfavorable atmospheric conditions. Detection of odors in areas far removed from the original source has been reported by many investigators [2-3].

A major problem in the establishment of sensible odor laws arises from the lack of reliability of odor measurements. Because the human nose is the perceptor, odor determinations involve psychological factors that are not entirely reproducible. This basic shortcoming in the measurement of odors plus a lack of reliable and objective sample collection methods has made it difficult to set acceptable standards. Both industry and control officials are currently faced with many difficulties associated with the quantification of atmospheric odors. Reproducible as well as accurate measurements are considered essential for defining the magnitude of a given odor problem. Some of the immediate concerns of researchers are:

i. establishment of criteria for enforcing legislation

ii. definition of acceptable guidelines for malodors and public odor nuisance

iii. determination of the effectiveness of control equipment in different applications, along with a study of the relative importance of various odoriferous processes

iv. measurement of the intensity of sources by determining odor levels in discharges

v. prediction of odor levels at various distances from an emission source based on stack height, gas temperature, topography and meteorology

vi. development of evidence needed for assessing the effects of odors

vii. projection of long-term environmental pollution trends.

The objective of this investigation was to

i. study the suitability of various commercially available synthetic polymer bags for sampling odorous gases with respect to their storability, aging, probability of adsorption, desorption and seepage characteristics, with special regard for convenience and ease of handling

ii. establish the precision with which odor threshold values of pure and mixed odorants can be determined routinely using a forced-choice dynamic dilution olfactometer

iii. develop a reliable and reproducible procedure for odor threshold measurement for a variety of odorous gas emissions.

II. ODOR DETECTION TECHNIQUES

The detection of odors often implies measurements at very low concentrations of odorants. Some chemicals can exhibit odor at concentrations as low as 0.1 parts per billion (approximately 10^{-9} grams per litre). Physico-chemical methods for measuring such low concentrations require cumbersome procedures. The instrumentation needed for such work is simply not practical for routine measurements. Fortunately, the human nose is so sensitive that it can respond to thousands of different odor stimuli and detect both low and high concentration of odorants simultaneously. However, all human noses do not have the same sensitivity for odor detection [4]. Therefore, it is common to use an odor panel consisting of individuals called "panelists", "judges", "observers" or "participants". In practice, panels are presented with odor samples. Members, by indicating their responses, serve as the measuring instruments.

Odor sensation has multidimensional characteristics, involving intensity, detectability, acceptability and quality. The qualitative aspect of odor sensation may be described as odor character notes or broadly as hedonics, that is, like or dislike. The quantitative aspect of odor sensation may be described in interrelated terms of intensity or detectability which are the basis of most ordinances and regulations.

An odor sample, when diluted with clean air, gradually becomes weaker until it finally reaches an odor level which is too weak to be consistently detected by the panelists, except by chance. A range of better than even chance detection is recognized to exist between the pure air and the diluted odor sample.

A. Threshold Concept

Human responses to odors have often been expressed in terms of thresholds. Many procedures and devices have been developed for such measurements [5].

The odor threshold of a given sample is a dilution level at which the correct identification of that sample reaches some statistical degree of reliability [6]. It is that concentration of odorant at which the intensity becomes zero [7-8]. The minimum concentration at which a given odorant is barely perceived by the nose is defined as its "odor threshold".

The odor threshold values reported in literature have usually been determined by odor panels consisting of four or more persons. The threshold concentration at which any percentage of the panel has detected odor is referred to as "effective dosage" [9]. For example, if 50% of the panel perceives the odor at a certain concentration, that level would be designated as ED_{50}. Although the threshold level may be taken at any arbitrary fraction, it has become customary to utilize the "50% threshold" which is the minimum concentration at which half of a population of subjects responds to or identifies an odor. This definition is parallel to the "median effective dose", ED_{50}, cited in the literature of toxicology.

Different bases of determining threshold concentrations have often been used in literature. The threshold concentrations are defined in terms of

i. Odor Detection Threshold - the concentration at which a certain fraction of the odor panel perceives an odor

ii. Odor Recognition Threshold - the concentration at which a certain fraction of the odor panel perceives the odor as being representative of the odorant being studied [10]

iii. Annoyance or Objectionable Threshold - the minimum acceptable level at which an odor becomes an annoyance or objectionable to the residents of a community.

It has been argued that the reproducibility of the recognition thresholds is greater than that of the detection thresholds [11]. The recognition threshold is usually determined by a panel of trained analysts who have had prior experience with odor quality and are able to identify the odor. However, it is more common to use absolute ED_{50} values in air pollution work.

The most commonly used unit to quantify odors is the "odor unit". It is defined as the volume of clean air necessary to dilute one cubic foot of odorous gas to the threshold concentration. By definition

$$\text{Odor Unit (O.U.)} = \frac{\text{volume of clean air}}{\text{1 cubic foot of odorous air}}$$

Although the odor unit, defined as above, is dimensionless, it is not uncommon to find units of odor measurement expressed in terms of O.U./ft^3.

In recent years it has been recognized that the threshold concept ignores some fundamental aspects of human responses to stimuli. The development of the signal detection theory [12-15] has increased awareness that human responses are decisions caused by a given sensation consisting of random background noise alone or some signal (odor) mixed with the noise, Responses such as "yes, I detected something" or "No, I don't detect anything", are not simply expressions of sensation but are also influenced by other factors such as expectations; the "wish not to miss an odor that may be present", or the "wish not to sound a "false alarm" by incorrectly detecting a blank odor sample" [15]. In view of the above considerations, it should be apparent that odor threshold values are definitely not absolute properties of odorants like boiling points. They are, therefore, not necessarily quantitatively transferable from one situation to another. Rather, they represent values within broader ranges and depend on factors such as social, psychological and physiological backgrounds as well as measurement techniques.

B. Complications in Odor Measurement

It is well known that the human olfactory system does not respond equally to similar concentrations of different odors. These variations complicate the task of performing consistent and reproducible odor determinations by sensory methods. Hemeon [16] believes that differences in odor perception among individuals are not too great. He maintains that the threshold values determined under ideal conditions rarely vary by more than a factor of three. On the contrary, Wilby [17] reports that the threshold values of 35 untrained observers varied widely from a minimum of 10 times to a maximum of 50 times.

Lindvall [18] has presented an excellent review and the results of his own experiments show the effect of psychological and physiological factors such as degree of personal adaptation, motivation, attitude, expectancy, previous experience, and variation in background on human response to odor. Controlled experiments performed by Lindvall [18] indicate that motivation can significantly increase an individual subject's response to a given stimulus. Monetary rewards and punishment can produce 20 fold variations in the true threshold and increase the probability of reporting an odor sensation when none is present.

It is generally accepted that untrained panelists lead to higher threshold values than experienced judges [19]. Lindvall's investigations [18], however, do not show any evidence of differences in repeated threshold determinations.

The effects of physical and biological variables such as age, health, sex, smoking habits and time of the day have been reported [20] to influence olfactory sensitivity, but studies of these parameters have produced contradictory and inconclusive results.

In addition to the previously mentioned factors there are many other experimental variables that contribute to the problem of conducting accurate odor measurements. It has been indicated in the literature that both temperature and humidity influence odor responses [21-23]. Therefore, odor measurements should be performed at constant temperature and humidity until the effect of these parameters is quantified. Other experimental factors which may affect odor determinations include background odors, sample preparation errors, panelist's failure to follow instructions, contamination of the measurement device (olfactometer, test chambers and accessories), odor sample deterioration, and equipment malfunctions. Any efforts expended in perfecting reliable and reproducible measurement techniques will help to make odor technology a more exact science.

III. ODOR MEASUREMENT DEVICES

All odor detectability measurements with the human olfactory system involve dilution of the odorant gas by clean air. The detection threshold is expressed as the number of dilutions required to render the odorous gas non-odorous. A number of devices and methods have been designed for field and laboratory use to control and measure the required number of dilutions. These instruments are called olfactometers, even though they do not measure odors, but simply aid in preparing and presenting the odors to the actual detector, the human nose.

Odor sample dilution devices can be subdivided into the following three groups involving:

i. dilution of odorous gas with odor free air by means of respiration. This method depends on mixing odorous gas with odor free air in a container, bringing the nose in contact with the container, and inhaling the mixture. Examples: osmoscope, scentometer

ii. static progressive dilutions of an odorous sample with odor free air in a container, and injecting the gas mixture into the nose. Example: syringe dilution

iii. mixing of odorous gas with odor free air in a duct with subsequent transport to an observer's nose. Example: dynamic olfactometer.

A. Respiration Dilution Methods

These methods are based on the dilution of odorants either directly from the atmosphere or vaporized from cold traps.

1. Osmoscope

Fair and Wells [24] developed an instrument which consists of two telescoping tubes. The middle section of the inner tube is formed with specially designed holes which are closed or opened by adjusting the outer tube for dilution with clean air. The odor is introduced through one end of the inner tube which terminates in a special nose piece providing the diluted sample. The observer controls the dilution of odorous gas with clean air through inhalation. This device has also been described by Mateson [25].

Prince and Ince [26] modified this device to make use of the relationship that odor perception varies in logarithmic increments. They arranged the holes of the inner tube in a geometric series so that the odor sensation either doubled or halved at each step.

2. Katz and Allison Odorometer

Katz and Allison [27] developed an odorometer which was also used by other workers [28-29]. This method produces odor levels on the basis of the odorant's vapor pressure at constant temperature. A known flow rate of odor free air is bubbled through the odorant contained in a U-tube which is maintained at constant temperature. The diluted air mixture of known concentration is then passed through a gas mask or hood for odor determination by a panel.

3. Scentometer

Estimation of odor levels in the field can be made with a portable instrument known as a "scentometer" [30-34]. In principle, the instrument operates by diluting odorous gas or air with a stream of ambient air that has been purified by passing through a bed of activated carbon. The amount of odorous gas passing through the device, with respect to the purified air, is controlled through selection of one of four orifice diameters. The observer simply breathes through the instrument at one of the four dilution ratios. The instrument is limited in its range of odor dilution ratios, usually from 1 to 128. Interference from background odor is also unavoidable.

B. Static Dilution Methods

The first attempt to evaluate odor levels by static dilution was made by Fox and Gex [35] in 1957. Their method was adopted as the standard ASTM procedure D1391 [36]. It was later modified by Mills et al [37]. The Mills et al version is essentially accepted by most legislative bodies.

The static dilution method requires progressive dilution of an odorous gas sample with odor free air by means of 100 ml syringes. The various dilutions in the syringes are presented to panelists for judgement on the presence or absence of odor. The panel threshold is determined in terms of odor units which have been defined earlier.

In 1973, a task force of the ASTM E-18 Sensory Evaluation Committee updated the method to bring it in line with modern sensory evaluation principles. The following changes were recommended:

i. odors should be presented in ascending concentration levels differing by a multiple of 2

ii. a panel threshold should be taken as the geometric mean of the individual thresholds

iii. at each concentration, one syringe containing odor and one blank should be presented in randomized order. The panelists should indicate to the panel leader which syringe they believe contains the odor (forced choice)

iv. the dilution level at which a panelist makes the correct judgement and continues to be correct for two successive concentrations is taken to be that panelist's threshold

v. prescreening of panelists should involve odorants similar to the odorous gas to be evaluated.

Some of the problems associated with the syringe method include adsorption of odorants, contamination of syringes and loss of sensitivity due to olfactory fatigue or anticipation of positive response.

C. Dynamic Dilution Methods

Numerous techniques have been developed for the determination of odor threshold values through the principle of dynamic dilution. In dynamic methods, an odorous sample is continuously mixed with odor free air in an attempt to overcome the difficulties encountered with the static dilution of small samples. By using larger samples the dilutions can be presented at more reproducible flow rates, and for longer durations during each evaluation.

1. Osmo Dilution Device

Gex and Synder [38] developed an Osmo device which provides dynamic dilution of an odorous gas in a cylindrical flow proportioning chamber with air passed through activated carbon. Different dilution ratios are achieved by adjusting the movement of an axially located piston inside a cylinder with 528 equal size holes along the perimeter. The diluted gas stream is fed to a face mask for panel evaluation.

2. U. S. Public Health Service Unit

Nader [39] at the United States Public Health Service (USPHS) developed a portable dynamic dilution device which measures odor threshold values for ambient air. The unit is portable enough to operate inside an automobile from a car battery. Odorous air is collected into the dilution system by suction and mixed with 1-2 ft^3/min of purified air and then fed to an enclosed plastic hood for panel evaluation. The hood provides the panelist with complete isolation from the environment during testing to minimize outside interference. An individual's sense of smell can be vitalized by purging clean air into the hood. Tubing and wall connections are constructed of either Teflon or glass to minimize odor adsorption.

3. Hemeon Odor Meter

Hemeon [16] developed a system similar to Nader's except that much higher air flow rates (30 to 70 cubic feet per minute) were used. The Hemeon instrument is not portable. Odor samples must be brought to the laboratory in flexible plastic bags. The odor is diluted in one step for ambient air or two steps in series for flue gas samples. A diluted sample is evaluated simultaneously by three panelists using three ports arranged circularly around the module. One concentration is evaluated at a time. The odor intensity is judged on a category scale and a plot of intensity versus log dilution is extrapolated to determine the group odor threshold. The Hemeon olfactometer yields a higher value of odor units than the ASTM test for low odor level samples [40]. At higher odor levels, the methods are comparable.

4. Odor Fountain System

Hellman et al [41] developed a different approach for presenting odors to a five member panel. The odor testing facility consists of a room which is equipped with a recirculating fan, a duct system and an odor presentation device, called an "Odor Fountain Olfactometer". The olfactometer consists of three ports which provide rapidly flowing jets or fountains of air. Two of the ports are blanks while the other may contain an odor. Air flowing at 20 to 80 litres per minute from one inch diameter openings produces the same sensation of air movement in each port. The odorous gas stream from the room is exhausted through larger ventilation ports located 14 inches above the jets. The panelist sniffs one port at a time, and indicates the presence or absence of an odor by mentally ignoring the mechanical effects produced by the rushing flow of air.

5. Odor Room Method

The Odor Room Method [42-43] used by Arthur D. Little, Inc., requires two chambers; an antechamber and the test room. The rooms are constructed of materials that are non-absorptive to odors. The test room is equipped with fans for rapid air mixing of additions of known concentrations of odorous specimens. This arrangement provides, in effect, a large static-dilution volume. In practice panelists rest in the antechamber to acclimatize themselves with the relatively odor free conditions and then enter the test room together to decide on the presence or absence of any odor. This method cannot provide rapid changes in odor concentrations. It is not practically feasible to provide conditions that prevent the panelists from influencing one another.

6. Ford Dynamic Olfactometer

Recently Ford Motor Company developed a Dynamic Dilution System [44] for evaluating paint emissions in the laboratory and on-site. This unit has a dilution range varying from 15 to 30,000. Odorous samples are collected in Tedlar bags for laboratory evaluation or taken directly from a stack during on-site determinations. A sample is mixed with purified air flowing at a rate of 14 to 140 liters per minute into a 5 centimeter diameter glass manifold consisting of two mixing chambers. Dilution air is maintained at a constant relative humidity by means of a humidifier. Five odor sensing ports connected to the mixing chamber provide a steady flow of the diluted mixture to the 5 panelists simultaneously, who indicate the presence or absence of an odor. Each successive dilution presented for approximately 30 seconds is preceded each time by at least 30 seconds of odor free air. Usually 4 to 5 presentations are required to reach the panel threshold.

7. Swedish Dynamic Olfactometer

The Swedish National Institute of Public Health [45-46] has devised a method which employs collection of industrial exhausts or ambient air in large, flexible plastic bags. After the bags are returned to the laboratory, the odorous gas is withdrawn by a diaphram pump at a low constant flow rate. It is then mixed with odor free air in a dynamic mixing chamber and transferred to an exposure hood for evaluation by an odor panel.

Lindvall designed a Mobile Odor Laboratory [47-49] consisting of two mobile trailers which can be brought to the odor source or location. One trailer unit provides a conditioning area for the panelists to recover from the olfactory fatigue resulting from breathing any outside ambient air. The other trailer is equipped with devices for producing various dilutions of odorous samples acquired from specific sources. Panelists are required to make evaluations on the basis of signal detection theory [13]. This procedure allows the individuals to judge the odor samples in terms of a two-way probability. The serious limitation of the probability approach is due to the difficulty of expressing the odor measurement results as a single physical value.

8. ORF Dynamic Olfactometer

The Ontario Research Foundation [50] has developed a dynamic dilution facility for evaluating odorous effluents in the laboratory. This system has a dilution range of

30 to 10,000. Odorous samples are stored in Tedlar bags for presentation to panel members who are seated in a series of booths. The arrangement of cubicles along one wall of the room provides for the six panelists to be separated from each other and the panel leader. The inside of the room is painted with materials that are non-absorptive to odors. The odorous sample is withdrawn from the bag under positive pressure and diluted with air deodorized by passing through charcoal. Essentially 1 cubic foot per minute of gas is passed through stainless steel lines for presentation to the panelists. This system provides two ports, one for a non-odorous air blank and the other for the diluted odor sample. The panelists are instructed to sniff one port at a time and signal their choice by pressing the button corresponding to what they believe to be the odorous port. Usually, five or six different dilutions of the original sample plus one air blank are presented to the panel. In practice, responses to the diluted odorous sample are recorded by the panel leader for evaluation.

9. TRC Mobile Odor Laboratory

The Research Corporation of New England (TRC) uses a 27 foot mobile van that travels to the odor source [20, 51-52]. The dynamic dilution system used in the mobile field laboratory is a replica of the unit used in TRC's Odor Research Laboratory. This dilution system is made of glass and Teflon.

It has a dynamic range approaching 4 x 10^6 dilutions. The van is equipped with an air conditioning system. Activated charcoal filters provide a continuous supply of odor free air to the panelists. A positive pressure minimizes panelist exposure to outside odors. Normally 6 to 8 panelists are required.

