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Validation of Passive Air Sampling Monitors Onboard United States Navy Submarines

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VALIDATION OF PASSIVE AIR SAMPLING MONITORS

ONBOARD U.S. NAVY SUBMARINES

by

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ABSTRACT

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An operating submarine creates a unique air quality mixture of compounds that result from a combination of human metabolism, construction materials, materials brought onboard and compounds created through the interaction of ship systems. A comprehensive study of submarine atmospheres is ongoing during deployments of U.S. Navy nuclear submarines. As part of the overall effort, a paired air sampling comparison field validation was conducted to compare the air sampling effectiveness of passive diffusive monitors compared to more traditional active air sampling methods when sampling for acrolein, formaldehyde and ozone in the enclosed submarine atmosphere. Acrolein monitors containing 2-hydroxymethylpiperidine (HMP) impregnated glass fibers and 2-HMP silica gel as sorbent media, formaldehyde monitors containing adsorbing media of 2,4-dinitrophenylhydrazine (DNPH) and ozone monitors with a sorbent bed of nitrite impregnated glass fibers were evaluated. Active sampling was conducted in accordance with NIOSH Method 2501, NIOSH Method 2016 and OSHA Method ID 214 for acrolein, formaldehyde and ozone respectively. Extended sampling periods ranging from 14 to 28 days for active sampling methods and 28 days for passive monitors were necessary due to the trace airborne concentration levels of these airborne contaminants. Validation tests of the resulting active and passive air sampling data indicated that the acrolein, formaldehyde and ozone passive monitors were not validated

to sample the very low concentrations of these contaminants aboard U.S. Navy nuclear submarines. Depending on the airborne contaminant, the passive monitors had an average estimated accuracy ranging from $\pm$ 82.1% to $\pm$ 237.4% and $\log_{(10)}$ transformed correlation coefficients ranging from 0.0043 to 0.5289 ($r^2 = 0.0043 - 0.5289$). Although the passive monitors as tested were not validated for the enclosed submarine atmosphere, minor modifications to the passive monitors and improved laboratory analytical sensitivity will likely improve their effectiveness and additional validation testing conducted using the guidelines provided by this study is warranted.

This thesis is dedicated to the officers and enlisted personnel of the

United States Navy Submarine Force, undoubtedly the finest group of professionals ever.

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INTRODUCTION

The atmosphere inside an operating U.S. Navy submarine is unique in that frequent submerged (closed) operating conditions allow the accumulation of trace amounts of air contaminants within the submarine atmosphere. These compounds, present in generally small concentrations, are the result of human and microbial metabolism, machinery, product and hardware off-gassing, lubricating oil vapors and aerosols, hydraulic fluid leaks, electrical overheating, miscellaneous materials brought onboard and compounds created through the interaction of ship systems or special mission needs (DiNardi, Greenwell, Woolrich, and Carlson, 1998). In 1995, the U.S. Navy determined that insufficient knowledge regarding the total spectrum of airborne constituents in submarine atmospheres and any associated long term health effects on submarine sailors was available (DiNardi, Greenwell, and Woolrich, 1999). As part of a proactive response to this situation, the Submarine Atmosphere Health Assessment Program (SAHAP) was established within the Department of Operational Medicine at the Naval Submarine Medical Research Laboratory (NSMRL). SAHAP's mission is to generate and transmit knowledge of atmospheric constituents' onboard U.S. Navy submarines to the fleet in order to proactively promote health, and prevent disease and disability in submariners (DiNardi et al., 1999).

In order to determine the potential health effects of these trace amounts of air contaminants, SAHAP developed a Comprehensive Exposure Assessment Strategy (DiNardi et al., 1998; DiNardi et al., 1999). Essential to this strategy is the determination of potential airborne contaminants and their respective concentrations within the

submarine atmosphere. In order to accomplish this, submarine atmosphere air sampling is required. SAHAP has accomplished to date, active air sampling and analysis, introduced passive sampling technology, and begun work on a database format to record air monitoring results in order to perform appropriate retrospective epidemiological studies (DiNardi et al., 1999).

Air sampling can be accomplished by a variety of methods. Active sampling, passive (or diffusive) sampling and grab sampling are all methods available for the determination and subsequent analysis of airborne contaminants. Active sampling involves the forced movement of air, generally by an electrical or battery driven pump, across or through some collection device. Solid sorbent tubes, treated or untreated filters, and liquid media are common collection techniques (Langhorst and Coyne, 1989; Dietrich, 1997). The primary advantage to active sampling is that many of the reference analytical methods published by the National Institute for Occupational Safety & Health (NIOSH), Occupational Safety & Health Administration (OSHA), and American Society for Testing and Materials (ASTM) are based on active sampling due to extensive evaluation and proven reliability (Dietrich, 1997). A reference air sampling method is a procedure that is recognized to reveal or determine actual or true airborne contaminant concentration values of a particular contaminant of interest. Subsequently, in many circumstances active sampling is often considered the "gold standard" to which other sampling methods are compared or tested. However, active sampling is often labor intensive with a high degree of technical knowledge required to calibrate and operate sampling equipment and collect samples. Further, active sampling equipment tends to be

cumbersome for personal air samples and active sampling equipment and analysis can be quite expensive (Godish, 1985; Levin and Lindahl, 1994).

Passive sampling involves using monitors that are capable of sampling gases or vapors from the atmosphere at a rate controlled by the physical process of diffusion through a static air layer or permeation membrane. Passive sampling does not involve the active movement of air through the monitor or sampler (Cao and Hewitt, 1994). According to Lindahl, Levin and Mårtensson (1996), passive (or diffusive) sampling is an efficient alternative to active sampling. Advantages of passive sampling monitors include, ease of operation allowing personnel to collect samples with less technical training (Dietrich, 1997). Passive monitors eliminate the need for expensive sampling equipment (Godish, 1985) and the need for intensive calibration and maintenance of that equipment (Langhorst and Coyne, 1989). In addition, a worker can wear passive sampling monitors with little or no interference as compared to active sampling equipment (Langhorst and Coyne, 1989; Dietrich, 1997). Passive samplers may also be susceptible to environmental parameters of air motion (air stagnation or high face velocities) and reverse diffusion (Dietrich, 1997). Passive sampling monitors are also sometimes referred to as passive dosimeters, diffusive monitors, diffusive samplers, personal dosimeters, passive badges and other like terms.

Grab samples are air samples that are taken to evaluate airborne contaminants at a single point in time. Common methods of grab sampling include vacuum evacuation flasks or bags, syringes and direct reading instrumentation. Grab samples are useful to identify unknown air contaminants and to provide preliminary hazard information, but for

the most part, they do not integrate the amount of contaminants detected over time (Dietrich, 1997).

The scope of data gathered by SAHAP to date has been insufficient to provide a positive correlation between active and passive sampling methods in submarine atmospheres; and, in fact, has shown inconsistencies between concentrations measured. Such a correlation or comparison is desirable because passive sampling is an attractive alternative to intensive active sampling in terms of ease of operation and cost and the space constraints presented by submarines.

Studies or research efforts to validate the use of passive monitors onboard U.S. Navy submarines have not been completed to date.

Statement of the Problem

Passive sampling is an attractive alternative to active sampling methods for monitoring trace airborne contaminants in submarine atmospheres. However, passive monitors must be evaluated for accuracy in the submarine environment in order to validate airborne monitoring obtained using this sampling methodology. These studies are complicated by the fact that contaminant concentrations are low, and the limit of detection (LoD) is not sufficiently low to allow an adequate sample mass to be collected in a reasonable amount of time.

Statement of the Purpose

This study will examine passive air sampling as an appropriate tool to accurately assess trace or very low level concentrations of airborne contaminants within the

submarine atmosphere. Thus, the purpose of this study is to validate passive monitoring as an alternative to active sampling methods.

Significance of this Research Area

Specifically, this project will assist the Submarine Atmosphere Health Assessment Program (SAHAP) to more readily assess and evaluate the potential airborne contaminants in the submarine atmosphere by validating the use of passive sampling monitors onboard submarines at concentrations far less than those typically measured by passive monitors and for periods of time far longer (weeks) than the typical workday (hours). Validating passive sampling technology will allow for more widespread and cost effective analysis of submarine atmospheres; thus enabling SAHAP to more accurately determine the concentrations of airborne contaminants and ultimately assess the health of submarine sailors. Another possible benefit of this research effort is the potential application of passive sampling technology to evaluate other long-term exposures, e.g., indoor air quality monitoring in any environmental setting.

Hypothesis

There is no statistically significant difference ($_p$<0.05) between the airborne concentration measured with passive air sampling monitors aboard operating submarines compared to active air samples collected in accordance with an accepted reference method when sampling for formaldehyde, acrolein and ozone.

Null Hypothesis

A statistically significant difference exists between the airborne concentration measured with passive air sampling monitors compared to active air samples collected in accordance with an accepted sampling and analytical method onboard operating submarines when sampling for acrolein, formaldehyde, and ozone.

Description of Experimental Methods

A paired air sampling comparison field validation was performed to compare the differences between active and passive sampling methods within the enclosed atmosphere onboard submarines. A series of active samples was concurrently taken side-by-side with a series of passive samplers during the same time interval. Air samples were analyzed and a field validation performed. Differences detected (if any) in airborne concentrations of target air contaminants (e.g., formaldehyde, acrolein, and ozone) represent the dependent variable. The two sampling methods (active vs. passive) represent the independent variables.

BACKGROUND

United States Navy Submarines

There are currently four classes of submarines of two different types within the U.S. Navy's inventory of submarines. The first distinct type of submarines is ballistic missile submarines. These submarines are designed to carry and deliver nuclear ballistic missiles in support of the country's strategic weapons strategy. Commonly referred to as 'Trident' (name of overall weapons system) or 'Ohio-class' (named for the lead ship in the class) submarines, the primary role of these submarines is strategic deterrence. These submarines are relatively large and are designed to operate undetected while on strategic patrol approximately two months in duration. The second type of submarine in the U.S. Navy's inventory are fast-attack submarines. Fast-attack submarines have a variety of missions that include aircraft carrier battle group support, anti-submarine warfare, intelligence gathering, and special operations. The U.S. Navy currently has three classes of fast-attack submarines. The oldest fast-attack submarines are known as 637-class (denoting the hull number of the first submarine in the class) submarines. Once the mainstay of the submarine force, most of these submarines have been removed from service. The current workhorse of the submarine force is known as the 688-class or LOS ANGELES class submarines. The newest class of submarines is known as the SEAWOLF class. These submarines are significantly smaller, faster and more maneuverable than ballistic missile submarines (U.S. Navy, 1999). The efficient design of submarines affords very little excess space for unnecessary machinery/equipment or crewmember personal items. When operating submerged the enclosed submarine cannot be replenished by outside air unless the submarine is operating at periscope depth.

Therefore, special attention is devoted to the maintenance and monitoring of the enclosed submarine atmosphere.

Submarine Atmosphere

The United States Navy has developed a comprehensive program to ensure the health, safety, and efficiency of submarine personnel and to prevent or minimize the deleterious effects of atmosphere contaminants on submarine machinery or equipment. The Technical Manual for Nuclear Powered Submarine Atmosphere Control (U.S. Navy, 1994), commonly referred to as the "Atmosphere Control Manual", outlines all the necessary requirements and actions to maintain a suitable submarine atmosphere. The Atmosphere Control Manual (U.S. Navy, 1994) describes atmosphere control equipment, administrative and monitoring programs and essential record keeping to ensure the submarine air quality is maintained within acceptable limits. It also contains reference information on the effects of an abnormal atmosphere on human physiology. The purpose of the submarines atmosphere control system is to maintain the submarine's submerged atmosphere as close as practicable to a normal atmosphere. This is accomplished through proper atmospheric monitoring, proper equipment operating procedures, and control of materials introduced into the submarine (U.S. Navy, 1994). Edge (1987), the Atmosphere Control Manual (1994) and a National Research Council (1988) report on Submarine Air Quality detail in full the exact operation of atmosphere control equipment. Briefly, electrolytic oxygen generators and oxygen candle furnaces provide oxygen. Carbon dioxide is removed by means of monoethanolamine (MEA) scrubbers and lithium hydroxide canisters. Carbon monoxide, hydrogen, and other hydrocarbon contaminants are removed by catalytic combustion in a CO-H_2 burner and an electrostatic precipitator

controls various aerosols generated from cigarette smoking, cooking and machinery operation. In addition to the equipment described above, submarines will periodically ventilate with outside air while at periscope depth depending on mission parameters and mission requirements. Such ventilation periods serve to bring in fresh outside air and exhaust the internal submarine atmosphere.

The Atmosphere Control Manual (U.S. Navy, 1994) also establishes atmosphere constituent and contaminant limits that must be maintained to ensure the submarine atmosphere and air quality remains safe and healthy. The prescribed atmospheric limits are based on prolonged exposures followed by prolonged non-exposure periods. Consequently, these limits vary from regulatory permissible exposure limits (PELs) or recommended Threshold Limit Values (TLVs) which are primarily based on a 'typical' eight-hour workday and a 40-hour workweek in the occupational environment. These limits also vary from established ambient air quality standards that establish limits on environmental air quality (air pollution). The age and relative fitness and health of submarine crew members are an additional exposure criteria aspect in which the submarine atmosphere vary from other limits established to a broader, more general population (U.S. Navy, 1994). In order to provide comprehensive exposure guidance to submarine personnel, the Atmosphere Control Manual (U.S. Navy, 1994) establishes three different concentration limits.

A 90-day exposure limit represents the allowable average airborne concentration of a particular airborne contaminant over an assumed continuous exposure period of 90 days. 90-day limits are established with the expectation that submarine personnel will experience a corresponding period of lower concentrations (U.S. Navy, 1994). A 24-hour

limit represents airborne concentration exposure values developed for use in the event of an accidental or unexpected release of a single airborne contaminant. The establishment of these 24-hour exposure limits also assumes that the contaminant concentration in question returns to normal levels within 24 hours (U.S. Navy, 1994). 1-hour emergency exposure limits are intended solely for the design of safe operational procedures in response to rare, catastrophic single events in the lifetime of any submarine crew member and are not to be exceeded (U.S. Navy, 1994). Table 1 provides the 90-day, 24-hour and 1-hour exposure limits for acrolein, formaldehyde and ozone excerpted from Tables 3.5 and 3.6 of the Atmosphere Control Manual (U. S. Navy, 1994).

Table 1 – U.S. Navy Submarine Exposure Limits (ppm)

Compound	90-day	24-hour	1-hour
Acrolein	0.01	0.01	0.05
Formaldehyde	0.50	1.00	3.00
Ozone	0.02	0.10	1.00

The Atmosphere Control Manual (U.S. Navy, 1994), the National Research Council's report on Submarine Air Quality (1988) and Edge (1987) also detail analytical principles and methods of operation of the atmosphere analysis equipment used to monitor the submarine atmosphere. The Central Air Monitoring System (CAMS) is the primary means by which submarine personnel monitor the submarine atmosphere. CAMS is a combination mass spectrometer and non-dispersive infrared spectrometer with the capacity to monitor the submarine atmosphere in various locations. The atmosphere is routinely monitored for oxygen, carbon dioxide, carbon monoxide,

refrigerants, and total hydrocarbons. The atmosphere throughout the submarine can be analyzed rapidly and an alarm will sound if out-of-tolerance conditions exist for any of the compounds being monitored, such as oxygen, carbon dioxide, carbon monoxide, nitrogen, hydrogen, benzene, and hydrocarbons including chlorofluorocarbons. In addition to CAMS, submarines are also equipped with various portable analytical monitoring instruments to monitor the submarine atmosphere. These include the Trace Gas Analyzer (a photoionization detector for total hydrocarbons), fluorocarbon, oxygen, hydrogen and torpedo-fuel (OTTO fuel) detectors, as well as various grab sampling detector tubes. The primary purpose of this monitoring equipment is to ensure the submarine atmosphere remains safe for submarine personnel and as such primarily monitors whether gases that affect life support are within prescribed limits at any given point in time. The monitoring equipment described above is generally not used to determine quantitatively the levels of any trace atmospheric contaminants. Thus, the overall impact on the safety and health of trace quantities of atmospheric contaminants remains largely unknown.

Previous studies that focused on the trace amounts of airborne contaminants in submarine atmospheres include Raymer, Pellizzari, Voyksner, Velez and Castillo (1994) and Holdren et al. (1995). Each of these studies reported results of submarine atmosphere sampling from a qualitative analysis of air samples from submarines. The purpose of their efforts was to qualitatively characterize air samples aboard submarines to identify what trace airborne compounds were present in the submarine atmosphere. These studies identified many organic compounds present in the air of submarines, but did not specifically quantify their airborne concentrations. The results of these studies

however, enabled SAHAP to develop a list of target compounds for future study. In Memorandum Report 98-01, A Comprehensive Exposure Assessment Strategy for the U.S. Navy Submarine Atmosphere Exposure Health Assessment Program (DiNardi et al., 1998) reported results of ongoing submarine atmosphere air monitoring (both passive and active), but their findings to date are preliminary in nature and do not draw any final conclusions regarding the overall quality of the submarine atmosphere.

Active Air Sampling

Active air sampling is generally defined as the collection of air and entrained contaminants by some forced or 'active' movement of air by a sampling pump. The sampling pump draws the air through or across some form of collection device that can later be analyzed. Various collection devices include sorbent tubes, treated filters, or impingers containing a liquid collection media (Dietrich, 1997). Modern air sampling pumps are equipped with a variety of features that allow for variable flow ranges, constant flow capability, and data logging functions. Air sampling pumps must be able to provide or maintain a desired flowrate over the duration of the sampling period in order to allow for accurate determination of sampling volume. Precise determination of sample volume is necessary to derive the airborne concentration of a particular contaminant. Sample volume is determined by multiplying the operating flowrate times the duration of time the sample was collected. The resulting product provides the collected sample volume, as shown:

$$V = Q \times T$$

where

Q = volumetric flowrate (in liters per minute or milliliters per minute)

T = time of sample duration (in minutes)

Sample flowrates and required collection volumes are generally established or outlined by the appropriate sampling and analytical method for the contaminant of concern. In order to accurately set the air-sampling pump to the desired air sampling flowrate, the air sample pump must be calibrated. Accurate calibration depends on calibrating the pump with the representative collection media in-line to duplicate the entire sampling train as it will be used when conducting actual field measurements. Various types of calibrators include spirometers and bubble meters (primary standards) and flowmeters, wet test meters, and dry gas meters (secondary standards) (Dietrich, 1997).

The use, reliability, and accuracy of active air sampling are well reported. Sampling and analysis conducted in accordance with the appropriate reference method is considered to yield the true airborne concentration of that particular airborne contaminant. Eller and Cassinelli (1994) of the United States Department of Health and Human Services, published the National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods that contains many of the reference sampling and analytical methods used to evaluate the concentration of specific airborne contaminants. In addition, the United States Department of Labor (1990) has published the Occupational Safety and Health Administration (OSHA) Analytical Methods Manual that also contains several reference sampling and analysis methods for airborne contaminants. Other organizations that have published air sampling analytical methods include the United States Environmental Protection Agency (1984) who has published the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air; and the American Society for Testing and Material (ASTM) has published

several separate air sampling analytical methods. Since most of the sampling and analytical methods published in each of these major publications are based on the use of active air sampling as described earlier, extensive testing and documentation of reliability have been conducted (Dietrich, 1997). Often several different methods may be available for the evaluation of specific contaminants. Sampling and analytical methods utilizing active air sampling developed to determine the airborne concentration of acrolein, formaldehyde and ozone include:

ASTM Method D5014-94	(Standard Test for the Determination of Formaldehyde and Other Carbonyl Compounds in Air)
ASTM Method D5156-95	(Standard Test Methods for Continuous Measurement of Ozone in Ambient, Workplace and Indoor Atmospheres)
EPA Method TO-11	(Method for the Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Pressure Liquid Chromatography (HPLC))
NIOSH Method 2016	(Formaldehyde)
NIOSH Method 2501	(Acrolein)
NIOSH Method 2539	(Aldehydes, Screening)
NIOSH Method 2541	(Formaldehyde by Gas Chromatography)
NIOSH Method 3500	(Formaldehyde by Visible Absorption Spectrophotometry)
NIOSH Method 5700	(Formaldehyde on Dust)

OSHA Method ID 214 (Ozone in Workplace Atmospheres – Impregnated Glass Fiber Filter)

NIOSH Methods 2016, 2501 and OSHA Method ID 214, which are sampling and analytical methods for formaldehyde, acrolein, and ozone respectively, are of particular interest to this project.

Applications and examples of active air sampling are extensively reported throughout the literature and well documented. The few following examples are mentioned merely to demonstrate the scope and widespread application of active air sampling. Emphasis is devoted to examples involving sampling and analysis of formaldehyde, acrolein or ozone. Although the following citations are limited to these three analytes, there are examples and reports of active air sampling in the literature of virtually every possible airborne contaminant.

Noble, Strang and Michael (1993) report the use of active sampling devices for full-shift and short-term monitoring of formaldehyde in the laboratory setting. Experiments were conducted in a laboratory Plexiglas® exposure chamber and heating alpha-polyoxymethylene in a refillable, high-permeation rate diffusion tube generated stable formaldehyde concentrations. NIOSH Method 3500 compared favorably to other means of sampling and analysis. In a separate study, Luker and Houten (1990) conducted an evaluation of potential formaldehyde exposures in a sewing/garment plant. Using active air sampling (10 ml of 1% sodium bisulfite in all-glass midget impingers) to conduct area samples, they reported mean formaldehyde concentrations of 0.92 ppm during the morning hours and 1.05 ppm in the afternoon. These values exceeded the

OSHA permissible exposure limit (PEL). As a result of their evaluation, lower free formaldehyde content fabric was used resulting in significant reductions of airborne formaldehyde concentrations and worker complaints.

Geyh, Wolfson, Koutrakis, Mulik, and Avol (1997) report the development and evaluation of a small active ozone sampler that utilizes a single glass denuder as the collection substrate. The denuder was coated with a solution containing nitrite ion that reacts with ozone to produce nitrate. They compared their Harvard ozone sampler to an ultraviolet (UV) photometer. Their active sampler demonstrated very good accuracy and precision under laboratory and outdoor ambient conditions at ozone concentrations ranging from 20 to 220 parts per billion (ppb) in the laboratory and from 20 to 40 ppb in the outdoor ambient environment.

Vainiotalo and Matveinen (1993) conducted active air sampling in food and catering industry workplaces to ascertain the potential for acrolein exposure from emission of cooking fumes. Utilizing air sampling pumps equipped with sorbent tubes containing XAD-2 resin impregnated with 2,4-DNPH they collected air samples during frying/grilling of meat or fish and during deep fat frying in the evaluated food service facilities. They discovered concentrations of acrolein ranged from 0.01 to 0.59 mg/m^3. Hirtle, Teschke, van Netten, and Brauer (1998) reported the presence of acrolein from pottery kiln emissions when they conducted area monitoring of professional art studios, recreation centers, public schools, and colleges and universities in Canada. Acrolein was collected by air sampling pumps equipped with sorbent tubes containing silica gel impregnated with 2,4-DNPH and analyzed using high-pressure liquid chromatography

(HPLC). Measured acrolein values exceeded the Canadian indoor air quality guidance of 0.2 ppm.

Passive Air Sampling

As discussed by Dietrich (1997), the development of passive sampling devices has unquestionably been among the most important air sampling developments within the last twenty years. Passive sampling is the collection of airborne gases and vapors at a rate controlled by a natural or physical process such as diffusion through a static air layer or permeation through a membrane without the active or forced movement of air by mechanical means (i.e., air sampling pump). Passive monitors are generally compact, lightweight and their basic appeal is simplicity of use, and the fact that a sampling pump and the associated calibration are not required (Rose and Perkins, 1982; Ellwood, Groves, and Pengelly, 1990). Diffusive samplers are ideal for field work and in recent years have been recognized as efficient alternatives to pumped sampling (Levin, Lindahl, and Andersson, 1989; Pengelly, Groves, Levin and Lindahl, (1996). The first such device reported in the literature was described by Palmes and Gunnison (1973). Since their development, passive monitors have been used widely throughout the world (Pristas, 1994) and passive sampling has been increasingly used for evaluation of low concentrations of organic compounds during recent years (Cao and Hewitt, 1994). NIOSH has generated a formal passive sampling method for toluene (NIOSH Method 4000) and OSHA has formally validated the use of 3M passive formaldehyde monitors (OSHA Method ID 205). However, since passive monitors are in most cases, alternatives to established sorbent tube techniques, no additional formal validation of passive monitor use is currently planned by either OSHA or NIOSH (Pristas, 1994).

Most commercially available passive samplers operate on the principle of diffusion. Diffusive samplers rely on the movement of contaminant molecules across a concentration gradient which for steady-state conditions, can be defined by Fick's First Law of Diffusion (Rose and Perkins, 1982; Posner and Moore, 1985; Dietrich, 1997):

$$W = -(DA)\, dc/dx$$

where: W = mass transfer rate, ng/sec,

D = diffusion coefficient, cm^2/sec,

A = cross sectional area of diffusion path length, cm^2,

dc/dx = the instantaneous rate of change in concentration over diffusion path, $(ng/cm^3)cm^{-1}$.

Considering the change in concentration $(C_1 - C_0)$ over the total diffusion path length $(X_1 - X_0 = -L)$, the above equation becomes:

$$W = D\,(A/L)\,(C_1 - C_0)$$

where: L = length of the diffusion (static) path, cm,

C_1 = ambient concentration of contaminant, ng/cm^3, and

C_0 = concentration of contaminant at collecting surface, ng/cm^3.

If an effective collection medium is employed, the contaminant concentration at the surface of the collector (C_0) can be assumed to be zero, and multiplying both sides of the equation by time, yields:

$$M = D\,(A/L)\,(C_1)\,t$$

where: M = total mass transferred, ng, and

t = total time that the monitor is exposed to the contaminated air, sec.

Rearranging the above equation as follows:

$$C_1 = ML/DAt$$

it becomes apparent that five factors affect the measurement of the ambient air concentration of a substance or contaminant (C_1). Two of the factors (L and A) are physical parameters associated with the construction of the monitor, one (M) is provided by analytically measuring the total mass of contaminant collected by the sampler, another is the duration (t) the sampler was exposed to the contaminated atmosphere, and the final factor (D) is an individual property of each vapor or gas.

Each gas or vapor being sampled has a specific diffusion coefficient (D). Therefore, a passive sampler or monitor will likely have a different sampling rate for different analytes based on its physical characteristics. Diffusion coefficients for various compounds can be determined experimentally or may be estimated using one of several equations (Dietrich, 1997). In a detailed review of passive sampling, Rose and Perkins (1982) report that the diffusion coefficient is directly proportional to the absolute temperature (T) of the vapor, raised to the three-halves power and inversely proportional to the atmospheric pressure (P).

$$D \propto T^{3/2}/P$$

Although utilized less frequently and generally not available commercially, passive samplers that rely on the principle of permeation through a membrane are especially useful where the contaminant of concern is usually found mixed with other interfering vapors or gases or when a liquid collecting medium is employed. The goal then becomes to identify a membrane material that is highly permeable to the contaminant of interest and impermeable to most other components in the atmosphere, and/or the collecting media (Rose and Perkins, 1982).

The determination of ambient concentrations of a contaminant using a permeation device can be determined from the formula (Rose and Perkins, 1982):

$$C = wk/t$$

where: C = concentration of contaminant, ppm

w = mass of contaminant collected, μg

k = permeation constant, ppm-hours/μg, and

t = exposure time, hours.

The permeation constant (k) is determined experimentally and is a function of the specific membrane material and contaminant of interest (Rose and Perkins, 1982).

Extensive studies have been accomplished to validate passive sampling monitors and to reliably assess their overall accuracy and precision. In 1987, Cassinelli, Hull, Crable, and Teass published a validation protocol for the evaluation of passive sampling monitors. This protocol evaluated several passive monitor performance characteristics such as: analytical recovery; sampling rate, and capacity; reverse diffusion; accuracy and precision; storage stability and shelf life; analyte concentration; exposure time; face velocity; relative humidity; interferents; monitor orientation; temperature; and behavior in the field (Cassinelli et al., 1987; Dietrich, 1997). This information provides manufacturers and other interested organizations with suggested experiments to address the performance characteristics listed above (Pristas, 1994). In a symposium presentation, Kennedy, Cassinelli and Hull (1987) reported that the most frequently seen problems validating passive monitors included variable sampling rates, high sensitivity to humidity and interferents, high bias for short sampling periods, and blank variability and liquid sorbent volume variations. The guidelines provided by Cassinelli et al., (1987)

state the general acceptance criteria for passive monitors is $\pm$ 25% accuracy with 10% differences at the 95% confidence level; that is, the absolute total error of the method should be less than 25% in at least 95% of the sample population. In some cases regulatory standards state acceptable passive monitor accuracy criteria that may vary from the general guidance stated above. For example, regulatory standards stipulate that passive monitors be $\pm$ 25% accurate when sampling for formaldehyde, benzene, ethylene oxide and vinyl chloride for concentrations at the PEL level, and that they be $\pm$ 35% accurate for concentrations at the action limit. Other regulatory guidance that stipulates passive monitor accuracy includes $\pm$ 35% accuracy for acrylonitrile at the PEL and $\pm$ 50% for vinyl chloride below the action limit and for acrylonitrile below the PEL (Pristas, 1994).

As outlined and described by Rose and Perkins (1982), when considering diffusive passive monitors and their corresponding diffusion coefficient, the three factors that have the greatest effect on variability are temperature, pressure, and the velocity of the air external to the diffusive monitor. Considering the following equation, discussed previously:

$$D \alpha T^{3/2}/P$$

it can be shown that a temperature rise from 5 to 35 °C (283.15K - 308.15K) would result in a 16% increase in the diffusion coefficient, while a rise in barometric pressure from 710 to 810 mm Hg would cause a 14% decrease. However, at the same time, the changes in temperature and pressure also are affecting the density of the contaminant in that density is inversely proportional to the temperature and directly proportional to the pressure. As a result, the total mass collected by a passive diffusion monitor is only

slightly affected by temperature ($M \alpha T^{1/2}$) and is independent of pressure. Movement of the air external to the passive monitor, often referred to as face velocity, can affect the concentration gradient ($C_1 - C_0$). Rose and Perkins (1982) report it is important to contain all the resistance to contaminant transport within the stagnant layer inside the passive diffusive monitor. When the air external to the badge is stagnant, C_1 can no longer be assumed to be the ambient concentration and the length of the diffusion pathway (L) is effectively extended decreasing the measured ambient concentration. Provided face velocities are greater than 7.5 cm/sec (15 fpm), no significant effect on monitor performance is expected (Rose and Perkins, 1982).