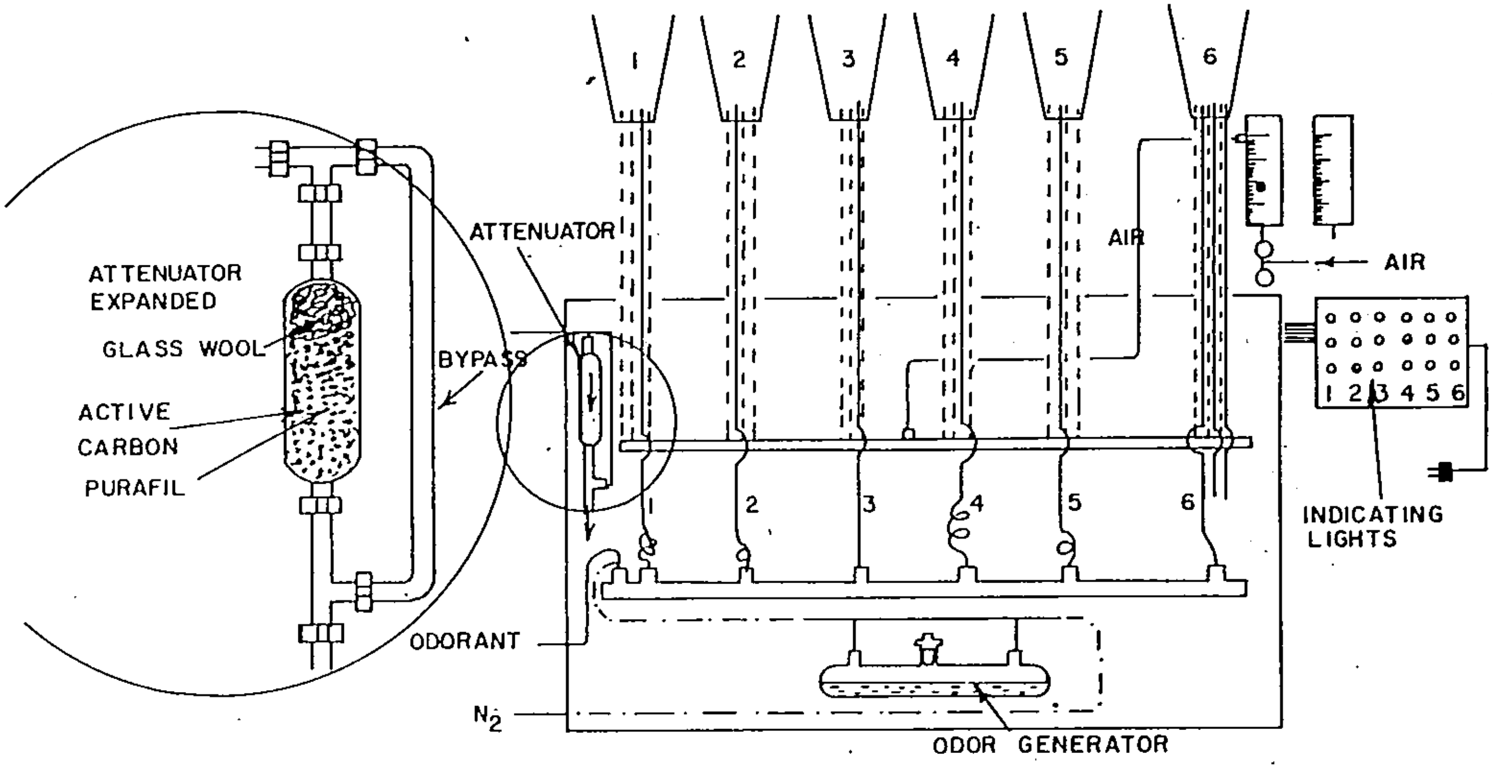
10. WSU Mobile Odor Perception Laboratory

Adams et al [53, 54], at Washington State University, designed an odor perception laboratory by converting a 35 foot bus into an air conditioned, mobile unit which travels to odor sources. The mobile laboratory evaluates the responses of diverse groups of subjects at fairs, expositions, hospitals, elementary schools and universities. Dynamic dilution of an odorous sample is performed in two stages. In the first step, an odorous sample, after continuous blending with charcoal filtered air, is stored in a vessel maintained at constant pressure. The second stage provides the desired dilution at the individual chamber inlets by blending a known flow of the odorous gas, collected in the first stage, with odor free air. This system provides a range of concentrations within the exposure chamber from 1 ppb to several ppm. The subjects smell diluted gas samples from six chambers in any order. The panel leader records whether or not an odor is detected at each chamber maintained at different concentrations. The data are fed to a computer for analysis.

11. IITRI Dynamic Triangle Olfactometer

The olfactometer illustrated in Figure 1 was designed by Dr. Dravnieks of the IIT Research Institute. It is based on the forced-choice triangle principle [55-56]. This device provides 6 dilution levels. Each level corresponds to a 3 sample "triangle" composed of two non-odorous air blanks and one odorous sample diluted with deodorized room air. In practice each panelist is instructed that one of the three ports of each dilution level may exhibit an odor different from the other two. The objective is to decide, through forced-choice, which port is delivering the odorous specimen. Each panelist signals his choice by depressing the button corresponding to his perception of the odorous port. The three ports are arranged in a circular, symmetrical, pattern to produce a double blind sample presentation. Neither the panelist nor panel leader knows the correct choice until a decision is made. This approach eliminates operator/panel leader interaction.

By design a panelist proceeds from the most diluted sample towards higher concentrations of the odorant in air. The dynamically diluted samples are presented at a constant flow of 500-600 ml/minute. The six odor levels increase each time by a factor of approximately 3. The dilution levels starting from Port 1 to Port 6, are approximately 1600, 540, 180, 60, 20 and 7. They can be increased by a factor of 27 with an attenuator (supplied with the olfactometer). An ascending order of presentation is necessary to prevent temporary loss of olfactory sensitivity which occurs if the stronger odor is smelled first [57].



PIGURE 1: Details of IITRI Dynamic Olfactometer [56]

The panel leader records the judgements on a specially developed form. The data are reduced according to a ranking procedure that provides the average panel odor threshold (ED_{50}) for each odor sample. The evaluation of one sample is routinely completed by a panel consisting of 8 to 9 members in less than 30 minutes. This method is less effective in providing accurate and reproducible test results at low odor levels due to the limitation caused by the very low flow of the odorous sample stream. If background odors become more obvious panelist indecision and confusion can result [58].

IV. PARAMETERS AFFECTING ODOR MEASUREMENT

There are many discrepancies in odor threshold values presented in the published literature [59-60]. The wide divergence in reported thresholds may be attributed to the wide variety of techniques and methods that have been used for odor determinations. Although sensory analysis is a convenient solution to the problem of odor measurement, this technique is far from being free of difficulties. Human beings generally differ in their responses to the same odorant with respect to the odor characteristics.

It is of practical importance to review the effects of various parameters on odor threshold measurements.

A. Purity of Odorant

The presence of trace impurities in an odorant can change the odor character significantly and make it difficult to determine the true threshold value. The purity of commercially available chemicals is usually not very high. The combination of the impurity with the odorant being studied may produce synergistic, counteractive or additive effects that could influence the odor threshold significantly.

B. Background Odors

Background odors may have the same effect on the odor threshold as the impurities in the commercially available chemicals. Leonardos [42] has observed a number of effects of the background on odor perception. For example, a background contaminated with trace impurities of diesel exhaust increased the threshold value of p-chlorophenol 40 times over that determined in a controlled background. The threshold value of ethyl mercaptan decreased by 10 times as a result of introducing 1 ppm of SO_2 into the background. Leonardos [42] further noted that the effect of the background odors was to increase the spread in the observed threshold values when trained analysts were used as a panel.

C. Sample Humidity and Temperature

It has been reported recently that temperature and humidity affect the perception of cigarette smoke and pure vapors [21]. The work of Kuehner [22] and Kerka et al [23] has also indicated that at constant temperature (dry bulb) an increase in humidity lowers the intensity level of cigarette smoke and pure vapors, while at constant specific humidity an increase in temperature lowers the odor perception only slightly.

The investigation on phenolic resin curing oven emissions at the Research Corporation of New England [20] has indicated that condensation during sampling results in a loss of odor with Saran bags, whereas the opposite was seen with Mylar bags. Schuetzle et al [44] report that as a result of condensation of hot gases from foundary operations a decrease in odor threshold values was observed.

D. Adaptation

Adaptation refers to the adjustment of the sense of smell to small variations in the environment. The sensitivity of the nose for a specific stimulus is thus reduced; that is, the threshold limit increases when adaptation has occurred [61-62]. It has been found that

i. the adaptation rate for humans is different for different odors

ii. the threshold limit increases more rapidly with an odor of high intensity than with one of low intensity

iii. the adaptation rate depends on the sequence in which an odor is presented.

Adaptation reduces human response to odors until a state of equilibrium or steady state is reached. The response can be reduced to zero (total fatigue) with increases in odor concentration. Work on adaptation has been discussed in detail elsewhere [63].

E. Odor Presentation Sequence

Pangborn et al [57] investigated the influence of odor presentation sequences on olfactory response to 2-heptanone stimuli. The samples were presented to a panel consisting of five subjects in a

i. randomized

ii. ascending, and

iii. descending fashion.

At all levels of detection of the odor stimuli, the descending sequential presentation yielded higher thresholds than the ascending sequential presentation. The descending method of odor presentation produces errors due to "adaptation", the tendency of reporting "yes", whereas the ascending method of presentation suffers from "anticipation" effects. A detailed discussion of these errors of judgement is covered by Swets [64].

The randomized method of presentation yielded a threshold value very close to the average of the ascending and descending modes of exposure. The median threshold value in the randomized presentation agreed with the value reported by Stone et al [65] who used a paired presentation method consisting of one blank and one stimulus sample.

The ascending method of limits [66] is the basis of odor detection criteria for the dynamic dilution measurement devices such as the IITRI Olfactometer developed by Dravnieks and Prokop [67].

F. Measurement Devices

The literature abounds with conflicting claims with respect to odor thresholds even for pure substances [59-60]. The different values of odor thresholds are due, at least in part, to the variety of equipment and procedures adopted for the odor measurements.

Leonardos [42] reports that the static odor test room procedure tends to give threshold values similar to those obtained by the dynamic dilution techniques. He also found that the ASTM syringe method produced considerably higher threshold values; sometimes 200 to 20,000 times greater, than the thresholds established by the odor test room or the odorhood techniques.

Dravnieks and Prokop [67] correlated ED_{50} values obtained by the dynamic dilution forced-choice triangle method to the values from the ASTM syringe dilution technique with a regression equation of the form

$$\log(ED_{50}) = 0.20 + 0.94 \log(\text{odor units})$$

This relationship yields dynamic dilution ED_{50} values that are higher than the ASTM odor values (at 1000 O.U. level the ED_{50} value is greater by 5%; at 100 O.U. by 20%; and at 20 O.U. by 33%).

A comparison of the Hemeon Odor Meter [16], another dynamic dilution method, with the ASTM static dilution method [36] shows a similar trend. The differences between the two threshold values increase at lower concentrations.

Dravnieks et al [68] have also developed a relationship between ambient odor measurements made with a dynamic dilution forced-choice triangle olfactometer and with a scentometer, a device commonly used for odor control regulation. Under controlled laboratory conditions, a scentometer reading of dilution to threshold (D/T) = 2 was equivalent to an ED_{50} = 4.8, and D/T = 7 was equal to ED_{50} = 9.5.

A study conducted by The Research Corporation of New England for the State of Illinois Environmental Protection Agency and U.S. Environmental Protection Agency on typical process emissions from rendering, pulp and paper, food processing, oil refining, steel mill, resin and enameling plants [51] has shown that

i. the reproducibility of the odor measurement systems varied with odor type and level. Dynamic dilution systems produced lower variations (52 to 78% based on a 95% confidence limit) than the static method (83 to 144%).

ii. the forced-choice dynamic dilution technique (IITRI) of presenting odor samples was the best method for minimizing panel guessing ("false positive" responses) and panel leader influence.

iii. high flow sample streams of 10 to 75 cubic feet per minute in the Hemeon Odor Meter created confusion among the panelists. They were not sure whether they were sensing odor or reacting to odorous gas stream pressure in their noses [69]. High odor flow rates also increased the chance of contaminating the background odor levels.

iv. low flow of the sample streams at low odor levels in the forced-choice dynamic dilution method (IITRI) tended to increase the effect of background air thus requiring a high degree of cleanliness.

G. Odor Panel Selection

It was mentioned earlier that no analytical instrument can measure the sensory characteristics of odors as well as the human nose can. Therefore the nose remains as the ultimate judge. However, the response of even a highly trained judge is extremely variable. This means that more than one panelist is essential for obtaining reliable odor data. An odor panel must be selected on the basis of careful consideration of the type of information and measurement desired. For example, an evaluation of community odor nuisance would require a panel representative of the entire population. On the other hand, odor intensity or threshold determinations could be conducted with only a few trained experts [42].

The selection of an odor panel can be considered in terms of

i. prescreening procedures
ii. number of panelists
iii. other factors (sex, age, smoking habits, eating habits).

1. Prescreening Procedures

Wittes and Turk [70-71] have presented various methods of screening candidates for odor panels and statistical procedures for evaluating odor results. They recommend that the selection of an odor panel should be based on the ability to

i. differentiate odors of different quality at low intensities
ii. differentiate odors of the same quality at various levels of intensity
iii. focus attention on more than one odor quality in a given sensation
iv. understand test procedures
v. exhibit satisfactory behavior during tests.

The Research Corporation of New England [20, 51] used a triangle test for screening odor panel candidates. Subjects were presented with three samples. Two were identical and one was of a different quality, but all were at low intensity. Each candidate was asked to sniff (inhale slowly through the nose for short periods) and pick out the odd sample. Dilute aqueous solutions of food flavors and other compounds such as oil of wintergreen, butyric acid and pyridine were used as odorants. These procedures can also be used for training an odor panel. Correct answers are disclosed after a group of trainees has completed the test. Repetition focusses attention on the elimination of errors.

2. Number of Panelists

In odor measurement work odor panels of widely varying sizes and compositions have been employed. Hemeon et al [16, 72] report that two or three subjects are convenient and adequate for reasonably consistent odor determinations. Sullivan et al [53] at Washington State University have converted a 35 foot bus into an air conditioned, mobile, odor-perception laboratory which uses test subjects from diverse populations found at fairs, expositions, schools and universities. Arthur D. Little, Inc. [11, 42] employed four trained staff members, each possessing more than one year of analytical experience, to measure the recognition threshold of 53 commercial chemicals. On the other hand, Wilby [17] at South California Gas Company, chose a 35 member untrained panel, to more closely approximate the total population, for threshold measurements on 18 sulfur compounds found in natural gas.

The size of a panel can significantly affect the cost of a venture as well as the complexity of data reduction. A practical panel size must represent a compromise between the measurement cost and the desired statistical confidence in the odor determinations.

For industrial odor measurements concerned with the evaluation of dilution thresholds, the panel must reflect odor sensitivity of a broader population, both with respect to the mean threshold value and to the distribution of sensitivities within the population [6]. Although trained subjects can discriminate small differences in odor characteristics they do not represent the response of the broader population. Dravnieks [6] states that training of subjects increases the ability to recognize odor character but does not enhance the ability to detect odors. Panels composed of subjects with average, lower-than-average, and higher-than-average sensitivities would provide more useful information than a carefully selected panel made up of individuals with similar sensitivities. The latter would produce very homogeneous and biased data.

3. Other Factors

In addition to the effects of prescreening procedures and panel size, other factors such as age, sex, smoking habits, social background, environment, occupation and pathological conditions must be considered with respect to their effects on the sensory perception of a panel. Summer [73] reports that the sense of smell varies with age, being highest at puberty or soon after. The Research Corporation of New England [20] has investigated the effects of age, sex and smoking habits on the odor response of a panel. No clear evidence was found that the age of a panelist was a significant factor although older persons did **respond** generally at the higher concentration levels. Male and female members did not seem to respond differently, but smokers were found to be less sensitive to odors.

H. Sampling Procedures

An ideal procedure for odor determination demands that the measurements be conducted by a panel directly at the source, where the odor sample can be continuously withdrawn without need for storage. This direct approach eliminates many possible sources of measurement errors and allows the collection of large amounts of data. However, the direct odor measurement techniques usually require a mobile laboratory, specially equipped for sensory testing. Consequently, direct measurement is impractical for most situations thus necessitating sample collection and storage. Collected samples must then be transported to an odor free laboratory for sensory evaluation.

Figure 2 illustrates some of the common sampling techniques for odor acquisition. The ASTM syringe method involves the collection of samples into 100-ml syringes or 250-ml glass bulbs. Dravnieks [74] reports that the relatively small volume of sample surrounded by a large glass surface area may lead to odor losses through adsorption, or sometimes catalytic degradation. On the other hand, Benforado et al [75] have not observed any loss of odor due to adsorption in a 250 ml glass sample tube even though the surface to volume ratio was relatively large.

Pre-evacuated stainless steel cylinders are conveniently employed for sampling but their use raises questions of adsorption and chemical losses [6, 20]. Cleaning of these containers is difficult. Undesirable chemical effects can be minimized if the containers are constructed of inert material such as Mylar, Teflon, Saran, Tedlar, or polyethylene and designed to give small surface to volume ratios.

The most widely used method involves sample collection in plastic bags. These are filled either by a lung technique or a peristaltic pump by which the sample is "milked" through disposable tygon tubing into a plastic bag [6]. Proper selection of bag material is mandatory in order to avoid adsorption and permeation losses.

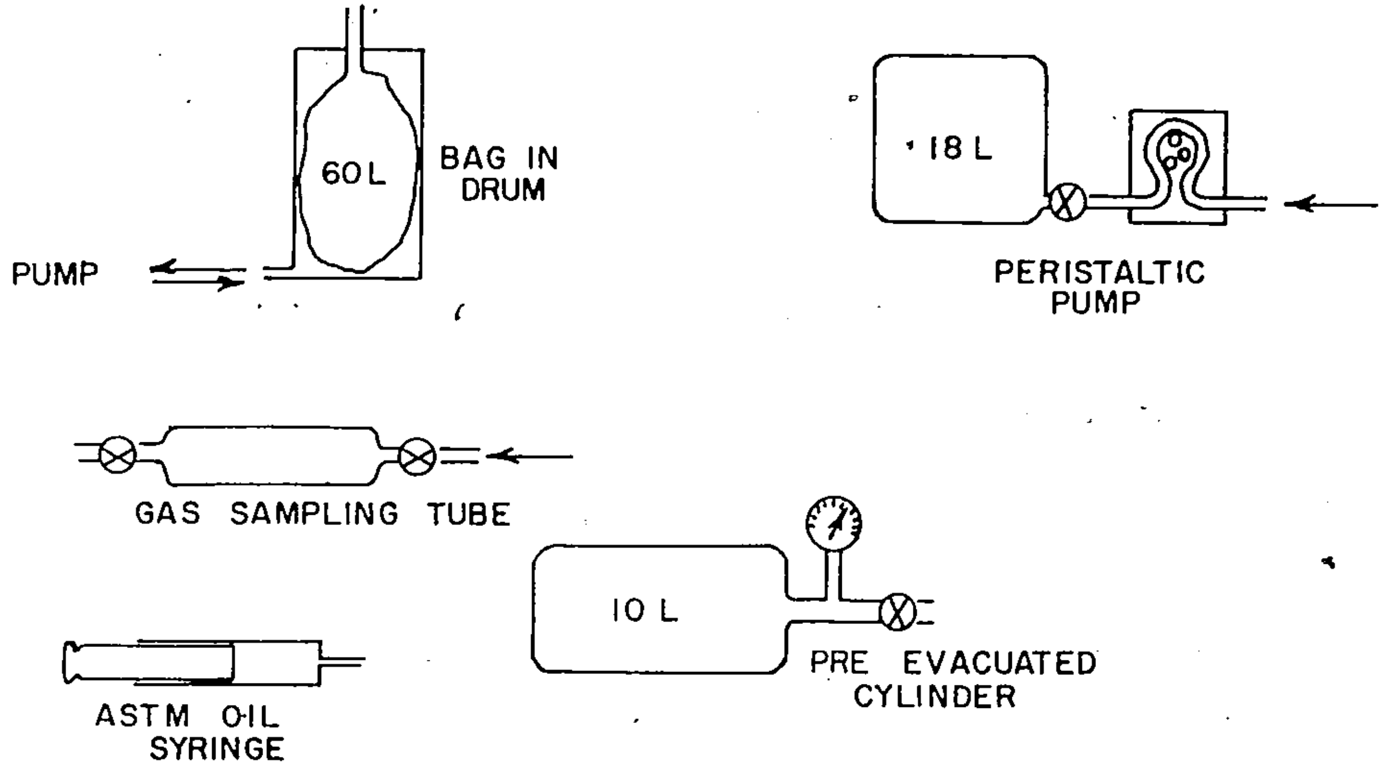


FIGURE 2: Sampling Techniques for Sensory Evaluation of Odorous Emissions [6]

Duffee and coworkers [20] have indicated that Saran, Mylar, Tedlar and thick-walled polyethylene containers will maintain phenolic resin process odor integrity for one to three hours. After this time interval there is a rapid decrease in odor level. They found that for levels higher than or equal to 1000 O.U., the odor level loss was 50% or greater after 24 hours. For low odor unit levels, little change was observed in the odor levels after a 72 hour aging period. A recent study at the Research Corporation of New England [51] has indicated that while varnish emissions can be stored, paint solvent vapors and bake oven emissions cannot be stored for more than 5 hours without decreasing the odor level by as much as a factor of 2. Glass and stainless steel containers have proven to be unacceptable for pulp and paper process emissions containing sulfur compounds. In an earlier study, Duffee et al [52] compared the storage characteristics of a 75 litre Tedlar bag with a 100 litre Saran container. They found that the Tedlar bag maintained its integrity for rendering process odors up to 20 hours while the Saran bag suffered a decrease in odor level of 50% in 20 hours.