According to Rose and Perkins (1982), when considering passive permeation monitors, accurate determination of the permeation coefficient for each monitor is necessary for obtaining accurate and valid results. Factors that influence permeation include thickness and uniformity of the membrane, affinity of the membrane for the analyte, swelling or shrinkage of the membrane, and possible etching by corrosive chemicals.

The previous paragraphs have focused on potential sources of error and causes of passive monitor variability specific to either diffusive or permeation passive monitors. Potential sources of error for both types of passive monitors (diffusion and permeation) are the determination of the mass of contaminant or analyte collected and the time of the passive monitor to the contaminated atmosphere (Rose and Perkins, 1982). Problems associated with the accurate determination of the mass of contaminant collected by passive monitors are essentially the same as those associated with other collection devices such as sorbent tubes used for active sampling or methods in which the collection

of the contaminant involves a chemical reaction with the collection medium (Rose and Perkins, 1982). Using known amounts or concentrations of contaminants to determine collection and/or desorption efficiency is as critical to passive sampling and analysis as it is for other collection methods. The overall accuracy of the analytical method and the potential saturation of sorbent in high analyte/contaminant concentrations are also factors to consider when evaluating aspects of measurement error (Rose and Perkins, 1982; Dietrich, 1997). The potential for interferences (negative or positive) from other constituents of the sampled atmosphere is a potential source of error for all types of air sampling (active and passive, including diffusive and permeation sampling). As evaluation and validation of passive monitors has evolved, both occupational hygienists and analytical chemists are paying increased attention to potential interferences in multi-contaminant exposure situations. In evaluating the potential for such interferences, it is important to realize there are several potential sites for interference from another contaminant to occur. Interference effects from absorption or adsorption efficiency of the sampling medium, chemical reactions of two or more contaminants prior to sample analysis, and the multitude of interferences associated with complex mixtures of vapors and gases all may affect the measurement accuracy of passive samplers. The interference issues listed above also apply to classic active sampling and analytical procedures (Rose and Perkins, 1982).

The final area for potential error that will affect the measurement accuracy of passive samplers is accurate time measurement. Accurately measuring the time the sampling device is exposed, whether active or passive, is essential in most occupational hygiene sampling procedures. Regardless of the sampling duration, whether it be short-

term (15 minutes), full shift (8 hours), or extended (28 days) sampling periods, measuring errors of less than one percent are reasonable (Rose and Perkins, 1982).

Therefore, although numerous factors may affect the final concentration reported by passive samplers, if face velocities are sufficient to avoid 'starvation' and the diffusion coefficient has been accurately calculated or experimentally determined, passive monitors should provide results comparable to active sampling methods and provide an efficient alternative to active sampling (Rose and Perkins, 1982; Levin, Lindahl, and Andersson, 1989; Pengelly, Groves, Levin and Lindahl, (1996); Dietrich, 1997).

Concurrent with this increased use of passive sampling methodologies, many research studies have been published validating the use of passive sampling monitors. Data from these articles have in general shown passive monitors comparable to traditional sorbent tube and pump samplers for many compounds, especially aliphatic and aromatic hydrocarbons (Rose and Perkins, 1982; Pristas, 1994; Dietrich, 1997). The following citations provide some examples of the extensive number of studies available in the published literature. Most of the examples cited outline validation studies of passive monitors when compared to another sampling methods, generally involving formaldehyde and ozone. Unfortunately, few data or examples on aldehydes other than formaldehyde are available (Brown, Crump, Gavin, and Gardiner, 1991). Specific and detailed description of the various validation or correlation methods discussed or utilized is provided in the following section.

Lindahl et al., (1996) report the evaluation of a diffusive sampler for the determination of acetaldehyde. Acetaldehyde was trapped on a filter impregnated with 2,4-dinitrophenylhydrazine (DNPH) and the hydrazone derivative collected on the filter

was analyzed. Prior to that study, Levin and Lindahl (1994) reported a review of diffusive air sampling of reactive compounds comparing sorbent samplers, liquid samplers and filter samplers; each evaluated as an acceptable alternative to active sampling. Eriksson and Levin (1995) report the field validation of a diffusive sampler used to sample personal exposure to monoterpenes generated during the handling and sawing of pine in the sawmill industry. Activated charcoal solid sorbent was used both in the passive monitor and the active sampling reference method.

Several studies (Kennedy and Hull, 1986; Levin, Lindahl and Andersson, 1989; Grosjean and Williams, 1992; Dillon and Gao, 1994; Kollman, 1994; among others) report successful validation of passive sampling monitors when compared to active sampling for evaluating airborne formaldehyde concentrations. These report a variety of passive methods, some of the advantages of passive sampling monitors and some of the limitations as well. The bulk of these studies evaluated passive sampling monitors containing a 2,4-DNPH impregnated sorbent bed or filter.

Several studies (Monn and Hangartner, 1990; Grosjean and Hisham, 1992; Koutrakis et al., 1993; Liu, Olson, Allen and Koutrakis, 1994) have also successfully validated passive sampling monitors when compared to active sampling reference methods for determining ozone concentrations. The passive sampling methodology varies with regard to the collection method. Grosjean and Williams (1992) and Grosjean and Hisham (1992) report using a filter impregnated with indigo carmine, an ozone-fugitive colorant. Color differences before and after sampling are measured by reflectance spectrophotography, and the color change (fading) varies in proportion to the ozone concentration. These passive sampling monitors have been tested in forested

mountain locations to assess oxidant damage to forests and other wilderness vegetation. Surgi and Hodgeson (1985) and Monn and Hangartner (1990) report using 10,10'-dimethyl-9,9'-biacridylidene and 1,2-di-(4-pyridyl)-ethylene impregnated film badges to determine ambient ozone exposure. One advantage reported for this method was minimal interferences from nitrogen dioxide and sulfur dioxide, common airborne pollutants. Finally, Koutrakis et al., (1993), Liu et al., (1994) and Brauer and Brock (1995) report using nitrite impregnated glass fiber filters to determine atmospheric ozone concentrations.

In regard to passive validation studies for acrolein, Goelen, Lambrechts, and Geyskens (1997) report that passive sampling and analysis is not yet commonplace. However, three studies (Otson, Fellin, Tran, and Stoyanoff, 1993; Levin and Lindahl, 1994; Goelen et al., 1997) have conducted examinations of passive sampling comparisons for aldehydes including acrolein using 2,4-DNPH impregnated filters or sorbent to evaluate airborne concentrations. Goelen et al. (1997) report that using 2,4-DNPH impregnated collection media for acrolein passive sampling yields incomplete recovery and that using 2-(hydroxymethyl)piperidine (HMP) instead provides a stable acrolein derivative and much more accurate results. Pristas (1994) conducted a survey to determine how passive sampling monitors are used for compliance monitoring internationally and reported passive monitors are accepted in varying degrees for occupational exposure monitoring throughout the world.

Validation Methods/Statistical Considerations

Interpretation of passive monitor validation studies requires the appropriate application of statistical techniques to draw sound conclusions regarding the performance

of passive sampling monitors. Validation data, both field and laboratory, can be evaluated by numerous tests (Rose and Perkins, 1982).

The Multiple Comparison Method [described and outlined by Rose and Perkins (1982), Noble, Strang, and Michael (1993), Kollman (1994), and Dillion and Gao (1994)], is a common validation method used to determine passive monitor accuracy relative to a respective corresponding active air sampling method. As part of this method an active air sample time-weighted average (TWA) concentration for the respective analyte is calculated for the entire sampling duration for each sampling period using the following calculation:

$$TLV - TWA = \frac{C_1T_1 + C_2T_2 + \ldots + C_lT_l}{T_1 + T_2 + \ldots + T_l}$$

where: TLV = established Threshold Limit Value (TLV)

TWA = Time Weighted Average (TWA)

C_1 = airborne concentration of first sampled period,

C_2 = airborne concentration of second sampled period,

C_L = airborne concentration of individual sample,

T_1 = sample time of the first sampled period,

T_2 = sample time of the second sampled period,

T_L = sample time of individual sample period.

Dietrich (1997) describes this well-known calculation procedure. The result of this calculation is a single airborne concentration value that has been time-weighted that is used as a basis of comparison for passive sampling result validation. Then using the passive sampling data, the mean and standard deviation are determined for each sampling period. The precision (or variation of passive air sampling values about the mean) for

each sampling period is estimated, as a percentage, by determining the coefficient of variation (CV) or relative standard deviation (RSD) of the data as follows:

$$CV = 100\frac{s}{X}$$

where: s = standard deviation of the passive air sample data set, and

X = mean of passive air sample data set.

From here the difference between the passive sampling mean and the TWA active sampling value, commonly referred to accuracy but more appropriately termed bias (as a percentage), is defined as follows:

$$b = \frac{X_P - X_A}{X_A}100$$

where: b = bias (%),

X_p = mean of the passive air sample data set, and

X_a = calculated active air sampling TWA.

Finally, the overall passive air sampling monitor accuracy can be determined as follows:

$$\text{Estimated accuracy (\%)} = B + (2 \times CV)$$

where: B = absolute value of the mean bias (|mean bias|), and

CV = coefficient of variation of the respective passive air sample data set.

The calculated estimated accuracy can be used to determine whether the passive sampling monitor being evaluated is validated using the NIOSH criteria protocol provided by Cassinelli et al. (1987) (Rose and Perkins, 1982; Noble, Strang, and Michael, 1993; Kollman, 1994; and Dillion and Gao, 1994).

A second validation method is to determine a correlation between the active air sampling TWA and the passive air sampling mean for the corresponding sampling period. This validation technique is used extensively in field passive sampling validation studies. For a direct correlation, used when the air sampling data is normally distributed, the sampling period average passive air sampling result concentration is plotted on the y-axis against the corresponding active air sampling TWA concentration on the x-axis. This one-to-one correlation is graphically depicted by trend analysis and the slope of the line, y-intercept and correlation coefficient is determined using linear regression and the results used to determine validation based on the NIOSH validation protocol provided by Cassinelli et al., (1987). Examples in the published literature of this validation technique include: Levin, Lindahl, and Andersson (1986); Levin, Lindahl, and Andersson (1988); Levin, Lindahl, and Andersson (1989); Mulik, Lewis and McClenny (1989); Levin and Lindahl (1994); and Brauer and Brook (1995). When the air sampling is not normally distributed, a log transformation of the data is necessary before a correlation can be conducted. Kollman (1994) outlines the use of this statistical evaluation. Prior to plotting both the passive and corresponding active air sampling result concentrations as outlined above, the results are $\log_{(10)}$ transformed. The appropriate $\log_{(10)}$ transformed data is then plotted and linear regression used once again to determine the correlation coefficient, slope and y-intercept of the resulting line and the results used to determine validation based on the NIOSH validation protocol provided by Cassinelli et al., (1987).

The last statistical means of validating passive air sampling data collected in support of validation research is the use of a direct statistical comparison such as a t-test.

This statistical application tests the differences of sample means and compares equality of sample group means to determine whether significant differences exist between sample group data at a particular confidence level (generally 95%). This type of statistical evaluation is most frequently used when evaluating large groups of data or when comparing different (non-matched) data sets (Kollman, 1994; Liu et al., 1994).

Effects of Exposure to Acrolein, Formaldehyde and Ozone

At higher concentrations, acrolein is a reactive and irritating aldehyde that is toxic by all routes of exposure (Ghilarducci and Tjeerdema, 1995). Respiratory system exposure causes local irritation in the upper respiratory tract due to direct chemical burns, respiratory distress from hypoxia caused by bronchoconstriction, pulmonary edema, cellular necrosis, and increased susceptibility to microbial diseases (Rorison and McPherson, 1992; Ghilarducci and Tjeerdema, 1995). Liquid contact with the skin causes irritation, erythema and chemical burns (Rorison and McPherson, 1992). Contact with the eyes causes severe irritation, intense lacrimation, cloudy or opaque corneas, and localized epidermal necrosis (Rorison and McPherson, 1992; Ghilarducci and Tjeerdema, 1995).

Formaldehyde is a common airborne contaminant that is ubiquitous in nature. At higher concentrations, it is a potent dermal and respiratory irritant (both to the upper airways of the nose and throat and the lower airways of the lung) as well as a sensitizer (Horvath, Anderson, Pierce, Hanrahan, and Wendlick, 1988; Rorison and McPherson, 1992). Respiratory system exposure results in local mucosal irritation, pulmonary edema, and in some individuals, a hypersensitivity response at airborne concentrations as low as 0.1 ppm (Horvath, Anderson, Pierce, Hanrahan, and Wendlick, 1988; Liu, Huang,

Hayward, Wesolowski, and Sexton, 1991; Rorison and McPherson, 1992). Extended respiratory system exposure at airborne concentrations approaching 5.0 ppm results in a pronounced cough, sore throat, wheezing and chest tightness (Liu et al., 1991). Airborne concentrations of formaldehyde can also cause eye irritation, headaches, fatigue, dizziness, nausea, vomiting, sleeping disorders, and memory loss at airborne concentrations ranging from 0.2 ppm to 10 ppm (Liu et al., 1991; Rorison and McPherson, 1992).

Also, at higher concentrations, ozone is an atmospheric oxidant formed through photochemical reactions of volatile organic compounds and nitrogen oxides and by electrical discharges or arcing in the presence of oxygen (Koutrakis et al., 1993; DiNardi et al., 1998). Ozone is a potent irritant that causes eye irritation, mucosal membrane irritation, pulmonary edema, and chronic respiratory disease, including changes in lung capacity, flow resistance and epithelial permeability (Koutrakis et al., 1993; U.S. Department of Health and Human Services, 2000). Changes in lung function can occur at airborne concentrations as low as 0.5 ppm when exposed for extended periods of time (3 hours per day, 6 days a week, for 12 weeks) (U.S. Department of Health and Human Services, 1999).

At extremely low concentrations, as measured in submarines, any non-carcinogenic effects of acrolein, formaldehyde, and ozone, which may occur are expected to be completely reversible.

METHODS

Description

Formaldehyde, acrolein, and ozone were the analytes sampled. These analytes were selected based on the following criteria:

- Previous sampling efforts (DiNardi et al., 1998; DiNardi et al., 1999) have identified these analytes present in enclosed submarine atmospheres.
- NSMRL requires more data on these contaminants in order to more effectively quantify the potential health risks to submarine sailors (DiNardi et al., 1998; DiNardi et al., 1999).
- These analytes are quite chemically reactive in the submarine atmosphere (DiNardi et al., 1998).
- Proposed new occupational exposure limits for these analytes onboard submarines may be problematic. The U.S. Navy is currently evaluating new occupational exposure limits. One of the contaminants being considered for a lower 90-day exposure limit is formaldehyde. Available submarine sampling to date indicates this may be problematic and additional air sampling data is needed (DiNardi et al., 1998).

Based on previous sampling efforts (DiNardi et al., 1998) trace or very low level concentrations of these analytes were expected, therefore the sampling period was extended considerably beyond the 'normal' eight-hour sampling period in order to more effectively capture and quantify these airborne contaminants.

In order to confidently quantify the amount analytes of interest collected by active sampling at the trace levels expected, an active sampling exposure duration model was

developed using the guidance provided by Mulhausen and Damiano (1998). They recommend an initial monitoring threshold of 10% of the occupational exposure limit (OEL), in this case the applicable 90-day exposure limit established by the U.S. Navy (1994). They also recommend the use of an analytical safety factor (10 times the limit of analytical detection (LoD)) to provide an acceptable level of quantification (LoQ). This duration model provides the minimum volume of air to collect by active sampling. This duration model is expressed as:

$$V_{MIN\,(liters)} = \frac{(ANALYTICAL\ \ SAFETY\ \ FACTOR)(LoD, \mu g)\left(\frac{mg}{10^3\ \mu g}\right)\left(10^3\ \frac{l}{m^3}\right)}{(EXPOSURE\ \ PROTECTION\ \ FACTOR)(OEL, \frac{mg}{m^3})}$$

$$V_{MIN}(liters) = \frac{(ANALYTICAL SAFETY\ FACTOR)(LoD,)}{(EXPOSURE PROTECTION\ FACTOR)(OEL,)}\ liters$$

where:

V_{MIN} = The minimum volume needed for collection of a sample, in liters,

LoD = The limit of detection for an analytical method, μg,

ASF = Analytical safety factor that when multiplied by the LoD = LoQ

e.g.: 10(LoD) = LoQ, unitless,

OEL = The Occupational Exposure Limit to which one wishes to assess compliance (e.g., 90-day exposure limits established by the U.S. Navy), ppm,

PF = Exposure protection factor that when multiplied by the OEL yields an "acceptable exposure concentration", unitless.

Table 2 provides a summary of the information determined by use of the active sampling exposure duration model to satisfy the requirements of the applicable sampling and analytical method for each of the respective analytes (Eller and Cassinelli, 1994; U.S. Department of Labor, 1990). It should be noted that although the 90-day occupational exposure limit for formaldehyde is 0.50 parts per million (ppm) as listed in Table 1, an occupational exposure limit for formaldehyde of 0.04 ppm was used in the above model. This decision was based on official U.S. Navy proposals to lower the formaldehyde 90-day limit to that value. These proposals are based on the establishment by the National Research Council (NRC) Committee on Toxicology of a Spacecraft Maximum Allowable Concentration (SMAC) for formaldehyde of 0.04 ppm (National Research Council, 1994). Note also that for acrolein, an exposure protection factor of 0.1 (or 10%) yields a minimum sampling volume of 8722 liters of air and an associated sampling flowrate of 216 ml/min. However, NIOSH Method 2501 (Eller and Cassinelli, 1994) requires the sampling flowrate not exceed 100 ml/min, therefore the exposure protection factor of acrolein was modified to 0.25 (or 25%) in order to achieve an acceptable level of quantification and meet the requirements of the sampling and analytical method. Active sampling for formaldehyde and ozone can be accomplished in accordance with the respective analytical method without any modifications to the duration model.

All passive sampling was conducted as directed by the passive monitor manufacturer (Assay Technology, Pleasanton, CA). A sampling period of 28 days was selected in order to be able collect the trace amounts of selected analytes and provide a satisfactory basis of comparison to the active sampling methods.

Table 2 - Active Air Sampling Exposure Duration Model Results

CHEMICAL NAME	CHEMICAL FORMULA	MOLECULAR WEIGHT	90-day limit (OEL) AIRBORNE CONC. (ppm)	90-day limit (OEL) AIRBORNE CONC. (mg/m^3)	EXPOSURE PROTECTION FACTOR	METHOD LOD (ug)	ANALYTICAL SAFETY FACTOR	AIR SAMPLE VOLUME (liter)	DURATION OF SAMPLING (days)	DURATION OF SAMPLING (minutes)	METHOD AIR SAMPLING FLOWRATE (ml/min)
formaldehyde	CH_2O	30.00	0.04	0.050	0.10	0.09	10.00	180.00	14.00	20160.00	8.93
acrolein	CH_2=CHCHO	56.06	0.01	0.023	0.10	2.00	10.00	8695.65	28.00	40320.00	215.67
acrolein	CH_2=CHCHO	56.06	0.01	0.023	0.25	2.00	10.00	3478.26	28.00	40320.00	86.27
ozone	O_3	48.00	0.02	0.040	0.10	2.00	10.00	5000.00	14.00	20160.00	248.02

Instrumentation

For all active sampling, low-flow SKC Pocket Pump® 210 Series (SKC Inc., Eighty Four, PA) samplers were used. In order to accommodate the long-term sampling requirement necessary to detect and quantify low levels of trace contaminants, the pumps were operated from an A/C power supply with battery back-up. The battery back-up feature was necessary in the event of a short-term power loss onboard the submarine due to casualty control training exercises, transferring power from shore power to ship's power or an actual power casualty. All air-sampling pumps were calibrated before and after each sampling period using a Gilibrator (Gilian Instrument Corp., Wayne, NJ) flow calibrator with representative media in-line.

Active sampling for acrolein was conducted following the sampling and analytical procedures outlined in NIOSH Method 2501 (Eller and Cassinelli, 1994) using 2-hydroxymethylpiperdine (HMP) impregnated on XAD-2, 120mg/60mg (front/back section) solid sorbent tubes. The pump flowrate was set at 86.5 ml/min and the samples were collected for approximately 28 days. Active sampling for formaldehyde was conducted following the sampling and analytical procedures outline in NIOSH Method 2016 (Eller and Cassinelli, 1994), using 2,4-dinitrophenylhydrazine (DNPH) impregnated on silica gel, 120mg/60mg (front/back section) solid sorbent tubes. A nitrite impregnated glass fiber filter cassette was placed before the DNPH impregnated tube to remove any airborne ozone, to prevent interference with formaldehyde derivative formation on the solid sorbent. The flowrate was set at 9 ml/min and each sample was collected for approximately fourteen days. Active sampling for ozone was conducted following the sampling and analytical procedures outline in OSHA Method ID 214 (U.S. Department of

Labor, 1990), using two nitrite-impregnated glass fiber filters. During collection, ozone will react with the nitrite impregnated on the filter, converting it to nitrate via oxidation. The flowrate was set at 250 ml/min and each sample was collected for approximately fourteen days.

Passive sampling was conducted with monitors prepared and provided by Assay Technology (Pleasanton, CA). All passive monitors were prepared expressly for this study effort and shipped directly to Old Dominion University. To initiate sampling with passive monitors, the monitor is placed in the desired location and the cover removed to start the diffusive sampling process. At the conclusion of the desired sampling period frame, the covers are replaced and the monitors placed in shipment containers to be returned to Assay Technology (Pleasanton, CA) for analysis. The basic passive sampling protocol developed by NSMRL is provided in Appendix A. Passive sampling for acrolein during the first three submarine sampling periods (A-1, B-1, A-2) was accomplished with 2-HMP impregnated glass fibers in the sampling monitor and for the last sampling period (C-1) was accomplished with 2-HMP impregnated silica gel in the sampling monitor. This media change was made by NSMRL/SAHAP and Assay Technology personnel after concerns of collection efficiency were observed from the first three sampling periods. Passive sampling for formaldehyde was accomplished with 2,4-DNPH impregnated silica gel beads placed in the passive monitor. Glass fibers impregnated with nitrite were placed in the passive monitor prior to the 2,4-DNPH to remove ozone from the sample atmosphere forming a combination aldehyde/ozone sampling monitor. Additional passive sampling for ozone was accomplished with nitrite

impregnated glass fibers placed in a separate passive monitor. Each passive monitor collected samples for approximately twenty-eight days.

Sampling Procedures

A side-by-side sampling comparison was performed between the active sampling equipment (applicable reference method) and the passive sampling monitor. Sampling onboard the submarine was performed in the Engine Room, Middle Level on the high-pressure air compressor flat. Appendix B provides a diagrammatic layout of a submarine with designated sampling locations. Submarines selected for sampling were chosen based on convenience, taking into account operational schedules, maintenance periods, and underway availability. The designated sampling period onboard the submarine was 28 days of which at least 18 days were spent underway conducting submerged operations.

A series of passive monitors (1 ozone, 2 acrolein, and 2 combination ozone/formaldehyde) were placed out of the moving airstream in the designated sampling location. As nearby as practicable (approximately 12 inches), four low-flow active sampling pumps were connected to the A/C power supply, which doubles as a carrying case. One pump sampled for ozone; one sampled for formaldehyde and two sampled for acrolein. The appropriate sampling media, described above, was attached and the pumps started to commence active sampling followed by removal of the passive sampling monitor caps to start passive sampling. Table 3 provides a summary of analyte types, sample methods, sample duration, number of samplers and total number of samples collected per trip.

The submarine's Hospital Corpsman (HM) inserted a new ozone filtering cassette on the active pump sampling for ozone and new 2,4-DNPH solid sorbent tube on the

Table 3 - Summary of Sampling Requirements

Analyte	Sample Method	Sample Duration	Number of Samplers	Total Samples Produced per Trip
Ozone	Active	14 days	1	2
Ozone	Passive	28 days	6	6
Acrolein	Active	28 days	2	2
Acrolein	Passive	28 days	4	4
Formaldehyde	Active	14 days	1	2
Formaldehyde	Passive	28 days	4	4

active pump sampling for formaldehyde after 14 days during the sampling period in order to cover the entire designated 28 day sampling period. The initial ozone and formaldehyde active samples were placed in refrigerated storage ($\leq$ 4°C) until completion of the entire sampling period and collected by the primary investigator and/or his assistant. The primary investigator and/or his assistant accomplished all other sampling procedures (both active and passive). NSMRL staff and Commander Submarine Group 2 Medical personnel sampled submarines homeported in New London, CT. Upon completion of the 28-day sampling period, all samples were collected and returned to the appropriate laboratory for analysis.

Sample Analysis

Sample analysis for acrolein collected by active sampling was conducted as described in NIOSH Method 2501 (Eller and Cassinelli, 1994) by Environmental Health Laboratory of Cromwell, CT. The 2-HMP impregnated XAD-2 sorbent was desorbed with toluene in an ultrasonic bath to isolate the analyte derivative 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane. The sample aliquot was then measured by a gas chromatograph equipped with a nitrogen specific detector using helium as a carrier gas. The resulting peak area and height reported the mass of acrolein collected when compared to a calibration curve prepared from at least six standards. Dividing the reported mass by the sample volume results in determination of the airborne concentration of acrolein.

Sample analysis for acrolein collected by passive monitors was conducted as described in OSHA Method 52 (U.S. Department of Labor, 1990) by Assay Technology of Pleasanton, CA. Similar to NIOSH Method 2501 (Eller and Cassinelli, 1994), OSHA

Method 52 directs the passive air sample sorbent to be desorbed with toluene and the resulting aliquot was analyzed (or measured) by gas chromatography using a nitrogen selective detector. As mentioned earlier, the acrolein passive monitor sorbent media for the first three sampling periods (A-1, B-1, and A-2) was 2-HMP impregnated glass fibers and for the last sampling period (C-1) was 2-HMP impregnated silica gel. Regardless of the sorbent media, the analytical procedure remained the same. The resulting peak area and height reported by the gas chromatograph was used to determine the mass of acrolein collected when compared to a calibration curve prepared from at least six standards. The sample volume was derived using Fick's First Law of Diffusion. Using the reported mass and derived sample volume allowed for the determination of the airborne concentration of acrolein

Sample analysis for formaldehyde collected by active sampling was conducted as described in NIOSH Method 2016 (Eller and Cassinelli, 1994) by Environmental Health Laboratory (Cromwell, CT). The 2,4-DNPH impregnated silica gel from the sorbent tube was eluted with acetonitrile to isolate the 2,4-DNPH derivative of formaldehyde and the sample aliquot measured by high-pressure liquid chromatography (HPLC) with an ultraviolet (UV) detector. The resulting peak area reported the mass of formaldehyde collected when compared to a calibration curve prepared from at least six standards. As before, the resulting mass of formaldehyde divided by the sample volume yielded the airborne concentration.

Sample analysis for formaldehyde collected by passive monitors was conducted as described in EPA Method TO-11 (U.S. Environmental Protection Agency, 1984) by Assay Technology (Pleasanton, CA). Similar to NIOSH 2016 (Eller and Cassinelli,

1994), EPA Method TO-11 directs the passive air sampling sorbent (2,4-DNPH impregnated silica gel) to be washed by gravity fed elution of acetonitrile. The resulting sample aliquot containing the DNPH-formaldehyde derivative was measured using isocratic reverse phase high-pressure liquid chromatography (HPLC) with an ultraviolet (UV) absorption detector operated at 360 nm. The resulting peak area reported by the chromatograph was used to calculate the mass of formaldehyde collected when compared to a calibration curve prepared from at least six standards. As before, the sample volume was derived using Fick's First Law of Diffusion. Using the measured mass and derived sample volume allows determination of the airborne concentration of formaldehyde.

Sample analysis for ozone collected by active air sampling was conducted as described in OSHA Method ID 214 (U.S. Department of Labor, 1990) by Environmental Health Laboratory (Cromwell, CT). Ozone in the sampling atmosphere reacts with the nitrite impregnated on the glass fiber filters in the sampling cassette to form nitrate by oxidation. The nitrate was extracted using deionized water and analyzed by ion chromatography using an UV-vis detector at the 200-nm wavelength. The resulting peak area reported the mass of nitrate that can be converted to determine the mass of ozone using a direct mass balance conversion factor. Again, dividing the resulting collected mass of analyte by the sample volume yielded the airborne concentration.

As with active ozone sample analysis, analysis for ozone collected by passive monitors was conducted as outlined in OSHA Method ID 214 (U.S. Department of Labor, 1990) by Assay Technology (Pleasanton, CA). The only difference in the analytical procedure described above for active ozone sample analysis is that instead of using nitrite impregnated glass fiber filters as the collection media, separate nitrite

impregnated glass fibers were used in the passive monitor. As with other passive monitors the determination of the sample volume necessary to calculate the airborne concentration was derived from Fick's First Law of Diffusion.

Data Analysis/Statistical Considerations

Two primary areas of investigative concern, air sampling result distribution and the differences (or variation) between the reported airborne concentrations (measured in parts per million, ppm) of active and passive sampling methods, were addressed statistically. SPSS (SPSS Inc., Chicago, IL) and Industrial Hygiene Statistics Spreadsheet (Mulhausen and Damiano, 1998) software packages were used to determine air sampling result distribution normality (normal vs. log normal). Air sampling data distribution for each analyte examined (e.g., acrolein, formaldehyde, and ozone) was statistically evaluated both as a single group encompassing all sampling periods aboard all submarines and each individual sampling period aboard each submarine separately.