Hemeon [16] has suggested that odorant adsorption on the walls of a five cubic foot polyethylene bag is insignificant during a period of 2 to 3 hours. The bag, however, had to be disposed of after one odor measurement. Also, other workers [19, 76] do not think that polyethylene has adequate strength and impermeability for use in odor sampling.

Cormack et al [77] have found that a 55 litre Tedlar bag prepared from 200 gauge DuPont sheet is markedly superior to polyethylene. Their results with Tedlar bag material showed that

i. the odor threshold for butyric acid increased from 0.001 ppm after 1 hour to 0.003 ppm after 23 hours of storage (based on initial condition)

ii. the odor threshold for dimethyl sulfide (0.003 ppm) and acrolein (0.1 ppm) did not change after 23 hours of storage

iii. the odor threshold for diethylamine (0.02 ppm) did not change after 72 hours.

Dravnieks and Prokop [67] have investigated the storage capabilities of thick-walled polyethylene bags for valeraldehyde/odors, rendering plant effluents and dilute mixtures of hydrogen sulfide and air (5.5 ppm). Their findings indicate that odor samples can be stored in the polyethylene bags for 48 hours without degradation. A recent study by Dravnieks et al [68] has indicated that ambient air and weak rendering odors can be satisfactorily collected and stored in Teflon bags for up to 36-48 hours. Bags containing samples of weak rendering odors (ED_{50} = 30 O.U.) can be deodorized for reuse after 3 to 5 repeated flushes with non-odorous air.

Schuetzle et al [44] found that polyethylene, Saran, and Mylar are not suitable for collecting organic emissions from foundry operations (core oven), whereas Tedlar bags experience hydrocarbon losses of less than 10% over a period of several days. On-site hydrocarbon measurement results indicated hydrocarbon losses from 7.3 to 38.2% in Tedlar bags depending upon the nature of the organic emissions. These losses were directly related to the temperature and polarity of the organic gases. Odor losses of up to 82% were found with Tedlar bags for paint bake oven emissions by Scheutzle et al [44].

Attempts to minimize losses due to adsorption have included increasing the size of the bag [52, 77-78] and preconditioning the bag [16, 20, 44, 51-52, 67].

Although Tedlar seems to be a good container material for storing organic source emissions, there still exists the possibility of sample condensation. The losses due to condensation can be minimized by diluting the sample at the source [44].

V. EXPERIMENTAL DETAILS

The objective of this project was to

i. develop a reliable and reproducible procedure for odor threshold measurement for a variety of odorous gas emissions

ii. establish the precision with which odor determinations can be made for compliance purposes

iii. determine the suitability of various synthetic polymer bags for odor collection and storage, prior to source or ambient odor level determinations.

To reflect these basic aims, attempts have been made to

i. perform odor threshold determinations on odorous samples of known composition to establish the reliability of the measurement technique.

ii. evaluate the performance characteristics of synthetic polymer bags with respect to odorous gas collection and storage.

A. Odor Sample Preparation

Generation of odor samples for test purposes required the design and construction of

i. a clean air system

ii. a feed preparation system, and

iii. an odorous air sampling system.

1. Flow Diagram for Odor Sample Preparation

Figure 3 provides a schematic representation of the equipment used to prepare odor samples. Compressed air from the 40 psig laboratory air line, controlled by a pressure regulator, was passed through a filter where oil and dirt were removed. The filtered air was deodorized by a charcoal holder containing 6 inches of activated carbon prepared from animal bones.

The purity of the clean air stream was checked frequently by an olfactometric sniff test. Total hydrocarbon analyses showed a methane equivalent less than 4 ppm in the air from cleaned bags.

Liquid odorants were injected into the clean air line by means of a motor driven 30 ml syringe device equipped with a variable speed control and revolution counter. The variable speed controller permitted regulation of the odorant feed rate into the system. The volumetric flow rate of the air was measured by means of a calibrated rotameter and controlled with a needle valve. Since the odorous air concentrations were well below those corresponding to odorant vapor pressure values at standard atmospheric conditions, it was reasonable to assume that all of the injected odorant was completely converted into vapor. The air temperature was measured with mercury thermometers and static pressures with a U-tube manometer. A portion of the odorous air was diverted to the sampling system with the remainder being vented to the fume hood.

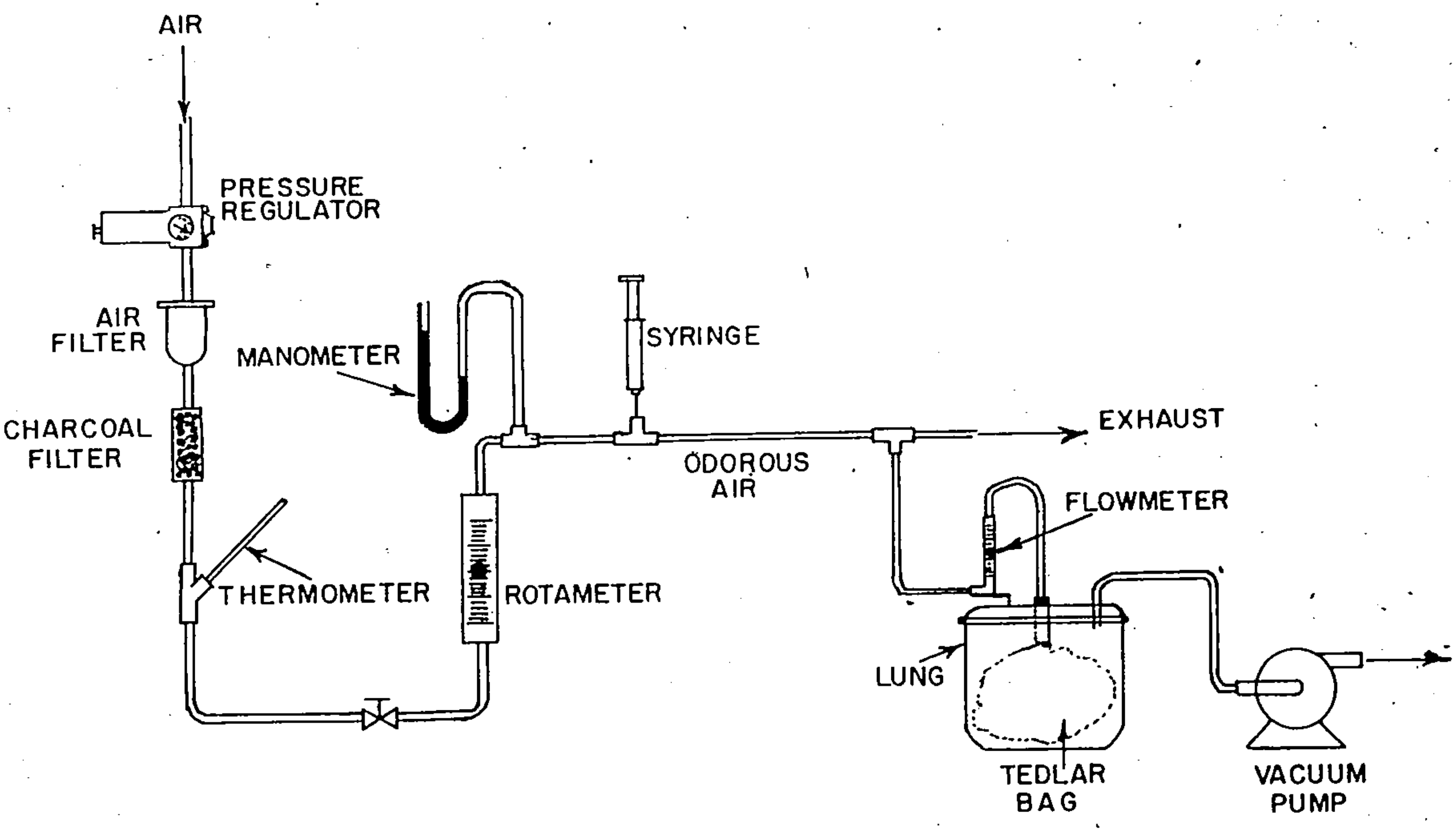


FIGURE 3: Flow Diagram for Odor Sample Preparation and Sampling

For any specific test, the odorant was introduced into the clean air after the desired flow was established. The system was allowed to operate for about 15 minutes to insure a steady state odorant flow. This was checked from time to time by sniffing a portion of the odorous air stream. The system was then ready for sampling. After termination of sampling, the odorant feed was turned off and the air was allowed to pass through the system at a reduced rate for several hours to deodorize the unit.

An odor sample from the odorous air preparation system was drawn through the regulated flow meter into a plastic bag, which was contained inside the lung. Sample acquisition was accomplished by evacuating the lung by means of a vacuum pump. When the bag was filled with an 8-10 litre sample in about 10 minutes, the valve at the flow meter inlet was closed and the pump was disconnected. The lid was then removed, the inflated bag detached and the diaphragm valve closed.

The positive pressure in the air line was more than sufficient to inflate the bag.

2. Equipment Details

a. Odorant Injection System

The odorant feed system consisted of a 1/6 H.P. electric motor, a gear reduction unit, a variable speed control, a syringe and syringe harness. A counter provided an additional check on the odorant flow in terms of the number of revolutions of the motor over any specific time interval.

The speed of the motor could be varied from 2.5 to 35 rpm. This range represented a ratiotrol scale from 0 to 100 respectively. A 30 millilitre glass syringe, manufactured by Becton, Dickinson and Company, equipped with needle no. 20, was used for introducing odorants into the clean air system through a Swagelok 'T' with a Teflon septum. Odorant injection rates were varied from 0.0267 to 0.0435 ml/min through ratiotrol settings ranging from 10 to 20 respectively.

b. Odor Sampling System

The odorous air sampling system consisted of a 20-litre stainless steel Presto Pressure cooker, a sample bag, and a vacuum pump. The National Presto Industries' pressure cooker, hereafter called the lung, was equipped with a flow meter and two bulk-head fittings passing through the air tight lid. The flow meter, supplied by Dwyer Instruments Inc., could measure odor sample flows up to 1.0 litre/min. The sample bag diaphragm valve was connected to the bottom of one of the bulk-head fittings as shown in Figure 3. A Cole Parmer Instrument Company vacuum pump (Model No. 7530-40) equipped with 1/4 H.P. motor was connected to the top of the other fitting. This was used to produce a vacuum inside the lung. The lung was essentially an air-tight rigid container large enough to hold a bag when inflated to a 10 litre capacity.

3. Calibration Procedures

a. Air Rotameter

The air rotameter was calibrated directly by means of a temperature compensated Rockwell bellows-type dry test meter which was previously calibrated with a wet test meter according to standard procedures. Air temperature, static pressure and atmospheric pressure data provided volumetric flow rates at standard conditions of 29.921 in. Hg. and 32°F. The rotameter calibration curve is given in Appendix I.

b. Odorant Injection System

The odorant injection system was calibrated by discharging the syringe contents into a rubber stoppered bottle (to prevent escape of the odorant vapors) and weighing the contents of the bottle. Ratiotrol settings ranging from 10 to 40 provided sufficient samples for weighing after 30 to 60 minute time intervals at each ratiotrol setting. The number of motor revolutions at each setting were also recorded by means of a counter which provided a check on the odorant flows. The calibration curve for the odorant injection system is illustrated in Appendix I.

B. Odor Threshold Measurement

1. Equipment

The odor measurement equipment consisted of a dynamic olfactometer and an odor test room. Figure 4 illustrates the flow patterns associated with the olfactometer which was located in the odor test room.

a. The Olfactometer

The olfactometer used in this study was purchased from IIT Research Institute, Chicago, Illinois 60616, U.S.A. It consisted of a dilution air pump, C, a peristaltic odor sample pump, B, a signal box, air rotameters, soap film (bubble) flow meters, deodorizer chamber, 6 sets of sniffing ports, splitters for air and odorous sample, attenuator, glass tubing and Teflon sample lines.

The dilution air pump was equipped with a Teflon lined neoprene diaphram. Supplied by Thomas Industries, 1419 Illinois Avenue, Sheboygan, Wisconsin 53081, this unit can deliver 9000 ml/min of deodorized air.

The peristaltic pump, supplied by Sigmamotor, Inc., New York, New York, was equipped with disposable Food Grade Tygon tubing for delivering 100 ml/min of odor sample.

The signal box had six triple sets of lights and operated on a 6.3 volt, 60 cycle electrical supply.

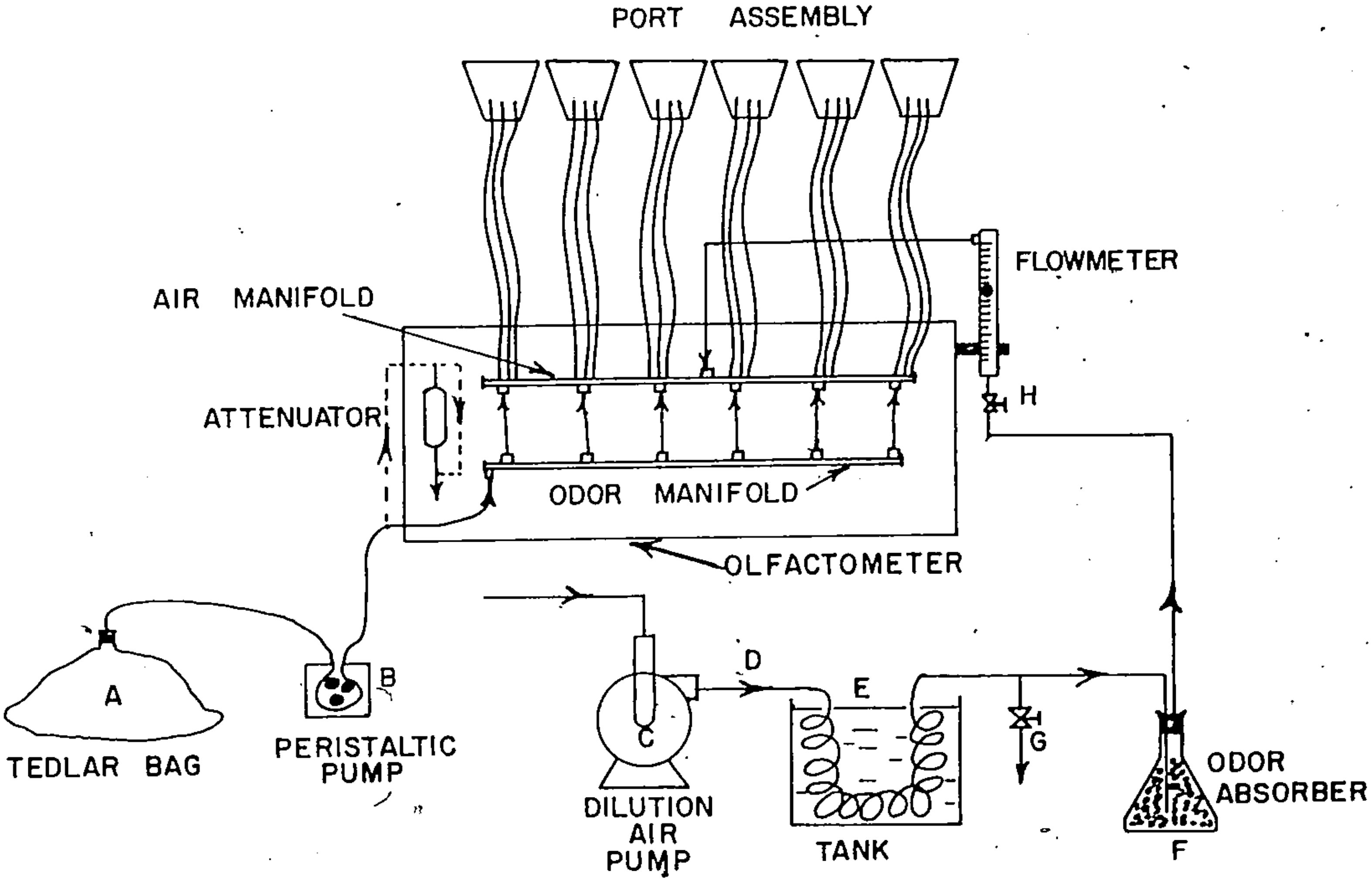


FIGURE 4: Equipment Flow Diagram for Odor Measurement System

Air rotameters No. RMA-SSV-16 (10,000 ml/min with stainless steel valve) and No. RMA-12 (500 ml/min) were supplied by Dwyer Manufacturing Company, Indiana. The 10,000 ml/min rotameter was used to regulate the dilution air flow to the six sets of ports. The 500 ml/min meter was used to calibrate the dilution air flow to each port.

The soap film (bubble) flowmeter (10 ml capacity), Cat. No, 96-000015-00, was supplied by Varian Associates, 5151 North Harlem, Chicago, Illinois 60068. This bubble flow meter was used for calibrating odor sample flow to each port.

The deodorizer chamber contained activated carbon and Purafil (permanganate-coated alumina) for deodorizing the dilution air. The Purafil was supplied by Purafil, Inc., Chamblee, Georgia 30361.

The splitters for air and odor distribution to the ports in the desired ratios were made by IIT Research Institute.

The glass sniffing ports used for delivering dilution air blanks and diluted odor samples to the panelists were developed by IIT Research Institute. Each port supplied approximately 500 ml/min of dilution air.

The olfactometer came equipped with one attenuator, normally supplied by Supelco Company, Bellefonte, Pennsylvania 16823 or Anallabs, Incorporated, North Haven, Connecticut 06473. Insertion of this attenuator in the odor sample line increased dilution levels by a factor of 27. During the progress of this project different attenuators were needed. Attenuator details are given in Appendix II.

Teflon tubing was supplied by Pennwalt Plastic Company, Clifton Heights, Pennsylvania. Tygon tubing was supplied by Auburn Plastic Company, Chicago, Illinois.

A detailed equipment description is given in the Instruction Manual for Dynamic Triangle Olfactometer, 1977 Model [56].

b. Odor Test Room

The odor test room was 4 feet long x 4 feet wide x 8 feet high. It was constructed as a totally enclosed double walled chamber, equipped with a door, a glass window, an interior light, a portable electronic air cleaner and an exhaust fan for ventilating odors. The test room housed the olfactometer and a wooden stool for seating the panelists during odor perception tests.