Evaluating differences between active and passive sampling results as part of the overall validation effort was accomplished using three different methods/tests. The multiple comparison method, a test of accuracy and precision, described by Rose and Perkins (1982) and Dillion and Gao (1994) was used to determine passive monitor accuracy relative to the respective corresponding active sampling method. A log-transformed correlation and linear regression analysis were used to determine the correlation coefficient between the two sampling methods. Log transformation of the average concentrations was done to normalize exposure distributions and to satisfy regression modeling assumptions. This validation method is well described by Kollman (1994), Liu et al., (1994), Dillion and Gao (1994), McGuire, Casserly, and Greff (1992)

and Levin, Lindahl, and Andersson (1988). Finally, SPSS (SPSS Inc., Chicago, IL) software was used to conduct a 2-sided significance level t-test where appropriate.

RESULTS

Four sampling periods were conducted on three different submarines to evaluate the enclosed submarine atmosphere. Two of the submarines were homeported in Norfolk, VA and one was stationed in New London, CT. The sampling period duration for the first, third and fourth sampling periods (A-1, A-2 and C-1) ranged from 28 to 30 days. The second sampling period (B-1) was limited to approximately 23 days due to submarine operational constraints.

Sample Distribution

All air sampling results, both active and passive were tested for distribution normality. Industrial Hygiene Statistics Spreadsheet (Mulhausen and Damiano, 1998) software was used to determine whether the air sampling data was normally or log-normally distributed. All sample data for each analyte of interest (e.g., acrolein, formaldehyde, and ozone) was grouped by sampling method (active or passive) and statistically evaluated. The pertinent air sampling data from each individual sampling period was also statistically evaluated for normality distribution. As seen in Table 4, the results of these particular evaluations varied. Individual Industrial Hygiene Statistics Spreadsheet (Mulhausen and Damiano, 1998) test result printouts are provided in Appendix C.

As a single data group, all the active air sampling data for acrolein was log-normally but not normally distributed. Passive air sampling data for acrolein as a single data group was neither log-normally nor normally distributed. However, when the passive acrolein air sampling data from the first sampling period (A-1) was removed because all the reported values were identically below the limit of detection (LoD),

Table 4 - Summary of Sample Distribution Normality Testing

Analyte	Sampling Method	Sample Group	Normal Distribution	Log-normal Distribution
Acrolein	Active	All	No	Yes
		A-1	Yes	Yes
		B-1	N/A	N/A
		A-2	Yes	Yes
		C-1	Yes	Yes
	Passive	All	No	No
		All (Modified)	Yes	Yes
		A-1	N/A	N/A
		B-1	Yes	Yes
		A-2	Yes	Yes
		C-1	Yes	Yes
Formaldehyde	Active	All	Yes	No
		A-1	Yes	Yes
		B-1	N/A	N/A
		A-2	Yes	Yes
		C-1	Yes	Yes
	Passive	All	Yes	Yes
		A-1	No	No
		B-1	No	No
		A-2	Yes	Yes
		C-1	Yes	Yes
Ozone	Active	All	No	Yes
		A-1	Yes	Yes
		B-1	N/A	N/A
		A-2	Yes	Yes
		C-1	Yes	Yes
	Passive	All	No	No
		A-1	N/A	N/A
		B-1	No	No
		A-2	No	No
		C-1	No	No

passive air sampling data for acrolein was both log-normally and normally distributed. When acrolein active air sampling data was evaluated separately by sampling period, the sample distribution was both log-normally and normally distributed for the first, third and fourth sampling periods (A-1, A-2, and C-1). However, distribution normality could not be evaluated for the active air sampling data from the second sampling period (B-1) because all values were identically below the limit of detection (LoD). Similarly, when acrolein passive air sampling data was evaluated separately by sampling period, the sample distribution was both log-normally and normally distributed for the second, third and fourth sampling periods (B-1, A-2, and C-1). As previously discussed, acrolein passive air sampling results for the first sampling period (A-1) could not be evaluated.

Evaluation of all active air sampling data for formaldehyde as a single group revealed that the results were normally distributed but not log-normally distributed. Passive air sampling results for formaldehyde from the four sampling periods evaluated as a single group, were both log-normally and normally distributed. When formaldehyde active air sampling data distribution was statistically considered separately by sampling period, the sample distribution was both log-normally and normally distributed for the first, third, and fourth sampling period (A-1, A-2, C-1). Distribution normality for active formaldehyde air sampling data from the second sampling period (B-1) could not be evaluated because only one active air sample was taken during this abbreviated (22.7 days) sampling period. Statistical evaluation of passive formaldehyde air sampling data by individual sampling period indicated that the results from the first two sampling periods (A-1 and B-1) were neither log-normally nor normally distributed. However, the

passive formaldehyde air sampling results from the third and fourth sampling periods (A-2 and C-1) were both log-normally and normally distributed.

Evaluation of active air sampling results for ozone as a single group revealed that they were log-normally distributed but not normally distributed. Similar grouping of all passive ozone air sampling data indicated the distribution was neither log-normally nor normally distributed. Similar to formaldehyde, when active ozone air sampling results were evaluated by sampling period, the sample distribution was both log-normally and normally distributed for the first, third, and fourth sampling periods (A-1, A-2, and C-1). As before, active ozone air sampling results from the second sampling period (B-1) could not evaluated for distribution normality because only one active air sample was taken during this abbreviated (22.7 days) sampling period. Distribution testing of passive ozone sampling data by individual sampling periods indicated that the sample distribution was neither log-normally nor normally distributed for the second, third and fourth sampling periods (B-1, A-2, and C-1). Sample distribution for passive ozone air samples from the first sampling period (A-1) could not be determined because all the reported values were identically below the limit of detection (LoD).

Finally, using SPSS (SPSS Inc., Chicago, IL) software a separate non-parametric statistical evaluation of the formaldehyde passive data from all sampling periods was tested for goodness of fit using an exact 2-sided (one sample) Kolmogorov-Smirnov Test. The significance level for normal distribution was 0.526 and the significance level for uniform distribution was 0.340. These results indicate that a normal or uniform distribution cannot be rejected but fall well short of confirming the air sampling distribution as normally or uniformly distributed. At least in the case of passive

formaldehyde air sample distribution, these results are similar to the parametric test results described earlier using the Industrial Hygiene Statistics Spreadsheet (Mulhausen and Damiano, 1998) software. The exact 2-sided (one sample) Kolmogorov-Smirnov Test was not appropriate for testing the passive air sampling data for ozone and acrolein due to the repeated limit of detection values and the exponential disparity between active and passive values.

Acrolein Monitor Validation

Table 5 provides a complete summary of all the active and passive sampling data obtained for acrolein during the validation study effort.

Utilizing the Multiple Comparison Method described by Rose and Perkins (1982) and Dillion and Gao (1994) and outlined in detail earlier, the overall estimated accuracy for acrolein passive monitors during the described sampling periods was $\pm$ 147.2%. Table 6 provides the pertinent information and corresponding results of this validation application.

The results of the $\log_{(10)}$ transformed correlation, described by Kollman (1994), Liu et al., (1994), Dillion and Gao (1994), McGuire, Casserly, and Greff (1992) and Levin, Lindahl, and Andersson (1988) and outlined earlier, are provided in Table 7. Graphical representation of the acrolein active and passive $\log_{(10)}$ transformed data correlation is provided in Figure 1. Trend analysis of this graphical comparison resulted in a line with a slope of –0.3979 with a y-intercept of –4.207 ($y = -0.3979x - 4.407$) and a corresponding linear regression analysis correlation coefficient of 0.4962 ($r^2 = 0.4962$).

Finally, comparison of the acrolein active and passive air sampling data provided in Table 5 was evaluated by means of a $\log_e$ transformed 2-sided significance level t-test.

Table 5 - Acrolein Air Sampling Summary

Hull/	Active				Passive			
Trip #	Sample #	Sample Vol. (L)	Mass(ug)	Conc. (ppm)	Sample #	Sample Vol. (L)	Mass (ug)	Conc. (ppm)
A-1	2-1	3519	34.2	0.0042	A-2(9412)	626.4	0	0.00034
	3-1	3563	45.8	0.0056	A--2(9413)	626.4	0	0.00034
					A-3(9414)	626.4	0	0.00034
					A-3(9415)	626.4	0	0.00034
B-1	1	2836.3	<2.0	<0.00031	A-2(9687)	510.2 L	1.4	0.00118
	2	2839.6	<2.0	<0.00031	A-2(9688)	510.2 L	1.17	0.00099
					A-3(9691)	510.2 L	1.26	0.00106
					A-3(9692)	510.2 L	1.21	0.00102
A-2	2-1	3728	4	0.00047	A-2B(5429)	357	1.53	0.0018
	3-1	3623	<2.0	<0.0002	A-2B(5430)	357	1.33	0.0016
					A-3B(5437)	357	1.14	0.0014
					A-3B(5438)	357	1.23	0.0015
C-1	2-1	3784	14	0.0016	A-2B(5301)	367	1.71	0.002
	3-1	3713	12	0.0014	A-2B(5302)	367	1.44	0.0017
					A-3B(5311)	367	1.28	0.0015
					A-3B(5312)	367	1.34	0.0016

Table 6 - Multiple Comparison Method (Acrolein)

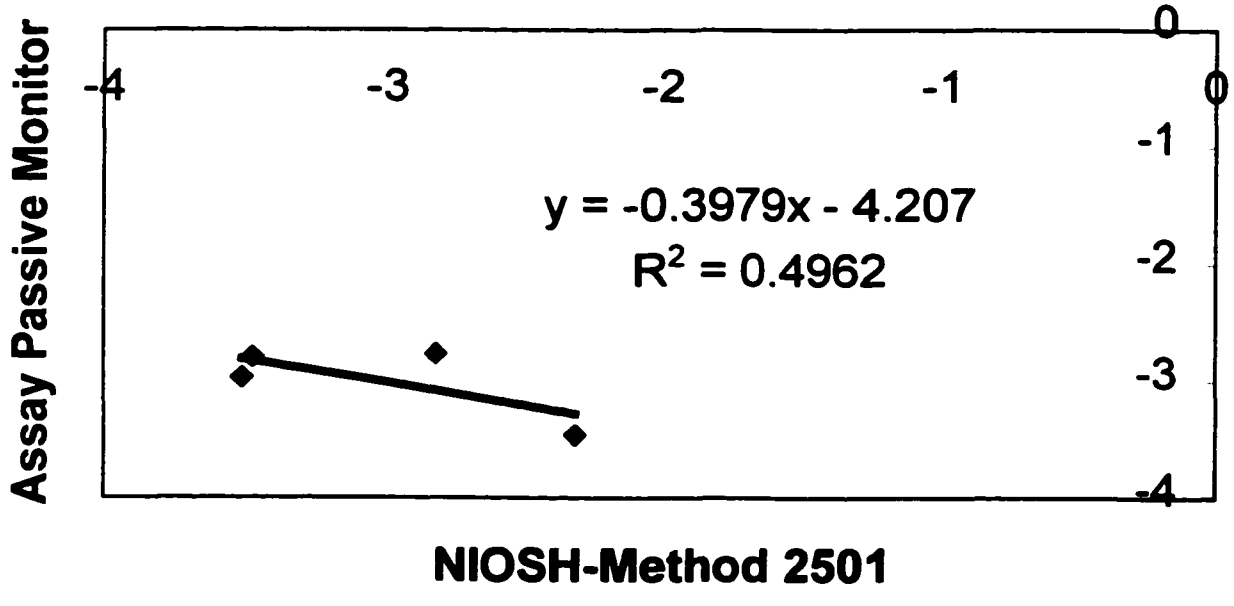
Hull/Trip#	Average Passive Reading, ppm (X_p)	Average Active Reading, ppm (X_a)	Bias, % ($b=X_p-X_a/X_a * 100$)	CV of Passive Readings, % ($CV=S/X * 100$)	Estimated Accuracy,% (|mean bias| + 2*CV)
A-1	0.00034	0.0049	-93.1	0	93.1
B-1	0.0010625	0.00031	242.7	7.9	258.5
A-2	0.001575	0.00034	363.2	10.8	384.8
C-1	0.0017	0.0015	13.3	12.7	38.7
		Average =	131.5	7.9	147.2

Table 7 - Log Transformed Data (Acrolein)

	Average Sampling Results, (ppm)		$Log_{(10)}$ Transformed Data		
Hull/Trip#	Passive	Active	Passive	Active	Difference
A-1	0.00034	0.0049	-3.47	-2.31	-1.16
B-1	0.00106	0.00031	-2.97	-3.51	0.54
A-2	0.00158	0.00034	-2.80	-3.47	0.67
C-1	0.00170	0.0015	-2.77	-2.82	0.05

Meaningful results from this statistical test were obtained only for the fourth sampling period (C-1). By means of this test, there was no evidence of significant variance between active and passive acrolein sampling methods based on p value of 0.281. The first sampling period (A-1) had identical limit of detection values for all the passive acrolein samples and therefore could not be evaluated. Conversely, the second sampling period (B-1) had identical limit of detection values for each active acrolein sample and could not be tested as described. The disparity between active acrolein samples on the third sampling period (A-2) did not allow statistical evaluation by this test for this sampling group.

Figure 1 - Log Transformed Data Correlation (Acrolein)



Formaldehyde Monitor Validation

Table 8 provides a complete summary of all the active and passive air sampling data obtained for formaldehyde during the validation study effort. It should be noted that active sample number 01 from the second sampling period (B-1) was disregarded because the initial 2,4-DNPH sorbent tube (active sample number 02) was used the entire abbreviated (22.7 days) sampling period. Utilizing only one 2,4-DNPH sorbent tube for formaldehyde collection was a deviation from the prescribed sampling procedure. This resulted in only one active sample result for formaldehyde from this sampling period (B-1).

Utilizing the Multiple Comparison Method described in detail previously, the overall estimated accuracy for formaldehyde passive monitors during the described sampling periods was $\pm$ 82.1%. Table 9 provides the applicable information and corresponding results of this validation application.

The results of the $\log_{(10)}$ transformed correlation described and utilized earlier, for formaldehyde air sampling data are provided in Table 10. Graphical representation of the formaldehyde active and passive $\log_{(10)}$ transformed data correlation is provided in Figure 2. Trend analysis of this graphical comparison resulted in a line with a slope of 0.0316 with a y-intercept of –2.8603 ($y = 0.0316x - 2.8603$) and a corresponding linear regression analysis correlation coefficient of 0.0043 ($r^2 = 0.0043$).

Lastly, comparison of the formaldehyde active and passive air sampling data provided in Table 8 was also evaluated by means of a $\log_e$ transformed 2-sided significance level t-test. Although meaningful results were obtained from each sampling period, the outcomes were mixed. For the first two sampling periods (A-1 and B-1),

Table 8 - Formaldehyde Air Sampling Summary

Hull/	Active				Passive			
Trip#	Sample #	Sample Vol. (L)	Mass(ug)	Conc. (ppm)	Sample #	Sample Vol.	Mass (ug)	Conc. (ppm)
A-1	4-1	176 L	0.614	0.0028	A-2(6775)	525 L	0.651	0.001
	4-2	183L	0.241	0.0011	A-2(6776)	525 L	0.763	0.0012
					A-3(6783)	525 L	0.807	0.0012
					A-3(6784)	525 L	0.79	0.0012
B-1	01	360.9 L	<0.04	0.0000895	A-2(8105)	428 L	0.656	0.0012
	02	360.9 L	1.96	0.0044	A-2(8106)	428 L	0.577	0.0011
					A-3(8139)	428 L	0.595	0.0011
					A-3(8140)	428 L	0.619	0.0012
A-2	4-1	196 L	0.988	0.0041	A-2(5427)	544 L	0.929	0.0014
	4-2	208 L	1.27	0.005	A-2(5428)	544 L	0.849	0.0013
					A-3(5435)	544 L	1.04	0.0015
					A-3(5436)	544 L	1.13	0.0017
C-1	4-1	203 L	1.19	0.0048	A-2(5299)	560 L	0.619	0.00089
	4-2	228 L	1.16	0.0041	A-2(5300)	560 L	0.579	0.00083
					A-3(5309)	560 L	0.639	0.00092
					A-3(5310)	560 L	0.699	0.001

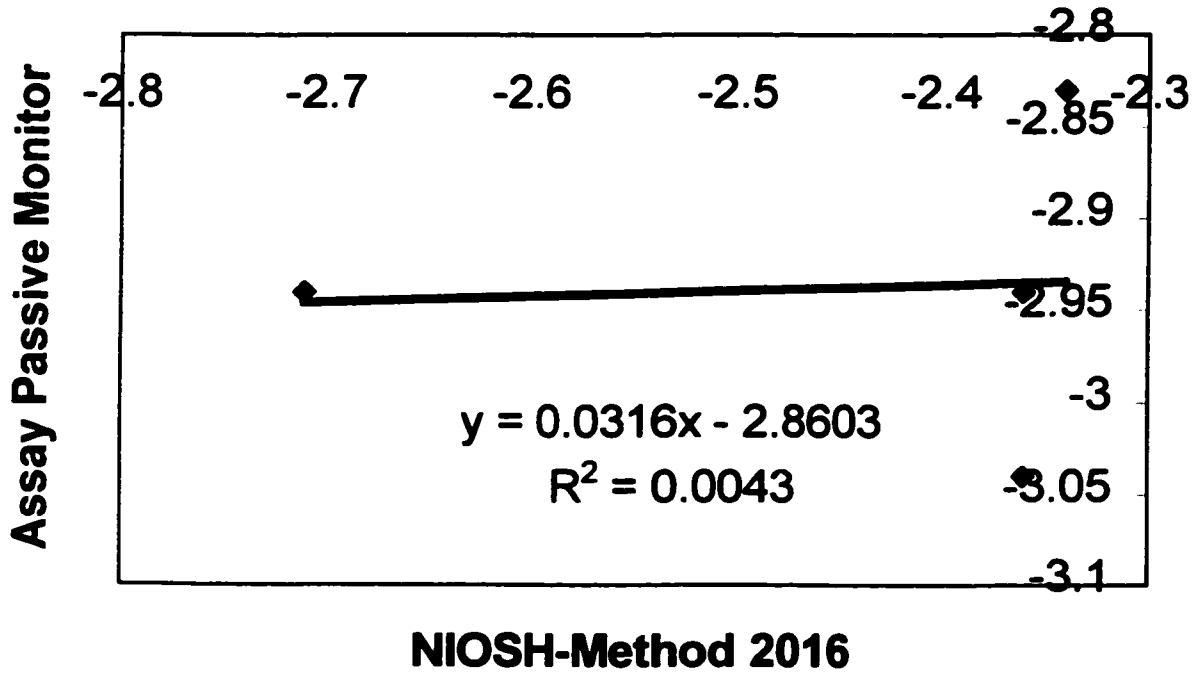
Table 9 - Multiple Comparison Method (Formaldehyde)

Hull/Trip#	Average Passive Reading, ppm(Xp)	Average Active Reading, ppm(Xa)	Bias, % (b=Xp-Xa/Xa * 100)	CV of Passive Readings, % (CV=S/X * 100)	Estimated Accuracy,% (|mean bias| + 2*CV)
A-1	0.00115	0.00195	-41.0	8.7	58.4
B-1	0.00115	0.0044	-73.9	5.0	83.9
A-2	0.001475	0.0046	-67.9	11.6	91.1
C-1	0.00091	0.0044	-79.3	7.8	94.9
		Average =	-65.5	8.3	82.1

Table 10 - Log Transformed Data (Formaldehyde)

	Average Sampling Results, (ppm)		$Log_{(10)}$ Transformed Data		
Hull/Trip#	Passive	Active	Passive	Active	Difference
A-1	0.00115	0.00195	-2.94	-2.71	-0.23
B-1	0.00115	0.0044	-2.94	-2.36	-0.58
A-2	0.00148	0.0046	-2.83	-2.34	-0.49
C-1	0.00091	0.0044	-3.04	-2.36	-0.68

Figure 2 - Log Transformed Data Correlation (Formaldehyde)



there was no evidence of significant variation between the reported active and passive formaldehyde concentrations based on p values 0.561 and 0.81 respectively. However, for the third and fourth sampling periods (A-2 and C-1) there was strong evidence of significant variation between the reported concentrations of formaldehyde from active and passive sampling methods based on p values of 0.001 and 0.000 respectively.

Ozone Monitor Validation

Table 11 provides a complete summary of all the active and passive sampling data obtained for ozone during the validation study effort. It should be noted, that as was the case with formaldehyde, that active sample 001 from the second sampling period (B-1)

Table 11 - Ozone Air Sampling Summary

Hull/	Active				Passive			
Trip #	Sample #	Sample Vol. (L)	Mass(ug)	Conc. (ppm)	Sample #	Sample Vol. (L)	Mass (ug)	Conc. (ppm)
A-1	1-1	4980	2.51	0.00026	A-2(9398)	503.2 L	0.05	0.00005
	1-3	4920	2.37	0.00025	A-2(9526)	503.2 L	0.05	0.00005
					A-2(9527)	503.2 L	0.05	0.00005
					A-3(9399)	503.2 L	0.05	0.00005
					A-3(9528)	503.2 L	0.05	0.00005
					A-3(9529)	503.2 L	0.05	0.00005
B-1	001	8125.4	<0.387	0.000024	A-2(9686)	409.9 L	6.3	0.0078
	002	8124.4	0.634	0.00004	A-2(0753)	409.9 L	0.05	0.00006
					A-2(0754)	409.9 L	0.05	0.00006
					A-3(9690)	409.9 L	0.05	0.00006
					A-3(0755)	409.9 L	0.05	0.00006
					A-3(0756)	409.9 L	0.05	0.00006
A-2	1-2	5410	<0.387	<0.000036	A-2(2453)	521.2 L	0.1	0.000098
	1-3	5090	1.22	0.00012	A-2(2576)	521.2 L	0.05	0.000049
					A-2(2577)	521.2 L	0.05	0.000049
					A-3(2454)	521.2 L	0.05	0.000049
					A-3(2578)	521.2 L	0.05	0.000049
					A-3(2579)	521.2 L	0.05	0.000049
C-1	1-1	4740	16.7	0.0018	A-2(2416)	536.4 L	1.31	0.0012
	1-2	5310	0.59	0.000057	A-2(2561)	536.4 L	0.05	0.000047
					A-2(2562)	536.4 L	0.05	0.000047
					A-3(2417)	536.4 L	2.56	0.0024
					A-3(2563)	536.4 L	0.05	0.000047
					A-3(2564)	536.4 L	0.05	0.000047

was disregarded because the initial nitrite impregnated fiber filter cassette (sample number 002) was used the entire abbreviated (22.7 days) sampling period instead of being replaced after 14 days as prescribed in the sampling procedure. Again, utilizing only one nitrite impregnated fiber filter cassette was a deviation from the prescribed sampling procedure. This resulted in only one active sample result for ozone from this sampling period (B-1).

The estimated overall accuracy of ozone passive monitors relative to the active sampling method was $\pm$ 237.4%. This was determined by once again using the Multiple Comparison Method validation test described earlier. Table 12 provides the pertinent information and corresponding results of this validation evaluation.

The results of the log $_{(10)}$ transformed correlation described and utilized previously, are provided in Table 13. Graphical representation of the ozone active and passive log $_{(10)}$ transformed data correlation is provided in Figure 3. Trend analysis of

Figure 3 - Log Transformed Data Correlation (Ozone)

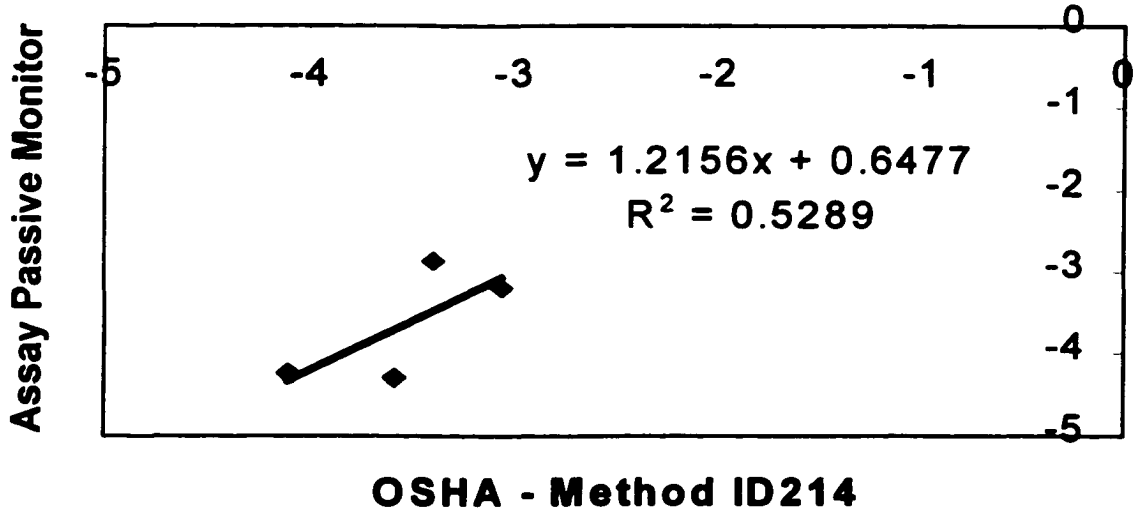


Table 12 - Multiple Comparison Method (Ozone)

Hull/Trip#	Average Passive Reading, ppm(X_p)	Average Active Reading, ppm(X_a)	Bias, % ($b=X_p-X_a/X_a * 100$)	CV of Passive Readings, % (CV=S/X * 100)	Estimated Accuracy,% (|mean bias| + 2*CV)
A-1	0.00005	0.00026	-80.7	0	80.7
B-1	0.00135	0.00040	237.5	234.1	705.7
A-2	0.000057	0.00008	-28.8	35.1	99.0
C-1	0.00063	0.00088	-28.4	155.8	340.0
		Average =	24.9	106.3	237.4

Table 13 - Log Transformed Data (Ozone)

	Average Sampling Results, (ppm)		$Log_{(10)}$ Transformed Data		
Hull/Trip#	Passive	Active	Passive	Active	Difference
A-1	0.00005	0.00026	-4.30	-3.59	-0.41
B-1	0.00135	0.00040	-2.87	-3.40	0.55
A-2	0.000057	0.00008	-4.24	-4.10	0.09
C-1	0.00063	0.00088	-3.20	-3.06	-0.12

this graphical comparison resulted in a line with a slope of 1.2156 with a y-intercept of 0.6477 ($y = 1.2156x + 0.6477$) and a corresponding linear regression analysis correlation coefficient of 0.5289 ($r^2 = 0.5289$).

Evaluation of the active and passive ozone air sampling data provided in Table 11 by means of a $\log_e$ transformed 2-sided significance level t-test was not performed for any of the four sampling periods. The use of this test was inappropriate because twenty of twenty-four passive air sample results were at or below the limit of detection.

DISCUSSION

Based on the air sampling data and the subsequent results of validation tests described herein, the passive air monitors evaluated during this research effort are not validated for use onboard U.S. Navy submarines to monitor the enclosed submarine atmosphere for acrolein, formaldehyde, and ozone. The alternative hypothesis that there is no statistically significant difference between the airborne concentration measured with passive air sampling monitors aboard operating submarines compared to active air samples collected in accordance with an accepted reference method when sampling for formaldehyde, acrolein and ozone is rejected. The null hypothesis that a statistically significant difference exists between the airborne concentration measured with passive air sampling monitors compared to active air samples collected in accordance with an accepted sampling and analytical method onboard operating submarines when sampling for acrolein, formaldehyde, and ozone is accepted.

Passive monitor accuracy for acrolein ranged from $\pm$ 38.7% to $\pm$ 384.8% with an average estimated accuracy of $\pm$ 147.3%. Examination of the acrolein air sampling data resulted in an average passive air sampling coefficient of variation (CV), an indication of passive measurement precision, of 7.9% and a bias of 131.5% when compared to the corresponding active air sample time-weighted average (TWA). A $\log_{(10)}$ transformed correlation between the average reported passive and active air sampling concentrations for acrolein resulted in a correlation coefficient of 0.4962 ($r^2 = 0.4962$) and a linear regression that did not approach unity ($y = -0.3979x - 4.207$). An evaluation of the significant differences between the passive and active acrolein air sampling data using a 2-sided significance level t-test was indeterminate. Only one set of air sampling results

(sample period C-1) could be evaluated. Therefore, no clear conclusion could be drawn from this test. These validation results fall well short of the validation acceptance criteria of $\pm$ 25% passive monitor accuracy and a correlation coefficient that approaches unity, as outlined by Cassinelli et al., (1987).

Passive monitor accuracy for formaldehyde ranged from $\pm$ 58.4% to $\pm$ 94.9% with an average estimated accuracy of $\pm$ 82.1%. Examination of the formaldehyde air sampling data resulted in an average passive air sampling coefficient of variation (CV), an indication of passive measurement precision, of 8.3% and a bias of –65.5% when compared to the corresponding active air sample time-weighted average (TWA). A $\log_{(10)}$ transformed correlation between the average reported passive and active air sampling concentrations for formaldehyde resulted in a correlation coefficient of 0.0043 ($r^2 = 0.0043$) and a linear regression that did not approach unity ($y = 0.0316x - 2.8603$). An evaluation of the significant differences between the passive and active formaldehyde air sampling data using a 2-sided significance level t-test produced mixed results. Two of the sampling periods (A-1 and B-1) indicated no significant differences between the reported active and passive formaldehyde airborne concentrations. However, the other two sampling periods (A-2 and C-1) indicated significant differences between the air sampling results of the two methods. In this circumstance as well, these validation results fall well short of the validation acceptance criteria provided by Cassinelli et al., (1987).

Passive monitor accuracy for ozone ranged from $\pm$ 80.7% to $\pm$ 705.7% with an average estimated accuracy of $\pm$ 237.4%. Examination of the ozone air sampling data resulted in an average passive air sampling coefficient of variation (CV), an indication of passive measurement precision, of 106.3% and a bias of 24.9% when compared to the

corresponding active air sample time-weighted average (TWA). A $\log_{(10)}$ transformed correlation between the average reported passive and active air sampling concentrations for ozone resulted in a correlation coefficient of 0.5289 ($r^2 = 0.5289$) and a linear regression that did not approach unity ($y = 1.21566x + 0.6477$). Virtually all of the air sampling data collected for ozone was at or below the analytical limit of detection. Accordingly, the use of a 2-sided significance level t-test to determine whether significant differences existed between reported active and passive airborne concentrations for ozone was inappropriate and no conclusions could be drawn from this test. As before, these validation results fall well short of the validation acceptance criteria provided by Cassinelli et al., (1987).