The inside walls and ceiling of the room were constructed of washable arborite. Washable vinyl tiles with neutral color schemes and low background odors were used as the floor lining. The outside walls were constructed of walnut colored wooden sheets. A remote control signal box was mounted on one exterior wall where the panel leader could record individual panelist responses during odor measurement. A telephone was provided for communication between panelists and the panel leader during odor testing. All electrical switches were placed on the outside walls. Precautions were taken to maintain the test room atmosphere free from any distraction or outside noise. However a low level noise was produced by the portable electronic air cleaner installed through one wall. The air cleaner was capable of delivering odor free background air into the test room at low and high flows of 100 ft^3/min and 150 ft^3/min respectively. It consisted of a two stage electrostatic precipitator for particulate removal down to 0.03 microns, a replaceable activated charcoal filter for smoke and odor elimination, and an outside lint screen for trapping larger dust particles.

An exhaust fan was used when required to evacuate the test room air completely. An odor free background could be restored inside this chamber in about 2 hours.

2. Measurement Techniques

a. ED_{50} Determination by Olfactometer

Odorous gas samples collected in Tedlar bags from either the odor preparation unit or from industrial sources were transported to the odor testing laboratory. All samples were analysed for total hydrocarbon content prior to the odor threshold determinations.

Single panelists interacted with the olfactometer in the enclosed odor test room while sitting on a stool. Each panelist began from the left side of the unit where the largest dilution (weakest odor) was available. The odor testing program involved decisions at six different odor levels. Each odor level was presented by an assembly of three identical glass ports arranged in a circular pattern in a plastic housing. The panelists smelled the effluents from the three ports of each odor level assembly. Any number of sniffs was permitted before deciding which port was odorous. Because this procedure is based on a ternary forced-choice principle the panelists were required to guess in case they were not sure that they could discriminate correctly. A decision was signaled by pressing the button (switch) corresponding to the port suspected of discharging the odorous stream. Each panelist started with the lowest odor level and proceeded to the next higher one, each time being forced to make a decision.

Eight or nine panelists were used for one complete test during a 30 minute time period. The panel leader kept records of individual observations on a pre-printed form. The evaluation of the odor test data is described in Appendix III. Complete details on this unit are given in the IITRI Instruction Manual [56].

b. ASTM Procedure

The standard ASTM method which follows the text of D-1391-57 (Reapproved 1967) [36] was also used for odor determinations to provide comparison with the IITRI dynamic olfactometer results.

Odor samples were collected in a 100 ml syringe, which was flushed with odorous gas, from either the odor preparation unit or the bag sample. The sample syringe, with cap on to prevent loss of odor, was taken to an odor free room where clean air was available for making dilutions. Measured quantities of the odorous sample were injected into dilution syringes partially filled with clean air either directly from the sample syringe or through a transfer syringe. The dilution syringes were filled with the clean air to their 100 ml capacity. Other dilutions, differing by a factor of 2, were prepared in the same manner. Each diluted odorous sample was presented to a panelist along with an air blank. According to the standard procedure the panelists were instructed to inject the contents of each syringe into one nostril by depressing the syringe plunger and then to indicate which of the syringes contained the odorous sample at each dilution level. The highest dilution (lowest odor concentration) at which a panelist made a correct judgement and continued to be correct at the next two higher concentration levels consecutively was taken as his threshold. The geometric mean of the individual thresholds gave the panel threshold. A detailed description of this method is given elsewhere [36].

All syringes and needles were thoroughly scrubbed with unperfumed detergent and chromic acid solution. They were washed with hot tap water, then rinsed with distilled water. After boiling in distilled water for half an hour they were dried in an oven at about 110°C. Before use, cleaned syringes and needles were allowed to cool and condition in room atmosphere.

3. Total Hydrocarbon Measurements

Total hydrocarbon measurements were performed during this investigation to

i. estimate the initial odorant concentrations and odorant losses from bags

ii. evaluate the extent to which bags can be cleaned by any procedure.

A Varian Aerograph series 1200-2 chromatograph, modified by Dr. S. J. W. Price, University of Windsor, was used for the determination of total hydrocarbon content (THC). This analyzer, equipped with a flame ionization detector, incorporated a six port gas sampling valve with a 2 ml sample loop and a recorder, Model No. 261, supplied by Linear Instrument Corporation. The recorder provided a 0-1 millivolt scale for data acquisition. Odor samples were transferred into the analyzer sample loop through copper tubing and air tight fittings by applying pressure on the odor sample bag. The THC analyzer measured the hydrocarbon content as butane which was interpreted in terms of equivalent methane concentration.

Before each analysis, the analyzer was calibrated with standard 97 ppm and 980 ppm butane gas. The analyzer response was a linear function of butane concentration. Analyzer sensitivity was checked at each odor concentration by measuring peak heights at different attenuator settings.

The peak heights were exact multiples of the attenuator factor, except at very low concentrations. These variations in peak heights were due to difficulties in reading the recorder chart when small pen displacements were involved. Every effort was made to calibrate the analzyer using the largest peak heights possible. All data were recorded on the basis of 3 constant peak heights.

C. Odor Sample Bags

The suitability of a vessel for the storage of an odor must be judged in terms of its ability to maintain a constant odor level for a specific length of time that may be needed to accomplish the required odor measurements. The present investigation was concerned with the study of bag characteristics as they depend on various physical and chemical properties of the plastic material of construction. In order to evaluate these bag performance parameters, it was essential to standardize the test procedures used.

1. General Description of Bags

Although a variety of bags are available on the market, some of them were ruled out on the basis of past experience and the work of other investigators [16, 20, 44, 67, 68, 76, 77]. Therefore, only three types of synthetic polymer bags were tested during this study. Tests were carried out on Teflon, vinyl-aluminum protected Polyester and Tedlar bags.

a. Teflon Bags

Nine litre rated capacity Teflon bags measuring 18" x 18" were purchased from

Pollution Measurement Corporation
P. O. Box 6182
Chicago, Illinois 60680

It has been reported that Teflon bags tend to come apart at the seams when filled too much [76]. In fact, the bags used in this study failed even earlier.

b. Polyester Bags

Single sealed Polyester bags were supplied by

The J. W. Ellis Industries
705 Progress Avenue
Scarborough, Ontario M1H 2X1

This type of bag can also be purchased from

Calibrated Instruments, Inc.
731 Saw Mill River Road
Ardsley, New York 10502

The fifteen litre rated capacity bags measuring 18" x 18" were designed with a single diaphram valve in one corner. The outside was protected by a vinyl-aluminum casing. Because of severe leakage when pure air was stored overnight, this type of bag was not considered very seriously for odor collection and storage.

c. Tedlar Bags

Tedlar bags with single seals and double seals were purchased from two sources

i. Pollution Measurement Corporation
P. O. Box 6182
Chicago, Illinois 60680

ii. Plastic Film Enterprises Inc.
429 East Elmwood
Troy, Michigan 48084

These bags were made from 2 mil thick transparent Dupont synthetic polymer sheet. For test purposes, bags were purchased in 3 and 9 litre manufacturer rated capacities. Each bag was provided with a diaphragm valve fitting in the centre of one face. When 2 valve fittings were specified, the second one was installed in the corner of the opposite face.

The 3 litre bags did not provide adequate samples for more than one odor measurement. Also, the surface area per unit volume was greater than that of the 9-litre bag. The 9 litre bag size was chosen as a potential odor container in preference to larger sizes because it

i. provided greater manageability and mobility
ii. just fitted the size of the odor collecting vessel (lung)
iii. provided adequate odor samples for 2 or 3 measurements.

2. Bag Testing For Leaks

Each new bag was tested for bulk leakage by filling with clean air and submerging under water. Frequently, bags leaked at the sealed edges or around the fittings. Only those bags without leaks were used for test purposes.

Prior to use as an odor container each new bag was cleaned of residual odors by flushing with deodorized air. Usually 3 or 4 fill-empty cycles were sufficient for bags equipped with a single valve.

Bags were conditioned by filling with the odorant to be tested and storing for 15 minutes. After evacuation of the odor, the bag was ready for sample acquisition of the odor with which it had been conditioned.

3. Bag Cleaning

Cleaning of used bags was a major problem if they were of the single valve type. The cleaning process involved filling the bags with charcoal deodorized air under positive pressure, and then evacuating by applying pressure on the bag by means of a square, wooden-board having a hole cut out in the centre to accommodate the valve and fitting. This sequence was repeated 11 times. On the eleventh cycle the air from the bag was tested by sniffing. If an odor was perceived, the cleaning process was repeated another 10 times. The cleaning of one valve bags was monotonous and very time consuming especially if trace odors persisted.

The cleaning of bags with two valves was accomplished by connecting the deodorized air line to the centre fitting and venting the contaminated air through the corner valve fitting on the opposite side. The exit end was connected to plastic tubing which was submerged in a beaker partly filled with water to indicate that cleaning was continuing. In practice, the bag was left on stream overnight. Total hydrocarbon analysis indicated that, by morning, air from the bag would contain no more than 4 ppm methane equivalent.

VI. RESULTS AND DISCUSSION

This chapter discusses odor measurement results in terms of

i. the suitability of bags for odor collection and storage

ii. the determination of ED_{50} values for odors of known composition

iii. the development of general procedures for odor threshold determinations.

A. Suitability of Bags for Odor Collection and Storage

Currently, numerous containers made of materials such as stainless steel, glass and different types of synthetic polymers are in use for odor collection and storage. These have been used by various investigators [16, 20, 44, 67, 68, 76, 77] according to their purpose and need. In the present study the general criteria for the selection of containers were

i. size considerations: a container must be filled in a reasonable time and hold adequate sample for 2 or more odor measurements

ii. ease in handling: a container should be easily transportable in a car trunk or rear seat

iii. ruggedness: a container should be sufficiently tough to withstand considerable abuse

iv. inertness: a container material should be chemically inert. This requirement is particularly critical in odor research since small amounts of impurities from the bag can change odor quality and threshold

v. temperature sensitivity: a container should be able to hold hot gases and be able to withstand high temperature surroundings

vi. permeation: a container should have adequate resistance to diffusion to minimize loss of sample during storage.

In view of the above requirements some of the commercially available containers were ruled out on the basis of experiences gathered from earlier published work. The specific reasons for eliminating particular containment vessels are discussed in terms of

i. stainless steel containers: such holders can withstand considerable abuse but are not convenient to handle. Their use also raises questions of adsorption and chemical losses [6, 20]

ii. glass containers: these are not convenient to handle and cannot withstand pressure and abuse. There is also the possibility of breakage at any time. Sample loss through breakage could be costlier than the container itself. Odor losses through adsorption are also high [20, 74]

iii. polyethylene (thickwalled) containers: these vessels are convenient to handle and can withstand abuse. However, they are heat sensitive and cannot be used where a chance contact with a hot pipe or duct may occur. They also lead to high odor losses through adsorption [44] and are high in residual odors

iv. polyethylene (thinwalled) containers: these are convenient to handle but cannot withstand pressure and abuse. They can be easily punctured by sharp objects. Because these bags are highly heat sensitive, their use could create problems in areas surrounding hot ducts and stacks and also in sampling hot gases [19, 76]. Hemeon [16] suggests that odor losses through adsorption are insignificant over 2 to 3 hour periods

v. Saran containers: Saran bags are convenient to handle but need protection from sharp objects. They tear and leak excessively [20]. Odor losses through adsorption are high [20, 44].

vi. Mylar containers: these holders are convenient to handle, but require protection from sharp objects. The sealed edges tend to come apart when filled too much [20, 76, 79]. Odor losses through adsorption [20] are lower than with polyethylene and Saran [44].

Overall, Tedlar and Teflon rank as the better bag materials [20, 44, 76, 77, 80]. Tedlar, Teflon and polyester bags were chosen for further evaluation during this research program. Tedlar bags were purchased from two sources. Both were made of the same thickness Dupont sheet but differed in their construction.

The three classes of bags were evaluated with respect to physical and chemical characteristics such as

i. ease of handling during and after sampling
ii. ability to retain an odor integrity for as long as necessary to complete an odor measurement
iii. loss of odors due to adsorption and/or permeation.

1. Bag Handling and Pressure Retention Characteristics

The bags from different suppliers were examined initially to determine their handling and pressure retention characteristics. Table 1 summarizes the findings of this evaluation. Almost all bags leaked when subjected to the leak test in water. This could be due to the unusually high pressures exerted on them when forced to stay under water during testing. In normal bag evaluation studies which are conducted at atmospheric pressures, the bags would not be subjected to such a rigorous treatment.

Bag Material	Supplier	Ease of Handling	Bag Characteristics
Teflon 9-litre capacity	Pollution Measurement Corp.	very convenient to use; needs protection from sharp objects	single sealed edges cracked by the odor pressure in the full bag at ambient conditions (after the bag was used 6 to 8 times).
Tedlar sheet 2 mil thick, 9 litre capacity	Plastic Film Enterprises	very convenient to use; needs protection from sharp objects	double sealed edges opened up or cracked, leaks developed at the seat of the fitting; the bag material wrinkled* after repeated use; may leak at the creases
Tedlar sheet 2 mil thick, 9 litre capacity	Pollution Measurement Corp.	very convenient to use; needs protection from sharp objects	single sealed edges did not crack or open up even under 50 lb pressure; the bag material wrinkled* after repeated use; may leak at the creases; leaks developed at the seat of the fitting after repeated use

*Although Tedlar bags are durable and rugged, the bag material wrinkled and cracked during usage due to the method adopted for filling and evacuation

TABLE 1: Comparison of Sample Bags from Different Suppliers

The double-sealed Tedlar bags supplied by Plastic Film Enterprises Incorporated should have shown better leak-free characteristics. On the contrary, the sealed-edges cracked and leaked. After completing several odor free air retention tests, the Tedlar bags from both suppliers were tested under water. Some condensation appeared in the form of drops inside the double sealed containers although these bags did not produce any visual air leak in the water. The water drops inside the bags evaporated when the bag was left in the room atmosphere over night. It was not likely that condensation from the contained air could have taken place because this phenomenon was not observed under identical conditions with bags supplied by Pollution Measurement Corporation.

The bag handling and pressure retention evaluations suggested that the Tedlar bags supplied by Pollution Measurement Corporation demonstrated superior qualities, as containers for odor collection, to those shown by the other bags evaluated in this program. Practically, Tedlar bags can be cleaned by heat treatment [44, 80] to remove residual plastic odors which are characteristic of all plastic bags. In addition, these bags proved durable and very rugged. With cautious handling they could be reused many times.

2. Odor Retention Tests

a. Effect of Storage Time on Odor Loss at Different Odor Levels

To study the effect of storage time on odor loss, odor samples were stored in various bags and analyzed for total hydrocarbon content (THC) at several time intervals. The decreases in total hydrocarbon content (THC) with respect to the initial content were expressed as odor losses. Prior to filling with any odor, each bag was conditioned with the odor to be tested for about 15 minutes to minimize any potential adsorption effects. The THC readings were determined with the analytical equipment discussed earlier. Possible sources of errors in these readings could be due to contamination as a result of hydrocarbon accumulation in or on

i. the container valves and fittings
ii. the THC analyzer connective copper tubing and fittings
iii. the fittings and lines provided with the lung
iv. the inside surface of the lung

through repeated use for long periods of time. It was shown experimentally that some accumulation of hydrocarbons occurs on the tubing, fitting and valve surfaces during analyzer operation.

Tables 2 and 3 summarize the results obtained with Tedlar bags holding n-butanol odors at high and low odor levels. Table 4 illustrates the retention capabilities for butyraldehyde odor. At low odor concentrations ranging from 334 to 554 ppm as methane equivalent no loss in butanol

Storage Time Hours	Total Hydrocarbon Content as CH_4 ppm	Odor Loss %
0	1575	0
3	1470	6.7
24	1400	11.1
49	1172	25.6

TABLE 2: Loss of n-Butanol Odor as a Function of Storage Time for PMC Tedlar Bags at High Odor Levels

Storage Time Hours	Total Hydrocarbon Content as CH_4 ppm	Odor Loss %
0	554	0
3	554	0
8	538	2.9
24	498	10.1
0	334	0
3	334	0
8	322	3.6
24	309	7.5

TABLE 3: Loss of n-Butanol Odor as a Function of Storage Time for PMC Tedlar Bags at Low Odor Levels

PMC - Pollution Measurement Corporation

Storage Time Hours	Total Hydrocarbon Content as CH_4 ppm	Odor Loss %
0	162	0
1	162	0
2	159	1.9
22	135	16.7
46	86	46.9

TABLE 4: Butyraldehyde Odor Loss as a Function of Storage Time for PMC Tedlar Bags

odor was observed for the first three hours, Small losses of 3.6% and 2.9% in THC levels were observed after 8 hour periods. These increased to 7.5% and 10.1% respectively with increase in storage time as shown in Figure 5. At the higher odor concentration, the butanol odor loss was much faster during the first eight hours. Further aging of the odor sample resulted in a rather high odor loss of 25.6% after 49 hours.

Preliminary tests carried out with butanol odors at initial THC levels of 618 and 656 ppm as methane (which are not reported in tabular form) indicated that rather high odor losses of 25% after 24 hour and 89% after 50 hour periods occurred with Tedlar bags. At higher initial concentration (3384 ppm as methane equivalent) a butanol odor loss of 55% was noted after a 44 hour storage period.

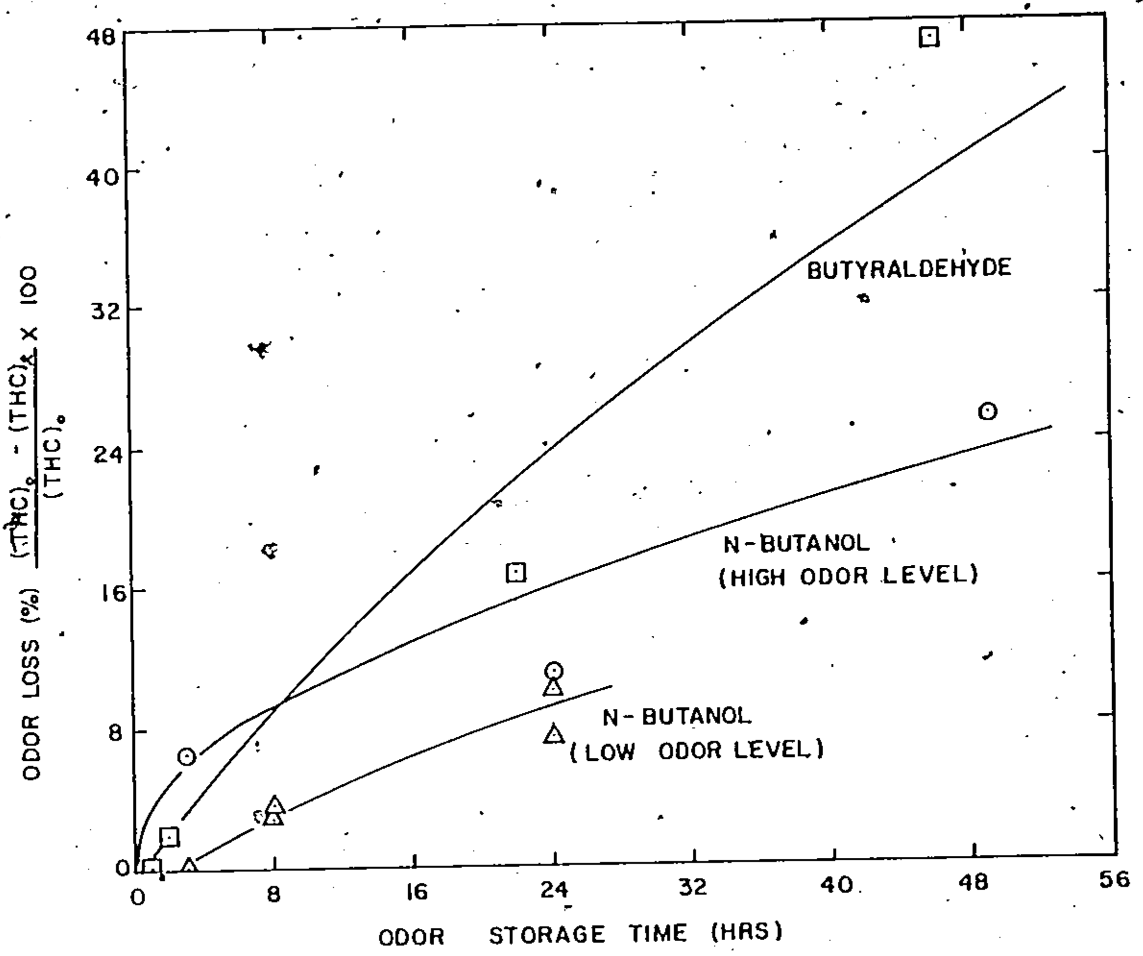


FIGURE 5: Effect of Storage Time on Odor Loss at Different Levels of n-Butanol and Butyraldehyde Odors with PMC Tedlar Bags.