This overall study outcome contradicts many of the reported validation studies from the published literature previously reviewed and discussed. Several possible reasons exist for this apparent disparity. The most obvious issue to consider is the quality of the air sampling data collected during the study. Due to the limited number of sampling periods (four) and the wide range of results, no clear determinations could be made regarding sample distribution normality. Secondly, statistical comparison was difficult and differences amplified by the limited amount of air sampling data. Consequently large variations were noted, especially in passive air sampling results. However, sampling periods were limited due to availability of submarines to conduct the prescribed air sampling. Each sampling period took approximately thirteen weeks to conduct from start to finish. This included time to liaison with and brief the crew of the submarine, the actual sampling period, and the time for the selected analytical laboratories to conduct the appropriate analysis and report the air sampling results. As a

result, the scope of time allowed for the study and operational schedule of submarines did not allow further air sampling and collection of additional data.

The protocol developed for this study specified an extended sampling time for passive monitors in order to sample a great enough volume to collect quantifiable amounts of subject analytes at the expected low airborne concentrations. However, Cao and Hewiit (1994) report that using passive sampling monitors for long sampling periods may result in blank build up and/or degradation of adsorbed organic compounds by reaction with ozone or other reactive compounds. The extended sampling periods prescribed by this study and any resulting blank build up and/or contaminant degradation may have impacted passive monitor performance compared to active sampling measurements.

Another factor that may have affected passive monitor performance is the process of reversion diffusion discussed by Posner and Moore (1985). As reported by Rose and Perkins (1982) and Dietrich (1997), the passive sampling model defined by Fick's First Law of Diffusion assumes an irreversible reaction between the contaminant in question and the adsorbing media. Hence, the concentration of the contaminant above the surface of the passive monitor sorbent bed (C_0) is assumed to be zero, as discussed previously. Posner and Moore (1985) state however, that C_0 is almost never zero in real world applications since the adsorptive process may be reversible in many cases depending on the physical characteristics of the contaminant in question and the adsorbing media and material. Consistent under reporting of passive airborne concentrations compared to other sampling methods may be accounted for by this reverse diffusion process.

In the case of acrolein measurement a likely and perhaps most important confounding factor in the failure to validate the acrolein passive monitor was the change of the passive monitor sorbent media. As previously discussed under Methods, the sampling sorbent in the acrolein passive monitor was changed from 2-HMP impregnated glass fibers to 2-HMP impregnated silica gel after the third sampling period. This decision was made by NSMRL and Assay Technology personnel based on concerns about the air sampling effectiveness of the 2-HMP impregnated glass fiber filters. Reviewing the acrolein air sampling results by sampling period tend to support such a decision. Considering the first three sampling periods (A-1, B-1, and A-2) the estimated accuracy of the acrolein passive monitor averaged $\pm$ 245%. However for the fourth sampling period (C-1) alone, the estimated passive monitor accuracy was $\pm$ 38.7, which readily approaches the validation acceptance criteria provided by Cassinelli et al. (1987). Unfortunately, additional acrolein air sampling data using passive monitors with the new adsorbing media was not available beyond the fourth sampling period. Further validation tests utilizing the new acrolein passive monitor with 2-HMP impregnated silica gel is warranted and should be pursued using the guidelines of this study.

In the specific case of formaldehyde a likely and perhaps important confounding factor in the failure to validate the formaldehyde passive monitor was the use of an ozone sampling pre-filter on the formaldehyde passive monitors. As discussed in the Methods section, an ozone pre-filter was placed in the diffusion pathway of the formaldehyde passive monitor to remove ozone from the sampled air. Grosjean and Williams (1992) state that ozone has been reported to introduce a negative bias when measuring formaldehyde using 2,4-DNPH impregnated silica gel. Based on these observations, an

ozone pre-filter of nitrite impregnated glass fibers was placed before the 2,4-DNPH impregnated silica gel in the formaldehyde passive monitor sorbent bed. However, preliminary results from recent laboratory studies using a permeation tube to introduce known concentrations of formaldehyde to the sampling atmosphere by Callahan (2000) indicate that for long-term sampling, formaldehyde passive monitors without the described ozone pre-filter demonstrate a greater accuracy (at or near $\pm$ 25%) than those passive monitors that have the ozone pre-filters installed. Based on these observations, rather than improving formaldehyde passive monitor accuracy the ozone pre-filter may in fact hinder the accuracy of the formaldehyde passive monitor and may be the cause for the disparate accuracy noted during this study. Validation of a formaldehyde passive monitor containing 2,4-DNPH impregnated silica gel in the sorbent bed without an ozone pre-filter is warranted and should be pursued using the guidelines of this study.

In the specific case of ozone, although the slope of the linear regression line of a $\log_{(10)}$ transformed correlation was 1.21, any positive correlation conclusion should be viewed suspiciously. Koutrakis et al., (1993) and Geyh et al., (1997) report passive monitor measurement of ozone is difficult due to its high reactivity and conditioning characteristics. As a result, ozone passive monitors suffer from a positive interference by nitrogen dioxide (NO_2) and yield very high limits of detection. The results in this study seem to bear this out. Twenty of twenty-four passive samples for ozone were at or below the limit of detection (LOD). Consequently, the available data for confident validation testing was suspect. Development of an ozone passive monitor capable of stable monitoring of very low airborne concentrations of ozone and/or improved laboratory

analytical sensitivity is necessary before substantive monitoring for ozone in the enclosed submarine atmosphere is feasible.

Nobel et al., (1993) emphasize a final important point. The performance of passive sampling monitors are optimized around current regulatory levels (e.g., published permissible exposure limits) and validation acceptance protocols (Cassinelli et al., 1987) are also derived at regulatory exposure limits. The performance of passive monitors deteriorates as airborne concentrations of contaminants decrease (Noble et al., 1993). Validation acceptance guidelines and protocols for passive monitors sampling airborne concentrations of contaminants well below current regulatory limits (such as found in the enclosed submarine atmosphere) should be pursued, especially in light of increasing interest in using passive sampling technology to monitor long term indoor air quality in various environmental settings where expected airborne contaminant concentration levels would be far below the established regulatory limits.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The completion of this study provides findings and new information important to the evaluation of the enclosed submarine atmosphere and ultimately any potential health implications to submarine sailors.

The designed validation study protocol is suitable for use onboard U.S. Navy nuclear submarines. Neither the operation nor the placement of the air sampling equipment (both active and passive) interfered with normal submarine operating conditions and minimal, if any, crew impact. Extended air sampling periods, necessary due to the low airborne concentration of the airborne contaminants of interest, were convenient to the submarine's Hospital Corpsman (HM) who monitored the sampling effort while underway. Using the Multiple Comparison Method to determine the estimated accuracy of passive monitors relative to the concurrent active air sampling method and using $\log_{(10)}$ transformed correlation coefficients to compare differences between active and passive air sampling results were effective validation tests. These statistical methods were relatively simple, yet they provided a direct evaluation of passive air sampling monitor effectiveness compared to traditional active air sampling methods.

Despite the fact that the average estimated accuracy of the passive monitors tested ranged from $\pm$ 82.1% to $\pm$ 237.4% and $\log_{(10)}$ transformed correlation coefficients ranged from 0.0043 to 0.5289 (r^2 = 0.0043 – 0.5289), depending on the airborne contaminant, passive air sampling monitors should not be prematurely dismissed as an appropriate tool to evaluate the enclosed submarine atmosphere. The acrolein passive monitors that contained 2-HMP impregnated silica gel performed significantly better than those that contained 2-HMP impregnated glass fibers. Although further evaluation of the revised

acrolein passive monitor is necessary, consistent performance as demonstrated during the one sampling period (C-1) that the revised acrolein passive monitors were used will likely result in their validation as an effective air evaluation technique in the enclosed submarine atmosphere. Likewise, removal of the ozone pre-filter on the formaldehyde passive monitor should also have a dramatic improvement on its performance. The encouraging results of recent laboratory validation testing of the formaldehyde passive monitors that contain 2,4-DNPH impregnated silica gel without the ozone pre-filter warrant continued validation testing with the expectation that they will also be validated for use in the enclosed submarine atmosphere. Finally, recent laboratory improvements in the analytical sensitivity for ozone lend hope that the ozone passive monitors will also eventually be validated for use onboard submarines provided additional validation testing is completed.

Therefore, further evaluation and validation testing of the appropriate passive air sampling monitor is recommended for each of the airborne contaminants evaluated during this study (e.g., acrolein, formaldehyde and ozone). In the case of acrolein and formaldehyde the revised passive monitors should be evaluated using the guidelines and protocol established by this study. Validation testing of ozone should also continue as described herein now that greater laboratory analytical sensitivity is available and greater ozone passive monitor accuracy is likely. Consideration should be given to expanding the scope of airborne contaminants evaluated to include organic amines, especially monoethanolamine (MEA), and oxides of nitrogen to ascertain their potential health impacts on submarine sailors as well.

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APPENDIX A

NSMRL PASSIVE SAMPLING PROTOCOL

PROCEDURE NOTES

- Maintain Monitors in a refrigerated environment ($\leq 4^{o}C$) upon receipt and after sampling. Annotate storage method.
- Set up and start sampling the day following receipt of materials.
- Do not hang Monitors on or near a ventilation source, near a heat source or flat against a bulkhead.
- Twelve (12) locations are sampled on board the submarine. Six (6) locations AFT and six (6) locations FWD.
- Five (5) different types of Monitors are sampled at each location.
- Monitors are sampled for 30 days.
- Current Monitor types provided are:

Type	Lot #	Exp. Date

- Record sampling information on the Passive Sample Data sheet.
- Record ventilation events during the deployment and sampling period on the Ventilation Record sheet.
- Include copies of the daily CAMS logs with return shipment to NSMRL.
- Use FED EX form provided to ship sampling materials back to NSMRL.
- Problems or questions contact: Com (860) 694-2544 or DSN (8) 694-2544.

SAMPLING LOCATIONS

FWD COMPARTMENT

Designator	Description	
F-1	Torpedo Rm	(Near Fire Control Station)
F-2	Aux Machinery Rm	(Near Workbench Area)
F-3	Crews Mess	

SSN_____ Trip # _____

F-4	Crews Berthing	
F-5	Fan Rm	(Aft Bulkhead Area)
F-6	Control	(Overhead Near Conn)

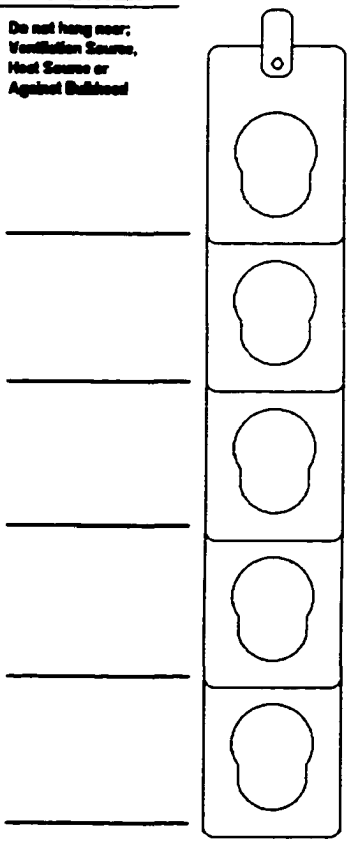
*Annotate actual locations sampled if different from above.

AFT COMPARTMENT

Designator	Description	
A-1	Eng Rm LL Aft	(ASW Bay)
A-2	Eng Rm ML Fwd	(High Pressure Air Compressor Flat)
A-3	Eng Rm	(High Pressure Air Compressor Flat)
A-4	Eng Rm UL Fwd	(Near Escape Trunk)
A-5	Eng Rm Maneuvering	
A-6	Eng Rm UL Fwd	(Near SSTG's)

*Annotate actual locations sampled if different from above.

MONITOR HOLDER ARRANGEMENT



IDENTIFY COMPONENTS AND

Naval Submarine Medical Research Laboratory

SSN_____ Trip # _____

ASSIGN MONITORS

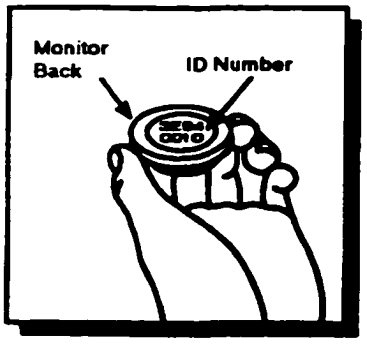
1. Obtain Monitor(s) (in foil pouch), Holder, and *Sample Data Sheet* for each location to be monitored.

2. Enter Sample Location to be monitored on *Sample Data Sheet*.

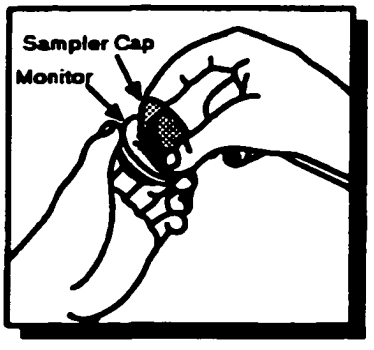
3. Tear open Foil Pouch and remove Monitor. Discard pouch and any product conditioners found within.

4. Locate the Monitor ID Number printed directly on back of Monitor (Fig. 1); record on *Sample Data Sheet.*

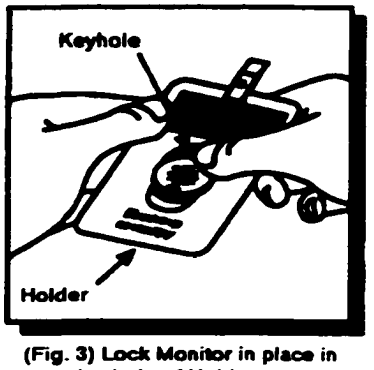
5. If sampling does not begin immediately, Monitor may be stored in tightly closed Return Container for up to one hour.



(Fig. 1) Locate Monitor ID No. on back of Monitor



(Fig. 2) Remove Sampler Cap from Monitor



(Fig. 3) Lock Monitor in place in keyhole of Holder

ASSEMBLE MONITOR FOR SAMPLING

1. Holding only edges of Monitor, remove Sampler Cap from Monitor face (Fig. 2). **DO NOT REMOVE Monitor back bearing Monitor ID Number**. Save Sampler Cap for later use; do not discard.