The effect of storage time on butyraldehyde odor loss (at 162 ppm as methane equivalent) is illustrated in Figure 5. The integrity of butyraldehyde odor could not be maintained in Tedlar bags for more than two hours. The odor loss increased rapidly with increasing storage time, reaching 16.7% after a 22 hour period and then increasing 3 fold after 46 hours. In another test with butyric acid odor at 416 ppm as methane equivalent an odor loss of 67% was recorded after a 30 hour storage period in a PMC Tedlar bag. Walter C. McCrone Associates [76] found that an 82% odor loss occurred after 48 hour storage of butyric acid, at 50 ppm as methane equivalent, kept in a Tedlar bag at 110°F.

b. Effect of Storage Time on Odor Concentration at Different Odor Levels

Figure 6 depicts the relationship between normalized odor concentration and storage time for different initial levels of n-butanol and a single level of butyraldehyde odor. The butanol data seem to follow the same relationship on a normalized basis. Even though the number of data points is limited, a relationship of this type, if verified, can lead to needed generalization of a specific odorant behavior. The butyraldehyde losses appear to be higher, but again, data are rather limited.

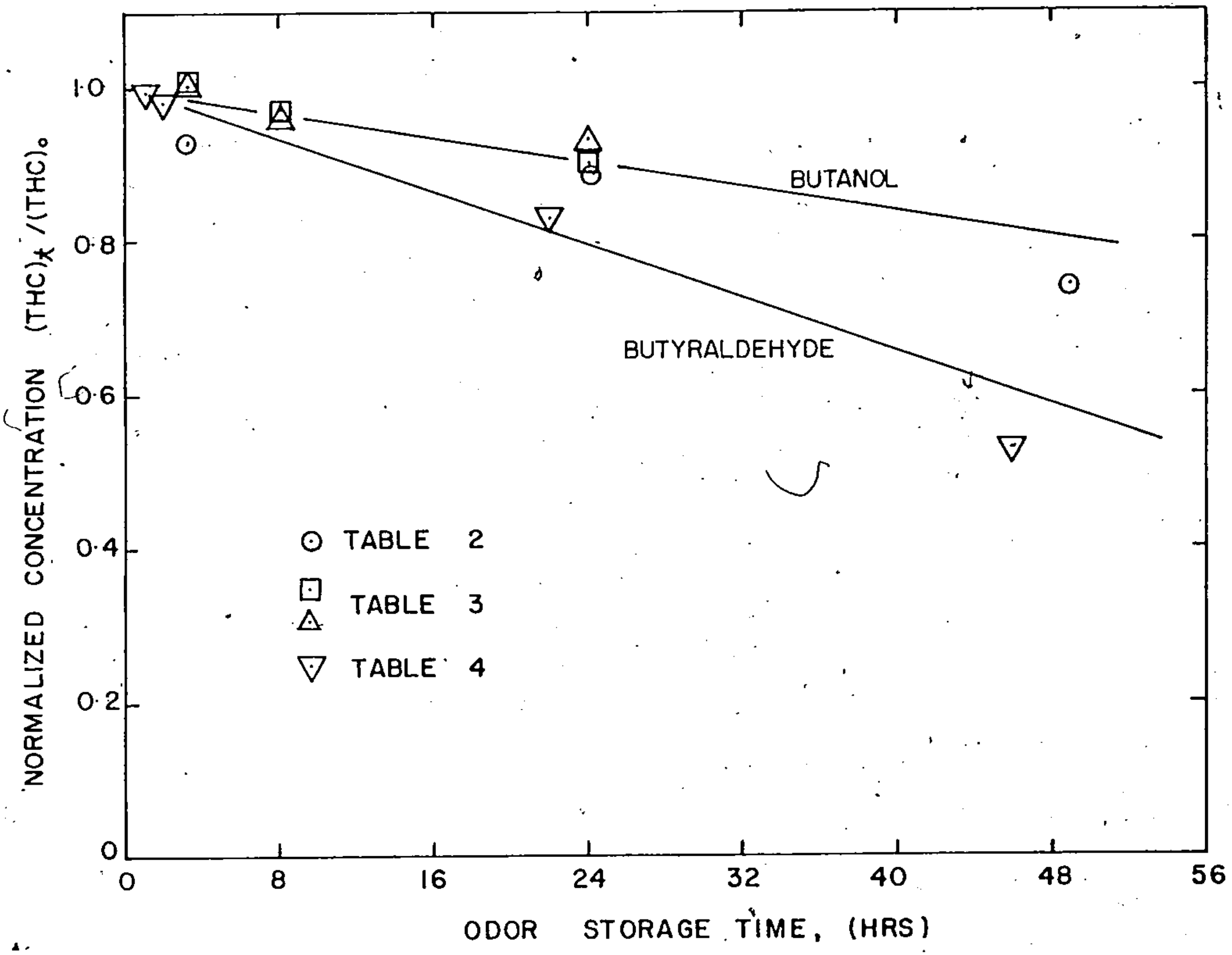


FIGURE 6: Normalized Concentration versus Storage Time in PMC Tedlar Bags

c. Effect of Odor Concentration on Odor Loss for Different Storage Times

The effect of odor concentration on odor loss for different storage times was examined with n-butanol, isopropyl acetate and acetic acid. The data are summarized in Tables 5, 6 and 7. For sample storage up to 48 hour periods the odor loss increased with increasing time as shown in Figure 7. It also appears that the odor loss of n-butanol will not be a significant factor in odor determinations for concentrations below about 600 ppm and up to 3 hour storage periods.

Initial Odor Concentration ppm as CH_4	% Odor Loss After			
	3 Hours	8 Hours	24 Hours	48 Hours
1575	6.7	--	11.1	25.6
554	0	2.9	10.1	--
334	0	3.6	7.5	--

TABLE 5: Effect of Initial n-Butanol Odor Concentrations on Odor Loss for Different Storage Times in PMC Tedlar Bags

Initial Odor Concentration ppm as CH_4	% Odor Loss After 4.5 Hours
11,968	16.5
814	3.7
763	5.3

TABLE 6: Effect of Isopropyl Acetate Concentrations on Odor Loss for 4.5 Hour Storage Times in PMC Tedlar Bags

Initial Odor Concentration ppm as CH_4	% Odor Loss After 6 Hours
1722	11.0
215	6.5

TABLE 7: Effect of Acetic Acid Concentrations on Odor Loss for 6 Hour Storage Times in PMC Tedlar Bags

A similar trend could be noted from Tables 6 and 7 for isopropyl acetate and acetic acid odors respectively. Odor losses were greater at higher odor concentrations than at lower concentrations.

d. Comparison of Tedlar Bags from Two Suppliers

The Tedlar bags purchased from Pollution Measurement Corporation (PMC) and Plastic Film Enterprises (PFE) were evaluated with respect to their odor retention characteristics. The results presented in Table 8 indicates that both bags were identical in terms of butanol odor loss for periods of 24 hours.

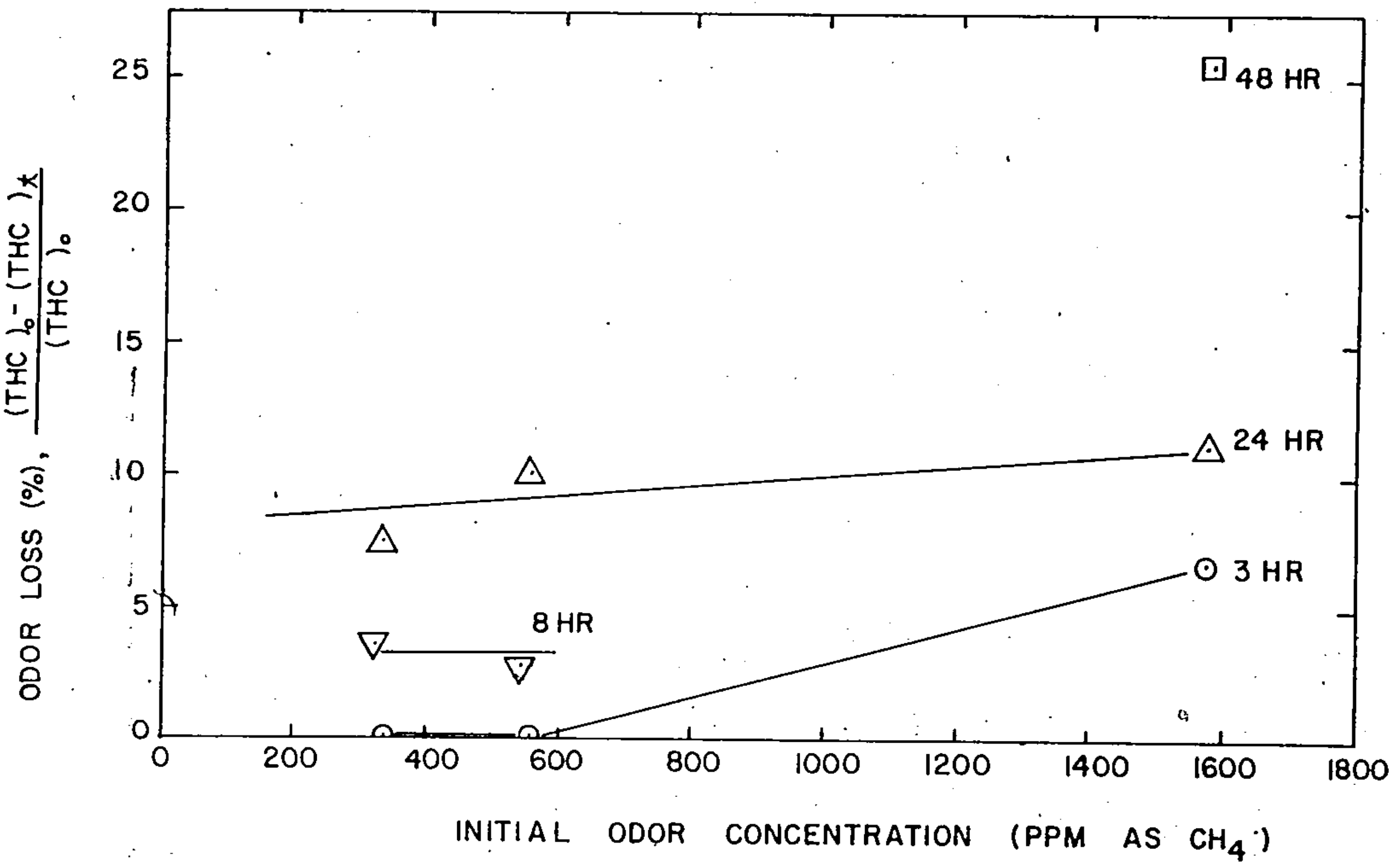


FIGURE 7: Effect of Initial n-Butanol Concentration on Odor Loss for Different Storage Times in PMC Tedlar Bags

Storage Time Hours	Odor Loss, %	
	PMC Bag	PFE Bag
1	0	0
3	0	0
8	3.6	3.1
24	7.5	8.0

TABLE 8: Comparison of 2 Mil Thick Dupont Sheet Tedlar Bags Purchased from Different Sources. (Tested for n-Butanol Odor Retention at 500 ppm as Methane Equivalent).

3. Adsorption and Permeation Characteristics of Tedlar Bags

The results discussed in the preceeding sections indicate that Tedlar bags do lose considerable amounts of stored odors. These findings are consistent with the work of other investigators [20, 44, 76, 77]. Studies at The Research Corporation of New England [20] suggest that the chemical characteristics of odors can change on aging in Tedlar, Mylar, Saran and polyethylene bags. Because of these possibilities an investigation to define the nature and magnitude of odor losses was initiated.

In principle odor losses could be due to adsorption on the inside walls of the container or permeation through them. In order to define the relative magnitudes of these phenomena a standardized experimental procedure had to be developed. The following steps outline the method adopted for the determination of adsorptive and permeative losses from Tedlar bags.

STEP 1: Testing bag for leakage under water

STEP 2: Filling the bag with the odorous gas and measuring its total hydrocarbon content (THC)

STEP 3: Measuring the THC of the ambient air inside the lung after placing the bag inside the air-tight container

STEP 4: Measuring the THC of the air inside the lung and odorous gas in the bag after 20 hours of aging with the lung kept at room conditions.

STEP 5: Calculating odor loss through seepage from the available THC data for the air in the lung and from changes in bag THC levels

The test results are presented in Table 9. According to these data the butanol odor loss from the Tedlar bag was 5.7% after 20 hours. On the basis of free space available in the lung and the increase in THC of the lung contents, the odor losses can be described by an 89.5% adsorptive component and a 10.5% seepage contribution. These preliminary results indicate that the odor loss is mainly through the process of adsorption rather than permeation.

During the early stages of this project total hydrocarbon measurements were carried on our samples collected from different sources. The results shown in Appendix VI, Table VI.1, indicate that background THC levels do not exceed 17 ppm as CH_4. In view of this observation the initial THC level in the lung appears to be unusually high. Some factors that can influence THC determinations have been discussed earlier. In addition to possible desorption from tubing, fittings and valves, the evaluation of THC levels inside the lung could be affected by desorption from the interior lung surface.

Storage Time Hours	Total Hydrocarbon Content ppm as CH_4		Total Odor Loss from Bag %	Odor Loss, % Due To	
	Bag	Lung		Adsorption	Permeation
0	1336	47.2	0	0	0
20	1260	54.4	5.7	89.5	10.5

TABLE 9: Results of n-Butanol Odor Loss from PMC Tedlar Bag Through Adsorption and Permeation

B. Precision and Accuracy of Odor Threshold Measurements

Experiments were conducted to determine the potential applicability of odor threshold measurements to regulatory actions that might involve provincial or federal environmental agencies. For legal purposes the creditability of odor data is determined by their

i. precision, which is a measure of their reproducibility

ii. accuracy, which is a measure of the closeness to the true value.

The determination of the accuracy of odor measurements is made difficult by the psycho-physical nature of the experiments. In practice identical odor samples subjected to the same measurement procedures and panelists often yield different odor thresholds. Consequently, it is necessary to emphasize precision as the major criterion for discriminating between various approaches to odor evaluation.

1. Precision

The precision of an odor measurement system is its ability to produce a consistent odor panel response to replicate runs on the same odor sample. The consistency of a panel response is dependent on the reproducibility of an individual's response to the same odor presented over a range of dilutions.

Table 10 presents typical data for individual panelist responses in terms of positive odor identification. For the IITRI dynamic technique, positive identification is interpreted as the first of three successive correct responses to odors presented in an increasing order of concentration.

Although individual responses appear to be different in the three tests, the observed differences are due primarily to the limitations imposed by the design of the olfactometer. The dilution levels provided at any port by the IITRI Dynamic Olfactometer in replicate tests are slightly different for the different starting conditions shown in Table 10. Recognizing this limitation, it may be concluded that an individual can repeatedly identify the presence of an odor at essentially the same level for a range of initial concentrations.

The responses of 8 different panels selected from a pool of 35 individuals, to n-butanol and isoproply acetate odors are summarized in Tables 11 and 12. There are significant differences in responses within a group, but differences between various panels do not appear to be significant. The sum, the arithmetic mean, the sum of squares of individual panelist responses (S.S.), standard deviation of the mean (S), and standard error of estimate of the mean (S.E.) were calculated for each odor determination. The analyses of variance for n-butanol and isopropyl acetate odors respectively are illustrated in Tables 13 and 14.

Odor	Panelist	Panelist Threshold (First Correct Detection) in ppm					
		75 ppm*		140 ppm*		84 ppm*	
		Test 1	Port No.	Test 2	Port No.	Test 3	Port No.
n-Butanol	EW	0.40	3	0.80**	3	0.47	3
	GPM	1.18	4	2.39	4	1.47	4
	KD	1.18	4	0.80	3	1.47	4
	AWG	3.41	5	--	--	4.18	5
	KA	1.18	4	0.80	3	--	--
		218 ppm*		166 ppm*		235 ppm*	
Isopropyl Acetate	SV	10.58	5	20.49**	6	11.99	5
	RA	10.58	5	7.79	5	4.04	4
	DS	10.58	5	7.79	5	--	--
	EW	0.40	2	0.31	2	--	--

*represents initial odor sample concentration as CH_4

**the next available dilution is one third of this value

TABLE 10: Precision of Individual Panelist Responses to n-Butanol and Isopropyl Acetate Odors with the IITRI Dynamic Olfactometer

	Panelist Threshold (First Correct Detection) in ppm							
	75 ppm*		140 ppm*		84 ppm*		71 ppm*	
	Panel 1	At Port No.	Panel 2	At Port No.	Panel 3	At Port No.	Panel 4	At Port No.
	1.18	4	0.80	3	1.47	4	1.15	4
	3.41	5	0.80	4	1.47	4	0.04	1
	1.18	4	2.39	4	1.47	4	1.15	4
	1.18	4	6.93	5	4.18	5	1.15	4
	0.40	3	2.39	4	0.47	3	1.15	4
	3.41	5	2.39	4	1.47	4	0.39	3
	0.40	3	0.80	3	0.47	3	1.15	4
	0.04	1	0.80	3	1.47	4	3.33	5
	1.18	4	0.80	3	--	--	8.88	6
Sum	12.38		18.10		12.47		18.39	
Mean	1.376		2.011		1.559		2.043	
S.S.	29.15		68.36		28.72		96.71	
S	1.23		2.00		1.15		2.72	
S.E.	0.41		0.67		0.41		0.91	

*represents initial odor sample concentration as CH_4

TABLE 11: Panelist Thresholds for n-Butanol Odors with the IITRI Dynamic Olfactometer

	Panelist Threshold (First Correct Detection) in ppm							
	218 ppm*		166 ppm*		235 ppm*		127 ppm*	
	Panel 1	At Port No.	Panel 2	At Port No.	Panel 3	At Port No.	Panel 4	At Port No.
	3.63	4	0.31	2	11.99	5	16.93	6
	10.58	5	20.49	6	11.99	5	2.20	4
	10.58	5	7.79	5	0.16	1	16.93	6
	1.22	3	20.49	6	30.10	6	2.20	4
	10.58	5	7.79	5	4.04	4	6.45	5
	3.63	4	20.49	6	30.10	6	16.93	6
	10.58	5			4.04	4	16.93	6
	0.40	2			11.99	5	16.93	6
Sum	51.20		77.36		104.41		95.50	
Mean	6.40		12.89		13.05		11.94	
S.S.	475.75		1380.98		2275.97		1484.41	
S	4.60		8.76		11.42		7.01	
S.E.	1.63		3.58		4.04		2.48	

*represents initial odor sample concentration as CH_4

TABLE 12: Panelist Thresholds for Isopropyl Acetate Odors with the IITRI Dynamic Olfactometer

Sources of Variation	Degrees of Freedom	Sum of Squares	Mean Square (Variance Estimate)	Calculated F_{ratio}	Tabulated F_{value} [81] @
Between tests Within tests	3 31	2.95 112.49	0.983 3.629	0.271	0.05 level: 2.91 0.01 level: 4.485
Total	34	115.44			

$F_{ratio} << F_{0.05,\ 3,\ 31}$ and $F_{0.01,\ 3,\ 31}$

Therefore, population means are not significantly different from the sample means.

TABLE 13: Analysis of Variance for n-Butanol Odors

Sources of Variation	Degrees of Freedom	Sum of Squares	Mean Square (Variance Estimate)	Calculated F_{ratio}	Tabulated F_{value} [81] @
Between tests Within tests	3 26	231.40 1789.29	77.13 68.82	1.12	0.05 level: 2.98 0.01 level: 4.64
Total	29	2020.69			

$F_{ratio} < < F_{0.05,\ 3,\ 26}$ and $F_{0.01,\ 3,\ 26}$

Therefore, population means are not significantly different from the sample means.

TABLE 14: Analysis of Variance for Isopropyl Acetate Odors.

According to this analysis the calculated F-ratios (the variance among tests/the variance within tests) are not significant at the 0.05 and 0.01 probability levels. The F-tests show that the population means are not significantly different from the sample means. On this basis, it can be concluded that no real variations exist in the mean panel responses from test to test. Therefore, the odor measurements made with the IITRI Dynamic Olfactometer are sufficiently precise for legal purposes.

In general, odor determinations are consistently repeatable by an individual panelist but there can be differences among various members of a group.

2. Accuracy

Because of the psycho-physical nature of odor stimuli it is not possible to talk about the true value of an odor threshold. Consequently, it is difficult to discuss accuracy quantitatively. The accuracy of an odor determination may be inferred from the degree of correlation between threshold values determined for different initial odor concentrations. This approach has been used in a previous work [58]. When odor concentrations are plotted against odor levels, the relationship must yield a slope of 1.00 for perfect accuracy. For the odor determinations made with the IITRI Dynamic Olfactometer, when initial odor concentrations were plotted against required dilutions to threshold a correlation coefficient of approximately 1.00 was obtained [58].

C. Factors Affecting Odor Threshold Determinations by Dynamic Dilution

Individual responses to an odor differ greatly [17, 20, 40, 82]. They can be influenced by

- i. physiological factors such as sex, age and health
- ii. psychological factors, that is, motivations and expectations
- iii. smoking and eating habits
- iv. odorant contamination
- v. sample humidity and temperature
- vi. background odors
- vii. noise conditions
- viii. measurement techniques.

The first three factors are believed to be responsible for large variations in individual responses. It is, therefore, common to utilize more than one individual to average out the influence of these factors. The number of individuals required thus becomes a parameter of practical significance. An attempt has been made to evaluate the effect of some of these factors on the measurement of odor thresholds.

1. Panel Size and Sensitivity

Training of panelists was not considered for the determination of odor threshold values in view of

i. the target population being the general public which is essentially untrained in this respect

ii. cost and time factors associated with training.

The number of panelists required to attain a specific level of confidence in the odor threshold value is a function of several variables. Usually, the confidence level of an odor measurement increases with an increase in the number of panelists subject to the limitations of precision and accuracy inherent in the measurement device itself.

The odor sensitivity of members within a panel can vary widely. Some show extreme sensitivity while others are incapable of smelling an odor [17, 40]. Figure 8 presents a typical panel response to n-butanol odor. Panelist KD detected the n-butanol odor at a dilution level of 8 while panelist SV detected the same odor at 1634 dilution levels. Such variations in human sensitivity to odors are not uncommon. Tables 11 and 12 show typical variations observed in tests carried out during the present program. Wilby [17] reported 10 to 50 fold variations in panels consisting of 35 untrained panelists subjected to 18 sulfur compounds. Similarly, Dravnieks [40] found variations of about 50 fold with isobutyric acid odor. In odor measurement work it is recognized that these variations in panelist sensitivities must exist in order to approximate the broader population both with respect to the mean threshold value and representation of the distribution of odor sensitivities with the population [6].

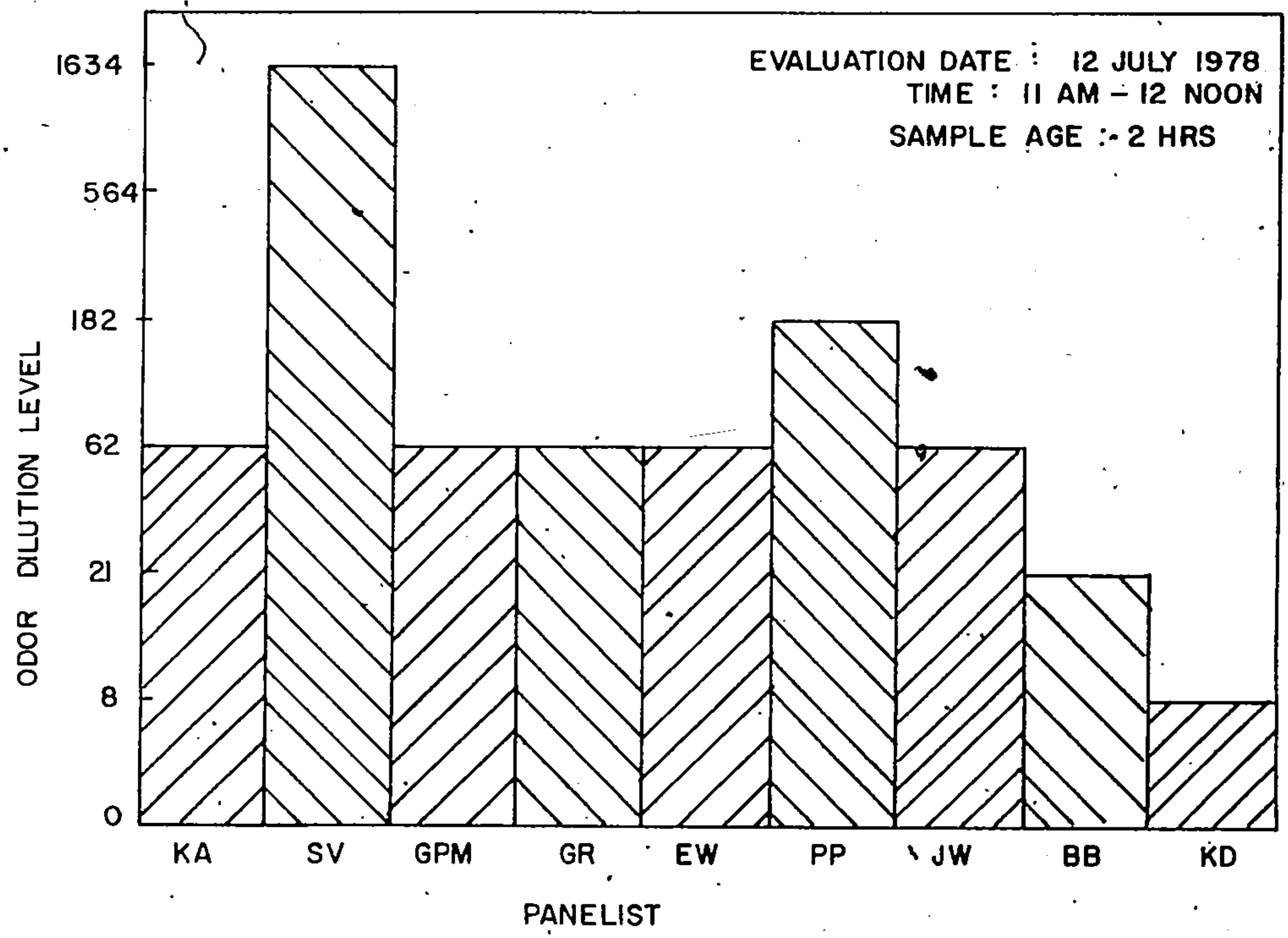


FIGURE 8: Typical Panel Member Responses to n-Butanol Odor

Individual responses of nine-member odor panels have been grouped into four categories for evaluating the effect of panel size and sensitivity on the arithmetic mean odor threshold values according to:

i. 3 lowest panel responses (least sensitive subjects)

ii. 3 highest panel responses (most sensitive subjects

iii. 6 lowest panel responses (least sensitive subjects

iv. 6 highest panel responses (most sensitive subjects)

The arithmetic means for each category were compared with the mean value determined from the full nine-member panel response to show the effect of panel size and sensitivity on the resultant odor threshold determination.

Table 15 provides the arithmetic mean (A.M.) and the estimate of the standard error of the mean (S.E.) for several panel sizes. The sensitivities of 3 and 6 member panels are compared with those of a 9 member panel. The arithmetic mean and the estimate of the standard error of the mean for the 35 panelists involved in the four test runs are also included in this table. The data show that panel size and individual sensitivities have a significant effect on the resultant group mean values. The 3 member and 6 member odor panel results are not in agreement with the responses of 9 member panels.

Test	Odor Concentration ppm *	Panel Sensitivity	3 Members		6 Members		9 Members		35 Members		
			A.M.	S.E.	A.M.	S.E.	A.M.	S.E.	A.M.	S.E.	95% Confidence Limits
1	71	Lowest ppm	2.70	1.43	1.68	0.79	1.22	0.56	0.97	0.19	(0.59, 1.35)
		Highest ppm	0.30	0.19	0.48	0.12					
2	75	Lowest ppm	1.58	0.45	1.13	0.29	0.81	0.25	0.97	0.19	(0.59, 1.35)
		Highest ppm	0.16	0.07	0.42	0.12					
3	140	Lowest ppm	1.83	1.09	1.19	0.57	0.95	0.38	0.97	0.19	(0.59, 1.35)
		Highest ppm	0.46	0	0.51	0.05					
4	84	Lowest ppm	1.37	0.55	1.10	0.28	0.89	0.24	0.97	0.19	(0.59, 1.35)
		Highest ppm	0.46	0.18	0.64	0.11					

*as CH_4

TABLE 15: Effect of Panel Size on Arithmetic Mean Odor Response Values for n-Butanol Odors

The mean threshold values of the 8 or 9 member panels are quite close to the mean value for all 35 panelists, as shown in Table 15. The standard errors of the means of 8 or 9 member panels also appear to be reasonable. Thus, it is possible to imply that the 9 member panels and their sensitivities approximate the response of a 35 member panel. Consequently, an increase in panel size beyond nine members is not called for. The published literature [6, 20, 51, 58, 67, 68, 83] supports the conclusion that a panel consisting of 8 to 10 members can produce consistent and reproducible odor threshold measurements. On the basis of factors such as time, cost and laborious evaluation procedures, nine member panels appear to be adequate for odor measurement work.

2. Effect of Measurement Techniques

Table 16 summarizes odor thresholds for 50% panel response, geometric mean thresholds and coefficients of determination (R^2) for two different measurement systems. The ED_{50} value determined by the IITRI Olfactometer for n-butanol odor is very close to the geometric mean threshold evaluated according to the ASTM syringe method. However, for butyric acid odor, the ED_{50} value determined by the IITRI Olfactometer is different from the ASTM geometric mean threshold by a factor of three. Both measurement systems show high correlation (R^2=1 for perfect correlation) indicating high reliability of the observed data. Threshold values from

Odorant	Odor Level ppm as CH_4	IITRI Dilution Method			ASTM Static Method		
		ED_{50}			Geometric Mean		
		O.U.	ppm	R^2	O.U.	ppm	R^2
n-Butanol	71	136	0.52	.941	125	0.57	.994
Butyric Acid	34	6668	0.0051	.998	2321	0.0165	.999

R^2 represents coefficient of determination

TABLE 16: Comparison of Threshold Values from Two Different Odor Measurement Techniques

both measurement systems are reasonably consistent with the literature as shown in Table 17.

The ASTM static method is not an effective means of presenting an odor to a panelist. Under poor supervision, panelists may not rigorously follow the rules related to expulsion of the sample into the nose for odor sensing. Since the method is a static one, only 100 ml of the odorant are available. This amount of sample is usually not adequate for the panelists to reinforce their original judgements.

Preparation of syringes for presentation to panelists may not necessarily provide reproducible dilution levels. The ASTM syringe method also requires significant time to

i. make up all the dilutions needed for an 8 to 10 member panel

ii. clean the syringes and the transfer needles to maintain them free from any contamination.

According to Research Corporation of New England studies [58] the performance of the ASTM method deteriorates with increasing odor levels, and is generally poor for sulfur compounds such as hydrogen sulfide and dimethyl disulfide, due to odorant adsorption onto glass surfaces of the syringes.

Dynamic dilution methods are simpler, faster and probably more accurate. They provide a continuous flow of odor sample. However, the choice of odor flow rate is difficult. Odor flow rates corresponding to normal inhalation rates seem to be desirable from a perceptual point of view

Odorant	Odor Threshold ppm	Measurement Technique	Investigator
n-Butanol	0.42-0.82	Dynamic (IITRI)	Present work
	0.56	Static (ASTM)	Present work
	0.30	Dynamic (odor fountain)	Hellman et al [10]
Butyric Acid	0.0051	Dynamic (IITRI)	Present work
	0.0165	Static (ASTM)	Present work
	0.001	Dynamic (MK 2)	Cormack et al [77]
	0.02	Dynamic (MK 1)	Cormack et al [77]
	0.001	Odor Room	Cormack et al [77]
	0.00047*	Odor Room	Leonardos et al [11]

*Recognition Threshold

TABLE 17: Comparison of Experimental Threshold Values with Literature Data

but high flows could confuse panelists if they are not sure whether they sense the odor or are reacting to odorous gas stream pressure in their noses [69]. High odor flow rates also increase the chance of contaminating the background. In addition, they consume the sample very rapidly.

The IITRI Olfactometer, which presents odor samples by the forced-choice, dynamic-dilution technique, is a method for minimizing some of the problems associated with the ASTM syringe technique. Continuous flow of odorant permits panelists to recheck their original judgement prior to signalling.

The low sample flows associated with the IITRI Olfactometer reduce panel fatigue and require only small amounts of sample. However, low sample flows can create confusion among panelists as to whether they are sensing the given odor or the background, especially at low odor levels.

3. Effect of Noise and Darkness on Odor Thresholds

In an industrial environment, people are constantly exposed to noise generated by heavy electrical and mechanical equipment. It may be suspected that in noisy environments the perception of odors could be affected. Also of some practical importance is the possible dependence of odor perception on the time of day.

In order to establish whether these parameters might affect odor complaints in a community, a study was conducted to evaluate the influence of noise and darkness on odor perception.

Tests were carried out with

i. engine noise at 89 dBA to simulate an industrial environment

ii. high frequency noise of 1000 Hertz at 94 dBA. This is a pure tone which is very unpleasant

iii. pink noise at 89.5 dBA. This is a constant-energy-per-octave band-width noise that is commonly used as a standard in noise testing.

Three series of odor measurements under standard, noise and dark conditions were conducted over six hour periods according to the following sequences:

TEST 1
  i. standard
  ii. dark
  iii. engine noise
TEST 2
  i. standard
  ii. dark
  iii. high frequency noise
TEST 3
  i. dark
  ii. standard
  iii. pink noise

Each test involved the same odor panelists and the same odor sample. The noise was created by means of a standard tape played on a portable recorder. In all tests, each panelist was exposed to the noise for 2 to 3 minutes prior to the odor measurement, as well as during the test. The experimental data from these tests are presented in Appendix IV.

The effects of noise and darkness on odor thresholds are evaluated using

i. parametric analysis
ii. non-parametric analysis

The first procedure is based on the assumption that an odor panel is a random sample of individuals from the general population. On this basis the data could be analyzed statistically. According to the second method, individual panel responses are compared to standard conditions. From the number of increases and decreases in individual sensitivities, a percentage change can be determined.

a. Effect of Noise on Odor Thresholds

Table 18 summarizes odor threshold data for the three noise conditions. These results show that the perception of the odor panels consistently increased when panelists were subjected to noisy environments. In

Test	Initial Odor Level ppm as CH_4	Standard Condition			Noise Condition			
		ED_{50}		R^2	Type	ED_{50}		R^2
		O.U.	ppm			O.U.	ppm.	
1	75	177	0.42	0.930	Engine Noise	299	0.25	0.994
2	140	170	0.82	0.992	High Frequency Noise	251	0.56	0.988
3	84	116	0.73	1.00	Pink Noise	305	0.28	0.988

Standard condition represents tests conducted in presence of light

R^2 represents coefficient of determination

TABLE 18: Comparison of n-Butanol ED_{50} Values for Noise and Standard Conditions

the presence of engine, high frequency and pink noises, ED_{50} values of panels decreased from 0.42 ppm to 0.25 ppm, 0.82 ppm to 0.56 ppm, and 0.73 ppm to 0.28 ppm respectively for n-butanol odors. These tests show high coefficients of determination which indicate that the observed differences in thresholds, though small, may not be due to chance. Of the three noises investigated, the maximum decrease in ED_{50} value occurred when panelists were exposed to the pink noise.

Table 19 provides individual panelist responses to n-butanol odors under standard and noise conditions. The data are analyzed by the non-parametric method. The change in each panelist's sensitivity is expressed as an increase (+), decrease (-) or no change (0) over the standard conditions. These results illustrate that noises generally increase a panelist's perception.

b. Effect of Darkness on Odor Thresholds

Table 20 compares odor results for standard (light) and dark conditions. The panel threshold values decreased in the absence of light (darkness) during tests 2 and 3 but increased in test 1. These results indicate that darkness does not consistently influence the panel perception.

The results of non parametric analysis are presented in Table 21. Once again these results illustrate that darkness did not influence odor perception to any significant degree.

Test	Panelist	Panelist Response in ppm		Change in Sensitivity		
		Standard	Noise	Higher	Lower	No Change
1 Engine Noise	KA	1.18	0.40	+		
	SV	3.41	3.41			0
	WJH	1.18	0.40	+		
	GPM	1.18	1.18			0
	EW	0.40	1.18		-	
	AWG	3.41	0.40	+		
	BCT	0.40	0.13	+		
	DSK	0.04	0.04			0
	KD	1.18	0.40	+		
Change in Panel Sensitivity				5	1	3
2 High Frequency Noise	EW	0.80	2.39		-	
	KL	0.80	0.09	+		
	RG	2.39	0.80	+		
	PD	6.93	6.93			0
	GPM	2.39	2.39			0
	GR	2.39	2.39			0
	KA	0.80	0.27	+		
	KD	0.80	0.80			0
	GD	0.80	0.80			0
Change in Panel Sensitivity				3	1	5
3 Pink Noise	SI	1.47	0.47	+		
	KC	1.47	0.17	+		
	MBP	1.47	0.47	+		
	AWG	4.18	0.47	+		
	EW	0.47	0.05	+		
	GPM	1.47	1.47			0
	VR	0.47	4.18		-	
	KD	1.47	0.47	+		
Change in Panel Sensitivity				6	1	1
Change in Panel Sensitivity for Three Tests			Total	14	3	9
			%	54	11	35

TABLE 19: Comparison of Individual Odor Panelist Responses Between Standard and Noise Conditions by Non-Parametric Method

Test	Initial Odor Level ppm as CH_4	Standard Condition				Dark Condition			
		ED_{50}		R	R^2	ED_{50}		R	R^2
		O.U.	ppm			O.U.	ppm		
1	75	177	0.42	-0.964	0.930	110	0.68	-1.00	1.00
2	140	170	0.82	-0.996	0.992	382	0.37	-0.992	0.984
3	84	116	0.73	-1.00	1.00	167	0.50	-0.991	0.982

Standard Condition represents test conducted in presence of light

R represents correlation coefficient

R^2 represents coefficient of determination

TABLE 20: Comparison of n-Butanol ED_{50} Values for Dark and Standard Conditions

Test	Panelist	Panelist Response in ppm		Change in Sensitivity		
		Standard	Dark	Higher	Lower	No Change
1	KA	1.18	1.18			0
	SV	3.41	1.18	+		
	GPM	1.18	1.18			0
	EW	0.40	1.18		-	
	AWG	3.41	3.41			0
	BCT	0.40	1.18		-	
	DSK	0.04	0.40		-	
	KD	1.18	1.18			0
Change in Panel Sensitivity				1	3	4
2	EW	0.80	0.09	+		
	KL	0.80	0.80			0
	RG	2.39	2.39			0
	PD	6.93	0.80	+		
	GPM	2.39	2.39			0
	GR	2.39	0.09	+		
	KA	0.80	0.80			0
	KD	0.80	2.39		-	
	GD	0.80	0.27	+		
Change in Panel Sensitivity				4	1	4
3	SI	1.47	0.17	+		
	KC	1.47	1.47			0
	MBP	1.47	1.47			0
	AWG	4.18	1.47	+		
	EW	0.47	0.47			0
	GPM	1.47	1.47			0
	VR	0.47	1.47		-	
	KD	1.47	0.47	+		
Change in Panel Sensitivity				3	1	4
Change in Panel Sensitivity for three tests			Total	8	5	12
			%	32	20	48

TABLE 21: Comparison of Individual Odor Panelist Responses Between Standard and Dark Conditions by Non-Parametric Method

D. Development of a General Procedure for Threshold Determinations

With any source odor of unknown strength it is difficult to measure odor thresholds with high precision. Because dynamic dilution olfactometers are mainly devices which provide a range of odor dilution for presentation to panelists, a threshold value can be measured with confidence only if the unknown ED_{50} value lies approximately in the middle of the dilution range available for a given test. For example, by design, the IITRI Olfactometer provides a range of six dilution levels according to the scheme:

Port number:	D_1	D_2	D_3	D_4	D_5	D_6
Dilution Level:	1600	540	180	60	20	7.
	maximum dilution					minimum dilution

Multiples of the above dilutions can be obtained through the use of attenuators. In conducting an odor test, the following situations can arise for an unknown odor:

i. overall panel detectability variation is greater than D_1/D_6. Therefore, some panelists would not detect any odor at either the minimum or the maximum dilution levels. Although this can produce inaccurate ED_{50} values there is no mechanism for changing the D_1/D_6 ratio in the IITRI instrument

ii. odor is too weak to be detected at the minimum dilution level of 7 - most panelists would miss detection at all dilution levels. Usually, this is not a problem with most source emissions.

iii. odor is too strong at the maximum dilution level - most panelists would detect odor at all dilution levels. This would make the test useless.

Some additional problems may also arise. Strong odors could contaminate the olfactometer to such an extent as to require several hours to restore the odor-free conditions within the instrument as well as the odor room. Also, the strong odors may damage the olfactory sensitivity of the panelists. This situation can be avoided by increasing the normal dilution levels by an attenuator. However, choosing the correct attenuator is an arbitrary exercise. No published data are available on how a correct attenuator should be selected for proper odor detection tests.

Problems arising as a result of arbitrary selection of attenuators are typified by the data in Table 22. The dilution range D_1-D_6 selection seems to affect the results significantly. Consequently, it becomes necessary to develop a consistent procedure by which the choice of dilution range can be made. Additional reasons for the development of a standard procedure for selection of an appropriate dilution range without trial and error arise from limitations on the total amount of sample available for testing and also from the degradation of the sample with time.

Test	Dilution Range Used D_1-D_6	Threshold Value, ED_{50}	
		O.U.	ppm as CH_4
1	1550-8	19.5	6.51
	9300-48	59.0	2.15
2	1640-8	85.9	2.54
	10,210-50	145.9	1.49
3	1520-8	68.0	3.46
	8520-48	187.0	1.26
4	1550-8	35.2	4.72
	19,940-105	187.5	0.89

TABLE 22: Effect of Attenuation (Dilution Levels) on ED_{50} Values of Isopropyl Acetate Odors Determined with the IITRI Dynamic Olfactometer

To minimize these difficulties, a procedure for determining ED_{50} values of unknown odors has been developed:

Step 1: Draw a 100 ml odor sample into a syringe from the odor container

Step 2: Determine the threshold value (dilution level) of the sample by the ASTM syringe method using the geometric mean of two panelists

Step 3: Select the attenuator corresponding to the measured dilution level using Table 23. Because the ASTM procedures generally underestimates the required dilutions, experience shows that when an overlapping range is encountered the higher dilution levels should be used for attenuator selection

Step 4: Install the correct attenuator in the olfactometer according to the IITRI Instruction Manual [56]

Step 5: Complete the odor measurement test with nine panelists and calculate ED_{50} of the odor according to the IITRI Instruction Manual [56].

Dilution Level	Attenuation Factor
60-180	1
180-540	3
360-1080	6
720-2160	12
1080-3240	18
2160-10,800	36

TABLE 23: Attenuators for Various Ranges of Dilution Levels

Step 2 provides a quick estimate of dilution level (threshold value in odor units) by the ASTM method. An attenuation factor is then chosen on the basis of the ASTM dilution level using Table 23, which has been designed to insure that individual panelist thresholds would fall in the middle of the D_1-D_6 dilution range.

The recommended procedure was tested with acetic acid odor whose initial concentrations varied from 47 to 13,000 ppm total hydrocarbon as methane equivalent. The results are presented in Table 24. The ED_{50} values determined by this procedure exhibit only minor differences. The observed variations in the measured threshold values are quite normal and are often expected in odor measurement work. However, Tests 3 and 7 show how improper selection of attenuators can affect the magnitude of an ED_{50} value. According to the instructions provided in Step 3 of the newly developed procedure, attenuation factors of 12 and above 36 should have been used during Tests 3 and 7 respectively.

The comparison of ED_{50} values determined by this procedure and the odor room method [11] shown in Table 25 suggests that there is good agreement between the values obtained by the two methods.

Odorant	ED_{50} ppm	Measurement Technique	Investigator
Acetic Acid	0.19-0.40	Dynamic (IITRI)	This work
Acetic Acid	0.21 (Recognition)	Odor Room	Leonardos et al [11]

TABLE 25: Comparison of ED_{50} Values From this Work and the Literature for Acetic Acid Odor

Test	Initial Acetic Acid Concentration ppm as CH_4	ED_{50} by ASTM O.U.	Attenuation Factor Used	ED_{50} by IITRI Olfactometer	
				O.U.	ppm
1	47	59	1	241	0.19
2	215	222	3	1076	0.19
3	1627	1110	6	2234	0.73
4	1836	1529	18	8110	0.23
5	2110	2638	18	5278	0.40
6	6992	3089	36	30,027	0.23
7	12,924	16,155	36	22,981	0.56

TABLE 24: ED_{50} Determination of Acetic Acid Odor Using Procedure Developed for the IITRI Dynamic Olfactometer

VII. CONCLUSIONS

On the basis of the results obtained in the present investigation, the following conclusions regarding odor storage and measurement procedures may be made.

A. Odor Storage

During this investigation Tedlar bags demonstrated satisfactory performance with respect to odor retention for a variety of odorants. These bags are reasonably strong and easy to manage. They did not leak appreciably at the sealed edges or around the fittings as compared to Teflon and polyester bags. Commercially, Tedlar bags are available in different sizes with one or two fittings. Tedlar bags with two fittings can be cleaned consistently to low levels of total hydrocarbons by flushing with non-odorous air overnight.

Tests with n-butanol, butyraldehyde, butyric acid, isopropyl acetate and acetic acid odors showed that Tedlar bags do lose some of the contained odors after 3 or 4 hours of storage time. The loss was greatest with butyraldehyde and lowest with n-butanol odors. For the odorants tested, the odor loss was proportional to the initial odor concentrations. There were no significant differences in the characteristics of the Tedlar bags supplied by Pollution Measurement Corporation at Plastic Film Enterprises. Preliminary studies tend to suggest that odor losses are due primarily to adsorption rather than permeation.

B. Reliability of Odor Measurements

Experimental evidence shows that an individual can consistently detect the presence of an odor at the same stimulus level for a range of initial concentrations. However, individual sensitivities can differ widely. The use of odor panels should be considered mandatory for legal or regulatory purposes.

The number of panelists required to attain a good level of confidence in an odor threshold determination was found to be 9. Mean threshold values from 3 and 6 member odor panels were not in good agreement with responses of 9 member panels. The results indicate that 9 member panel responses closely approximated the aggregate response of 35 individuals.

C. Effect of Noise and Darkness on Odor Perception

An individual's odor perception appears to be affected by noisy environments. In general, panel sensitivity was increased when subjected to three types of noises. On the average, absence of light seems to have little impact on odor perception.

D. Standardization of Procedures for ED_{50} Determinations

Odor thresholds can be determined with static or dynamic techniques. Both procedures were found to give reproducible detectability levels within the fundamental uncertainties of such measurements. The IITRI Dynamic Olfactometer is limited to six dilution levels for any particular test. If the ultimate threshold value does not fall in the middle of the dilution range, the instrument will produce an ED_{50} value of low confidence. Consequently, a number of different attenuators are needed to provide appropriate dilution ranges for odors of varying strengths. In practice attenuators ranging from 2 to 36 dilutions are generally sufficient.

A fast, reliable and practical procedure for odor threshold determinations of unknown samples has been developed. This procedure utilizes the static syringe method to guide the choice of dilution range for the dynamic evaluation. The threshold values determined with this procedure, for acetic acid over the range of 47 to 13,000 ppm total hydrocarbon as methane equivalent, show excellent reproducibility, as well as good agreement with literature.

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APPENDIX I

ROTAMETER AND SYRINGE CALIBRATION DATA

Rotameter Setting	Time sec.	Air Flow ft^3	Static Pressure in Hg	Temperature °F	ft^3/min as measured	ft^3/min at 32°F and 29/92 in Hg.
25	5616	78.4	0.6	73	0.8376	0.7791
40	1500	34.0	1.3	73	1.3604	1.2938
50	1562	45.0	1.9	73	1.7302	1.6780
60	1166	41.0	2.7	73	2.1103	2.1014
70	883	37.0	3.7	73	2.5153	2.5798
80	715	35.0	4.85	73	2.9381	3.1182
90	640	36.0	6.15	73	3.3732	3.7153
100	317	20.0	7.55	73	3.7855	4.3329

Tube No. FP-1/2-27-G-10/83
Barometric Pressure = 29.552 inches of Hg.

TABLE I.1: Rotameter Calibration Data

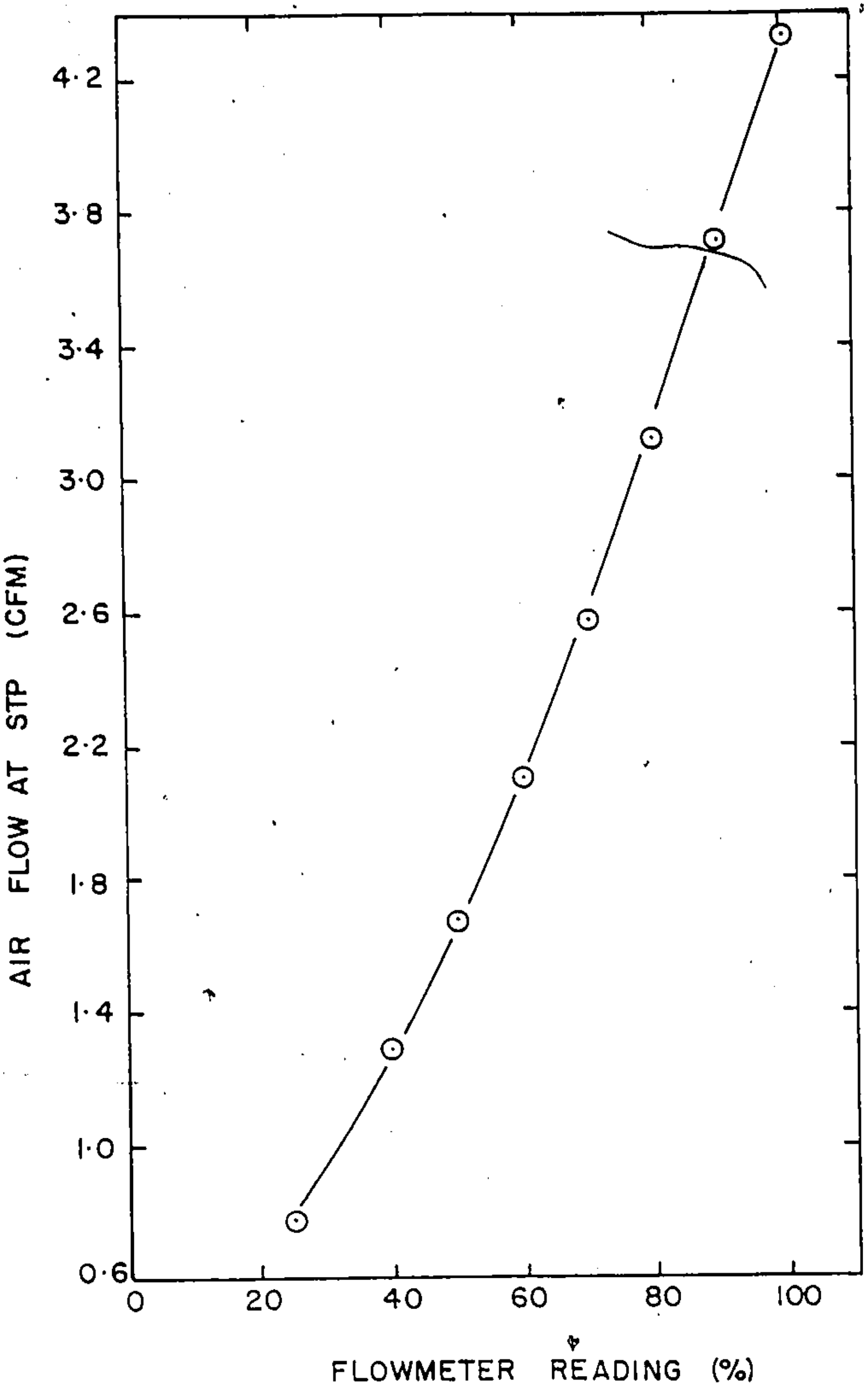

FIGURE I.1: Rotameter Calibration Curve

Ratiotrol Setting	Time min.	Butanol Collected gm	Butanol Flow gm/min	Counter Total	Revolution No/min	Odorant Flow ml/min
10	100	2.162	0.02162	524	5.24	0.0267
20	100	3.527	0.03527	863	8.63	0.0435
30	100	4.647	0.04647	1184	11.84	0.0574
40	80	4.860	0.06075	1235	15.44	0.0750

TABLE I.2: Syringe Calibration Data

Size: 30 ml, Needle No. 20

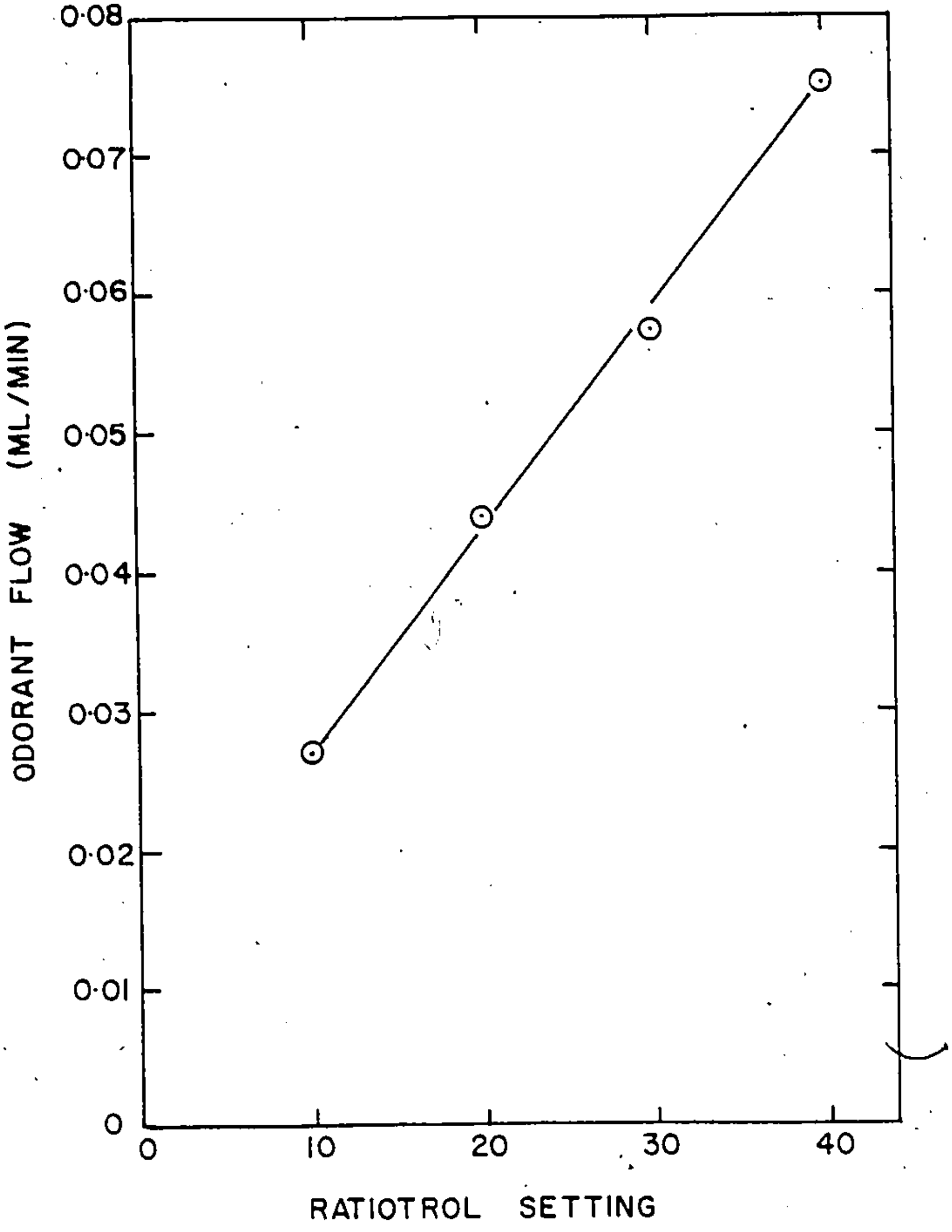

FIGURE I.2: Ratiotrol Calibration Curve

APPENDIX II

ATTENUATOR DETAILS

Attenuator Details

Attenuators were used with the IITRI olfactometer to provide various dilution ranges for strong odorant samples. This was accomplished by deodorizing a portion, (for example, 5/6 for an attenuating factor of 6) of the odorant sample by passing it through a deodorizing unit, which contained activated carbon and permanganate coated alumina (Purafil). The odor free gas was mixed with the remaining 1/6 of the odorant sample which by-passed the deodorizer. The total flow always remained the same but attenuation reduced the odorant concentration by a factor of 6. The adsorption capacity of Purafil was checked frequently by passing through a known concentration of the odorant which was removed with 99% efficiency based on THC determinations.

The IITRI Dynamic Triangle Olfactometer was supplied with only one attenuator which provided a dilution ratio of 27X. Therefore, several attenuators capable of establishing dilution ratios of 2X, 3X, 6X, 12X, 18X and 36X were fabricated to provide wider ranges of dilutions of odor samples. Attenuators were made from stainless steel capillaries of different lengths and diameters which were purchased from

i. Supelco Company
Supelco Park
Bellafonte, Pa 16823
U.S.A.

ii. Anallabs, Inc.
80 Republic Drive
North Haven, Conn. 06473
U.S.A.

These capillaries were calibrated after each odor test. Typical capillary sizes and corresponding attenuations are listed in Table II.1.

Capillary Size		Attenuation Factor (approximate)
Internal Diameter in.	Length in.	
0.05	12	2
0.04	12	6
0.03	12	7
0.03	25	12.7
0.02	12	17.5
0.02	17	36
0.02	26	52

TABLE II.1: Attenuator Details

APPENDIX III

ED_{50} EVALUATION FROM ODOR MEASUREMENT DATA

ED_{50} Evaluation from Odor Measurement Data

Individual response data were evaluated by the IITRI [56] and the ASTM D-1391 [36] recommended procedures to obtain an ED_{50} value for each odor determination. The panelist's threshold response was that dilution level at which the panelist first made the correct choice and continued to be correct at two consecutive higher concentration levels (1:27 probability of occurring by chance). The panel data were not corrected for positive responses that were followed by negative responses at higher odor concentration, that is, at lower dilution ratios.

The panelists' responses for the IITRI Olfactometer were recorded on a pre-printed form which is presented in Table III.1. The data were then evaluated by ranking triangle statistics developed by Dravnieks and Prokop [67]. The statistical results were plotted on a rectangular coordinate graph paper, with plotting values X along the X-coordinate, and the logarithm of the tolerance levels Y along the Y-coordinate. A straight line was drawn through the experimental points on the basis of a least square fit as shown in Figure III.1. The value of Y at X = 0 corresponds to log ED_{50} where ED_{50} is the dilution at which 50% of the panel would detect the odor under investigation. Alternatively, ED_{50} values can be calculated directly with a hand calculator equipped with at least square program.

Sample: n-Butanol Odor at 71 ppm
Evaluation Date: 12 July 1978; Time: 11:00 a.m.-12:00 noon, Age: 2 Hour
RESULT: Log ED_{50} = 2.132; ED_{50} = 135.5 O.U. =0.52 ppm

Cons. no.	Panelist	Dilution Level Number 1	2	3	4	5	6	"7"
		Correct Choice Would Be: (t = top, c = center, b = bottom						
		c	c	c	c	b	c	
		Panelist Indicated:						
1	KA	c	b	t	ⓒ	~~b~~*	~~c~~	—
2	SV	ⓒ	~~c~~	~~c~~	~~c~~*	~~b~~	~~c~~	—
3	GPM	t	b	t	ⓒ*	~~b~~	~~c~~	—
4	GR	c	c	t	ⓒ	~~b~~*	~~c~~	—
5	EW	b	t	b	ⓒ*	~~b~~	~~c~~	—
6	PP	b	b	ⓒ	~~c~~	~~b~~*	~~c~~	—
7	JW	b	c	t	ⓒ	~~b~~*	~~c~~	—
8	BB	c	c	c	b	ⓑ	~~c~~	—
9	KD	c	c	t	c*	c	ⓒ	—
10								
Frequency Tally		1		1	5	1	1	
Average Rank		1		2	5	8	9	
X=Plotting Value		-1.28		-0.84	0	+0.84	+1.28	
Y-Log .(Tolerance Level)		3.44	2.98	2.51	2.03	1.56	1.12	

Dilution Level No.	<1	1	2	3	4	5	6	"7"
Log (Dilution Factor)		3.21	2.75	2.26	1.76	1.33	0.90	

from connections in olfactometer

For Rank Count
1
2
3
4
5
6
7
8
9
10

*positively identified level

how many begin to detect

from frequency count

from average rank and table

average of Log(Dil. Fact.)

from flow calibration

Plot Y versus X

Y at X=0 is Log ED_{50}

Panel Leader SCV

TABLE III.1: Typical Odor Measurement Data Illustrating ED_{50} Evaluation by the IITRI Dynamic Triangle Method

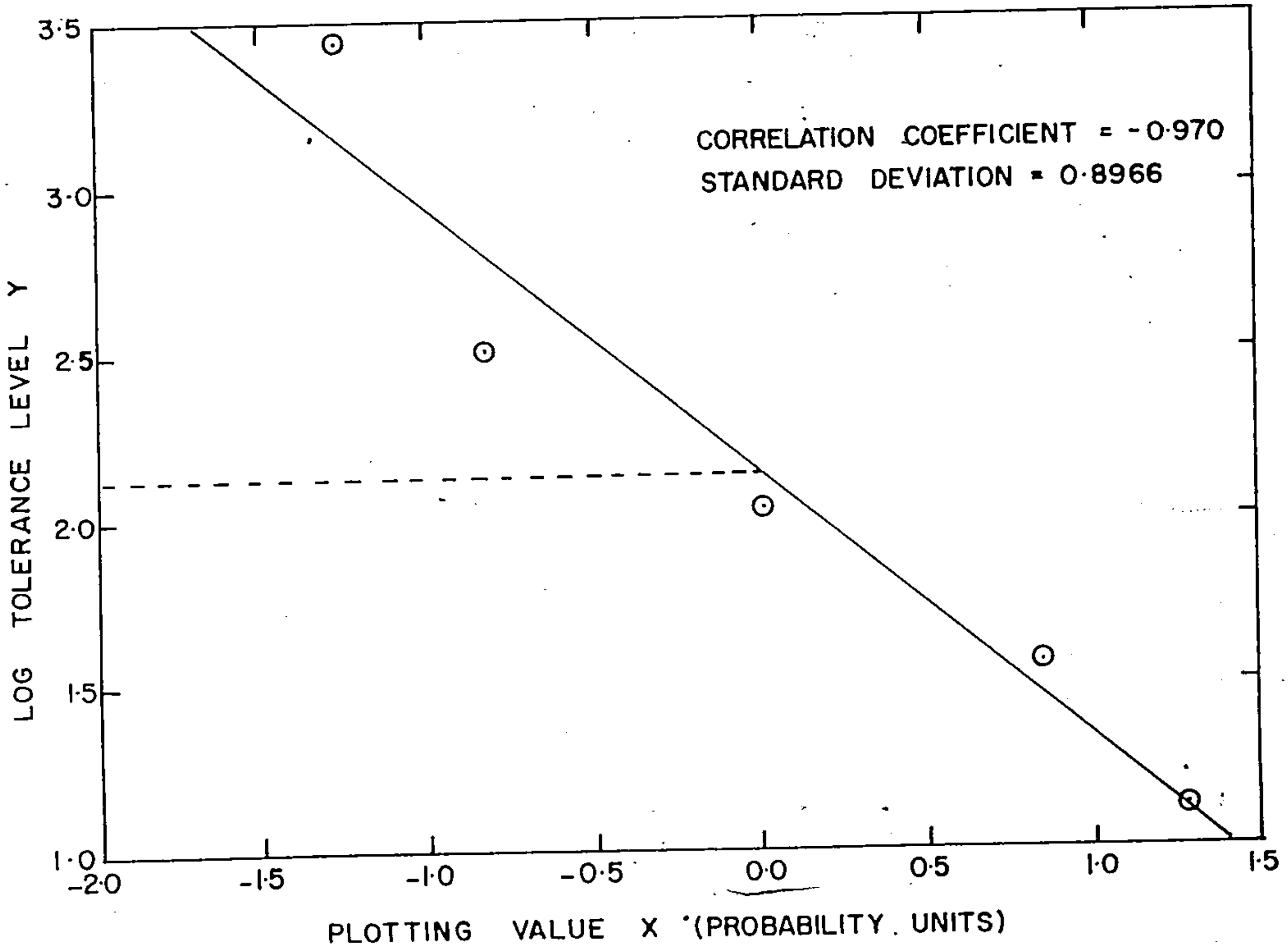

FIGURE III.1: ED_{50} Value Evaluation by Graphical Method

In the ASTM procedure, an individual panelist's threshold is determined as the lowest concentration of three consecutive correct responses at successive higher concentration levels. The ED_{50} is the geometric mean of the individual panelist's threshold values.

APPENDIX IV

ODOR PANEL RESPONSES UNDER STANDARD, NOISE AND DARK CONDITIONS

	Panelist Threshold (First Correct Detection) in ppm					
	75 ppm*		140 ppm*		84 ppm*	
	Panelist	Test 1	Panelist	Test 2	Panelist	Test 3
	KA	1.18	EW	0.80	SI	1.47
	SV	3.41	KL	0.80	KC	1.47
	WJH	1.18	RG	2.39	MBP	1.47
	GPM	1.18	PD	6.93	AWG	4.18
	EW	0.40	GPM	2.39	EW	0.47
	AWG	3.41	GR	2.39	GPM	1.47
	BCT	0.40	KA	0.80	VR	0.47
	DSK	0.04	KD	0.80	KD	1.47
	KD	1.18	GD	0.80		
Sum		12.38		18.10		12.47
Mean		1.376		2.011		1.559
S.S.		29.15		68.36		28.72
S		1.23		2.00		1.15
S.E.		0.41		0.67		0.41

*represents initial odor sample concentration as CH_4

TABLE IV.1: Panelist Thresholds for n-Butanol Odor at Standard Conditions (in presence of light, absence of noise).

	Panelist Threshold (First Correct Detection) in ppm					
	75 ppm*		140 ppm*		84 ppm*	
	Panelist	Test 1	Panelist	Test 2	Panelist	Test 3
	Engine Noise		High Frequency Noise		Pink Noise	
	KA	0.40	EW	2.39	SI	0.47
	SV	3.41	KL	0.09	KC	0.17
	WJH	0.40	RG	0.80	MBP	0.47
	GPM	1.18	PD	6.93	AWG	0.47
	EW	1.18	GPM	2.39	EW	0.05
	AWG	0.40	GR	2.39	GPM	1.47
	BCT	0.13	KA	0.27	VR	4.18
	DSK	0.04	KD	0.80	KD	0.47
	KD	0.40	GD	0.80		
Sum		7.54		16.86		7.75
Mean		0.838		1.873		0.969
S.S.		15.07		67.16		20.55
S		1.05		2.11		1.36
S.E.		0.35		0.70		1.64

*represents initial odor sample concentration as CH_4

TABLE IV.2: Panelist Thresholds for n-Butanol Odor Under Different Noise Conditions

	Panelist Threshold (First Correct Detection) in ppm					
	75 ppm*		140 ppm*		84 ppm*	
	Panelist	Test 1	Panelist	Test 2	Panelist	Test 3
	KA	1.18	EW	0.09	SI	0.17
	SV	1.18	KL	0.80	KC	1.47
	WJH	-	RG	2.39	MBP	1.47
	GPM	1.18	PD	0.80	AWG	1.47
	EW	1.18	GPM	2.39	EW	0.47
	AWG	3.41	GR	0.09	GPM	1.47
	BCT	1.18	KA	0.80	VR	1.47
	DSK	0.40	KD	2.39	KD	0.47
	KD	1.18	GD	0.27		
Sum		10.89		10.02		8.46
Mean		1.361		1.113		1.058
S.S.		20.14		19.15		11.28
S.		0.87		1.00		0.58
S.E.		0.31		0.33		0.21

*represents initial odor sample concentration as CH_4

TABLE IV.3: Panelist Thresholds for n-Butanol Odor Under **Dark** Conditions

APPENDIX V

GLOSSARY OF STATISTICAL TERMS

Glossary of Statistical Terms

1. Arithmetic Mean - the sum of all the observations $x_1, x_2 \ldots x_i, \ldots, x_n$ divided by their number, n:

   Arithmetic Mean (A.M.) = $\bar{x} = \sum_{i=1}^{n} x_i/n$

In the discussion of the experimental results, the arithmetic mean is used for two important reasons:

- i. the mean value provides a basis for the examination of the variation of the data in terms of the square of the deviations
- ii. the mean value permits the use of normal distribution in making probability statements about the population means.

2. Standard Deviation - measures the spread of the deviations from the arithmetic mean of a sample of n observations $x_1, x_2, \ldots, x_i, \ldots, x_n$ and is expressed mathematically as:

   Standard Deviation = s = $[\sum_{i=1}^{n} (x_i-\bar{x})^2/n-1]^{1/2}$

3. Standard Error - measures the standard deviation of the arithmetic mean and is calculated for n observations by the expression:

   Standard Error of the Mean = s.e. = $s/n^{1/2}$

4. Confidence Limits - the limits within which true mean (μ) can be said to lie with a given degree of confidence. For example, the confidence limits (confidence interval) at the 0.05 probability level of t-distribution usually specify the 95% confidence limits of the mean and is expressed as

$$\mu = \bar{x} \pm t_{0.05,f} \quad (s/n^{1/2})$$

where f is the degrees of freedom associated with standard deviation.

5. Total Sum of Squares - the sum of squares of all the nK observations (n-observations x K replicates) about the grand mean $\bar{x}$, which has (nK-1) degrees of freedom, is computed by the expression

$$\text{Total Sum of Squares} = SS_T = \sum_{i=1}^{n} \sum_{j=1}^{K} x_{ij}^{2} - \Big(\sum_{i=1}^{n} \sum_{j=1}^{K} x_{ij}\Big)^{2} / nK$$

6. Sum of Squares Between Replicates - it is computed by the expression

Sum of Squares Between Replicates = $SS_{Replicates}$ =

$$\sum_{i=1,j=1}^{K} \Big(\sum^{n} x_{ij}\Big)^{2} / n - \Big(\sum_{i=1}^{n} \sum_{j=1}^{K} x_{ij}\Big)^{2} / nK$$

7. Sum of Squares Within Replicates - is the difference between the total sum of squares and sum of squares between replicates and is obtained by the expression
Sum of Squares Within Replicates = Total Sum of Squares - Sum of Squares Between Replicates.

8. Degrees of Freedom - the number of independent measurements that can be made for estimating a statistical parameter. For the total nK observations, there would be (nK-1) degrees of freedom for estimating deviations from the mean.
9. Geometric Mean - the nth root of the product of n observations and is calculated by the expression

$$\text{Geometric Mean} = \text{G.M.} = (x_1 x_2 \ldots x_i \ldots x_n)^{1/n} \quad \text{or}$$

$$\log (\text{G.M.}) \doteq \frac{1}{n} \sum_{i=1}^{n} \log x_i$$

$$= \text{Arithmetic Mean of } \log (x_1 x_2 \ldots x_i \ldots x_n)$$

APPENDIX VI

TOTAL HYDROCARBON CONTENT OF AIR SAMPLES

Total Hydrocarbon Content of Air Samples

After cleaning the used and new Tedlar bags (one fitting) by flushing them with non-odorous clean air, residual odor levels were checked. The air samples were then collected from different locations inside and outside of Essex Hall, University of Windsor. The Total Hydrocarbon Contents of the air samples are presented in Table VI.1.

Bag	Bag - Past Odor History	Sample Location	THC as Methane Equivalent ppm
Tedlar	Used for Butanol Odor	Air from Laboratory Mains	15
Tedlar	Used for Butyraldehyde Odor	Air from Laboratory Mains	15
Tedlar	Used for Butanol Odor	Air from Laboratory Mains	15
Tedlar	New Bag Flushed with Clean Air	Air from Dr. Price's Lab	15
Tedlar	New Bag Flushed with Clean Air	Air from Laboratory Mains	17
Tedlar	Used for Butanol Odor	Air from Cylinder	12.4
Tedlar	Used for Butyraldehyde Odor	Air from Dr. Mathur's Room	13.2
Tedlar	Used for Butanol Odor	Air from South Side of Laurier Hall	11.5

TABLE VI.1: Total Hydrocarbon Content (THC) of Air Samples Collected in New and Used (Laboratory Cleaned) Tedlar Bags from Various Locations

APPENDIX VII

ODORANT SPECIFICATIONS

Odorant Specifications

1. 1-Butanol ($CH_3CH_2CH_2CH_2OH$)

Other Names:	Propylcarbinol, butyric or normal primary butyl alcohol, n-butanol
Molecular Weight:	74.12
Boiling Point:	117.7° ± 0.1°C
Purity:	99% Fisher Certified ACS
Density:	0.80978 at 20°/4°C
Vapor Pressure:	5.5 mm Hg at 20°C
Threshold Limit Value:	100 ppm
Lowest Published Toxic Concentration:	25 ppm
Human Toxicity:	May cause irritation of mucous membranes, contact dermatitis, headache, dizziness and drowsiness

2. Butyraldehyde ($CH_3(CH_2)_2CHO$)

Other Names:	butanal, butyl aldehyde, n-butyl aldehyde
Molecular Weight:	72.1
Boiling Point	75.7°C
Purity:	99% Fisher Certified ACS
Density:	0.817 at 20°/4°C
Human Toxicity:	May act as an irritant and narcotic

3. Butyric Acid ($CH_3(CH_2)_2COOH$)

Other Names:	Butanoic acid, n-butyric acid, ethyl acetic acid, propyl formic acid
Molecular Weight:	88.11
Boiling Point:	163.5°C
Purity:	99% Fisher Certified ACS
Density:	0.959 at 20°/20°C
Vapor Pressure:	0.43 mm Hg at 20°C
Human Toxicity:	Low toxicity, vapor is irritant to eyes, skin and respiratory tract.

4. Isopropyl Acetate ($CH_3COOCH(CH_3)_2$)

Molecular Weight:	102.13
Boiling Point:	88.4°C
Purity:	99% Fisher Reagent ACS
Density:	0.874 at 20°/20°C
Vapor Pressure:	40 mm Hg at 17°C
Threshold Limit Value:	250 ppm
Lowest Published Toxic Concentration:	200 ppm
Human Toxicity:	May be irritating to mucous membranes and, in high concentrations, narcotic. Prolonged exposure may result in liver injury.

5. Acetic Acid, Glacial (CH_3COOH)

Other Names:	Ethanoic acid, vinegar acid
Molecular Weight:	60.05
Boiling Point:	118°C
Purity:	99.7% Fisher Reagent ACS

5. Acetic Acid, Glacial (CH_3COOH) (continued)

Density:	1.0492 at 20°/4°C
Vapor Pressure:	10 mm Hg at 17.5°C
Threshold Limit Value:	10 ppm
Human Toxicity:	Ingestion may cause severe corrosion of the mouth and G.I. tract with vomiting, hematemesis, diarrhea, circulatory collapse, uremia, death. Prolonged exposure to the vapors may cause conjunctivitis and blepharitis in industrial workers.

VITA AUCTORIS

1934	Born in Badaun, India on July 10
1954	Obtained B.Sc. in Physics, Chemistry and Mathematics from Agra University, Agra, India
1958	Obtained Post Graduate Diploma in Chemical Engineering from Harcourt Butler Technological Institute, Kanpur, India
1964	Obtained M.Eng. in Metallurgical Engineering from McGill University, Montreal, Quebec, Canada
1979	Candidate for the Degree of Master of Applied Science in Chemical Engineering at the University of Windsor, Windsor, Ontario, Canada