2. Hold Monitor; face up, behind Holder. Put Monitor into top (larger end) of keyhole from back of Holder.

3. Slide Monitor down until it locks in place at bottom (smaller end) of keyhole (Fig. 3). Holder should slide into slot in white plastic grid, **not between white grid and clear back.**

BEGIN SAMPLING

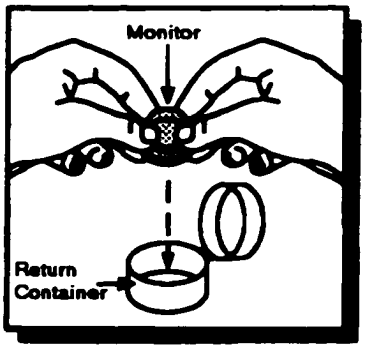
1. Record Start Time and Date on *Sample Data Sheet.*

Naval Submarine Medical Research Laboratory

SSN_____ Trip # _____

2. Attach Monitor by clipping Holder to a secure structure in designated location.

3. Sample Monitors for "30 Days".



(Fig. 4) Replace Sampler Cap and place Monitor in Return Container

END SAMPLING

1. At end of sampling period (30 Days) remove Monitor from Holder.

2. Immediately snap Sampler Cap back onto Monitor to stop sampling and place Monitor into Return Container (Fig. 4).

3. Record Stop Time and Date on *Sample Data Sheet.*

4. Place all Monitors (from same location) into the Foil Pouch marked for that sampling location and write the Start/Stop Dates on the label in the space provided.

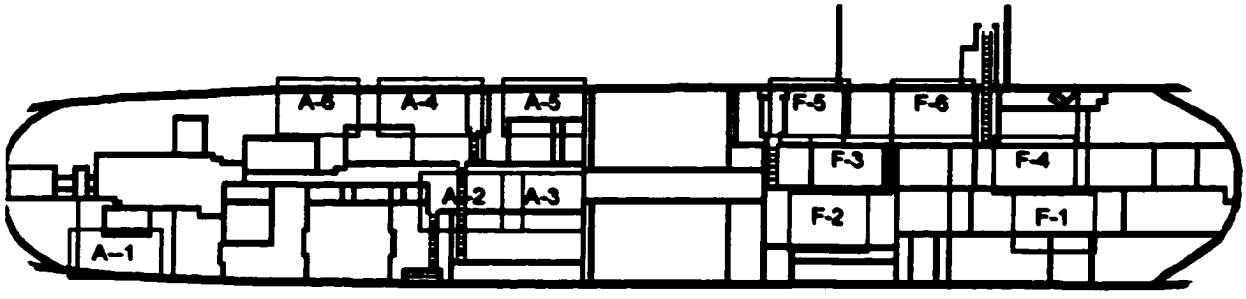
5. Store sampled Monitors in refrigerated environment ($\leq 4^{o}C$) until shipment to NSMRL.

SSN_____ Trip # _____

APPENDIX B

SUBMARINE PASSIVE SAMPLING LOCATIONS

The following diagram outlines the designated passive air sampling locations aboard a typical fast-attack submarine. All passive sampling monitors and the active sampling media used in this validation study effort were placed in sample locations A-2 and A-3 (Engine Room, Middle Level, Forward – High Pressure Air Compressor Flat).



Aft Locations

A-1 ER LL Aft (ASW Bay)
A-2 ER ML Fwd (HP Air Flat)
A-3 ER ML Fwd (HP Air Flat)
A-4 ER UL Fwd (Escape Trunk)
A-5 Maneuvering
A-6 ER UL Fwd (Near SSTG's)

Fwd Locations

F-1 Torpedo Room(Near Fire Control Station)
F-2 Aux Mach Rm 1 (Near Workbench)
F-3 Crew's Mess
F-4 Crew's Berthing
F-5 Fan Rm (Aft Bulkhead)
F-6 Control Room

APPENDIX C

AIR SAMPLING DISTRIBUTION TEST PRINTOUTS

Industrial Hygiene Statistics

Data Description:

0.01

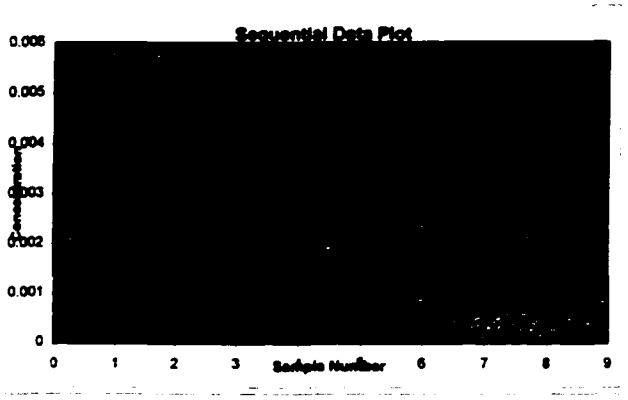
0.0042
0.0056
0.00031
0.00031
0.00047
0.0002
0.0016
0.0014

Number of samples (n)	8
Maximum (max)	0.0056
Minimum (min)	0.0002
Range	0.0054
Percent above OEL (%>OEL)	0.000
Mean	0.002
Median	0.001
Standard deviation (s)	0.002
Mean of logtransformed data (LN)	-7.001
Std. deviation of logtransformed data (LN)	1.265
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	3.542

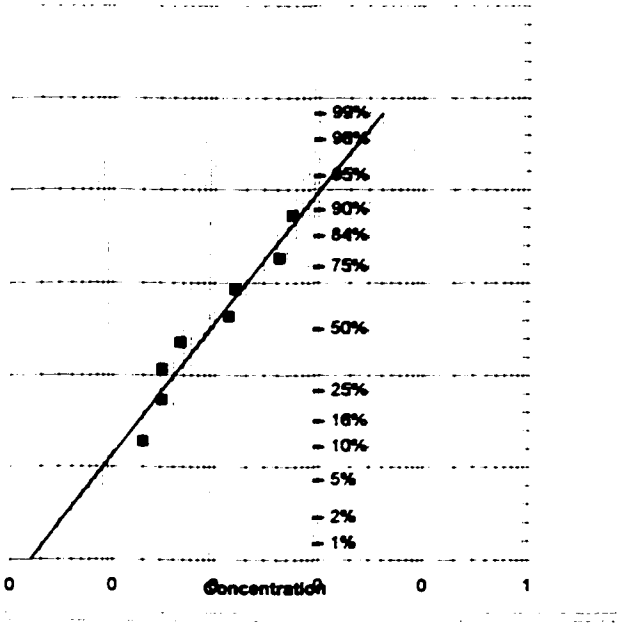
W-test of logtransformed data (LN)	0.908
Lognormal (a = 0.05)?	Yes
W-test of data	0.782
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.002
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.014
95th Percentile	0.007
$UTL_{95\%,95\%}$	0.051
Percent above OEL (%>OEL)	2.911
$LCL_{1,95\%}$ %>OEL	0.192
$UCL_{1,95\%}$ %>OEL	19.671

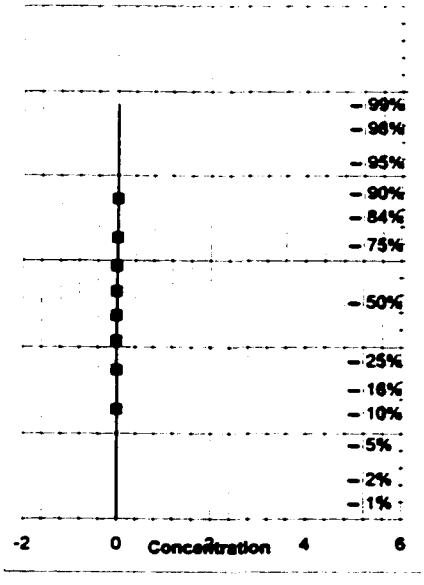
Mean	0.002
$LCL_{1,95\%}$ - t statistics	0.000
$UCL_{1,95\%}$ - t statistics	0.003
95th Percentile - Z	0.005
$UTL_{95\%,95\%}$	0.01
Percent above OEL (%>OEL)	0.003



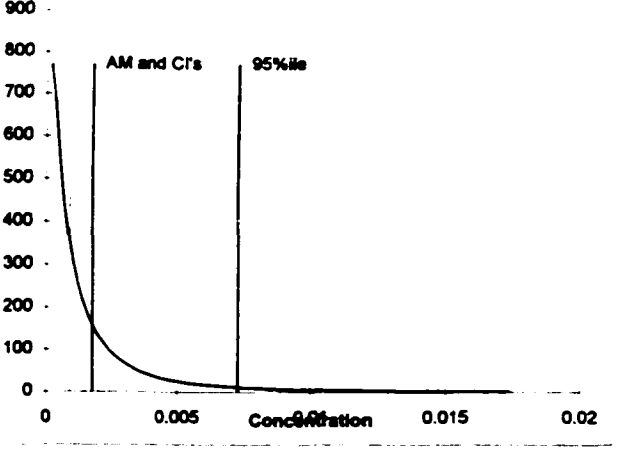
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

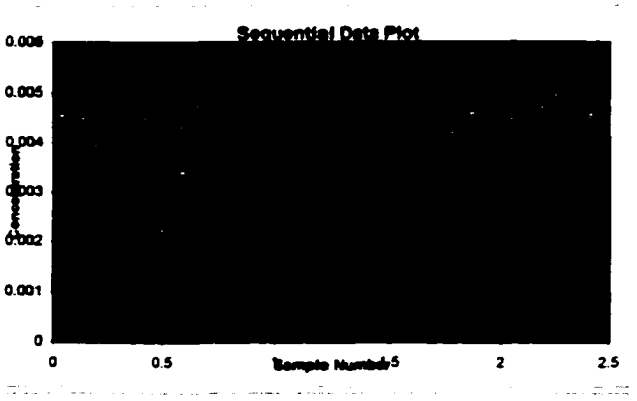
0.01	
0.0042	
0.0056	

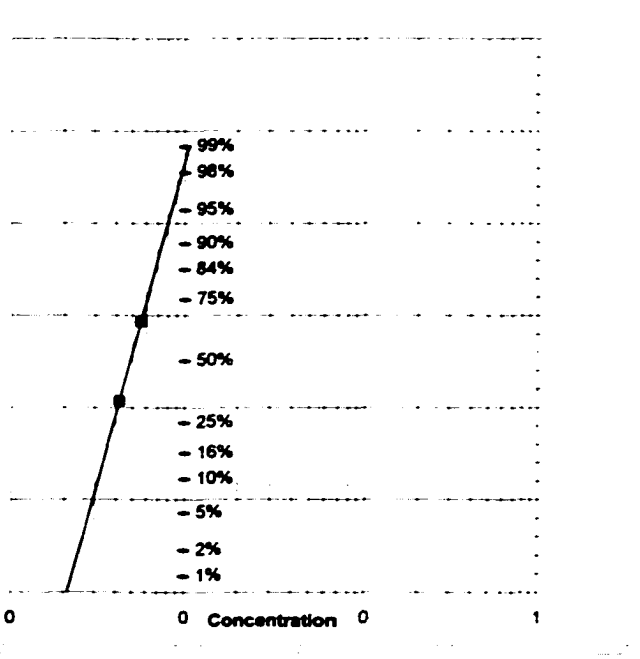
Number of samples (n)	2
Maximum (max)	0.0056
Minimum (min)	0.0042
Range	0.0014
Percent above OEL (%>OEL)	0.000
Mean	0.005
Median	0.005
Standard deviation (s)	0.001
Mean of logtransformed data (LN)	-5.329
Std. deviation of logtransformed data (LN)	0.203
Geometric mean (GM)	0.005
Geometric standard deviation (GSD)	1.226

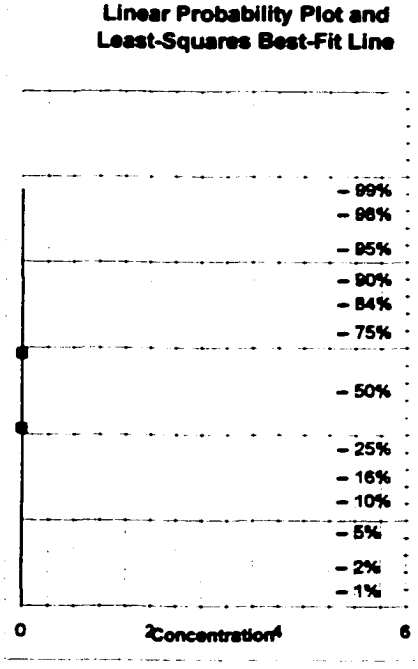
W-test of logtransformed data (LN)	1.000
Lognormal (α = 0.05)?	Yes
W-test of data	1.000
Normal (α = 0.05)?	Yes

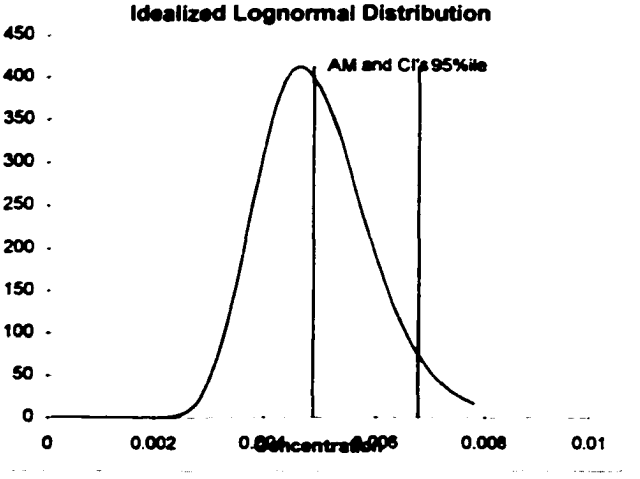
Estimated Arithmetic Mean - MVUE	0.005
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.007
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.019
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	54.832

Mean	0.005
$LCL_{1,95\%}$ - t statistics	0.000
$UCL_{1,95\%}$ - t statistics	0.009
95th Percentile - Z	0.007
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000







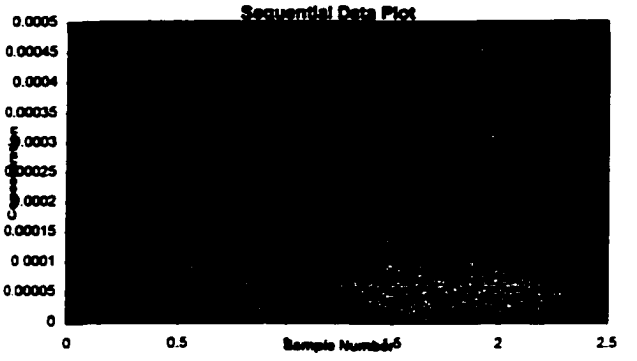


Industrial Hygiene Statistics

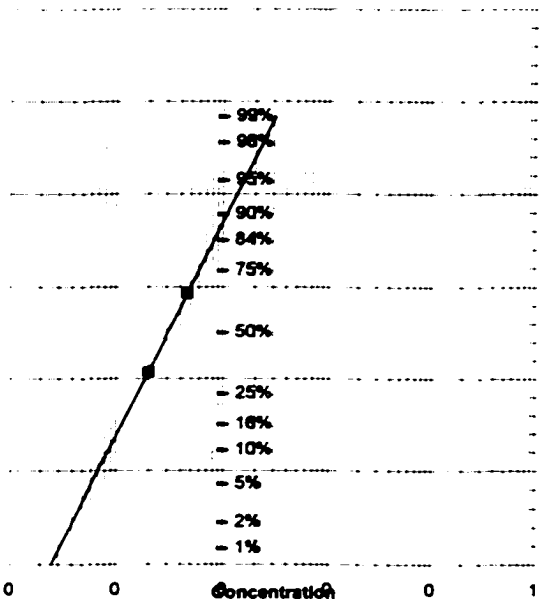
Data Description:

	0.01
	0.00047
	0.0002

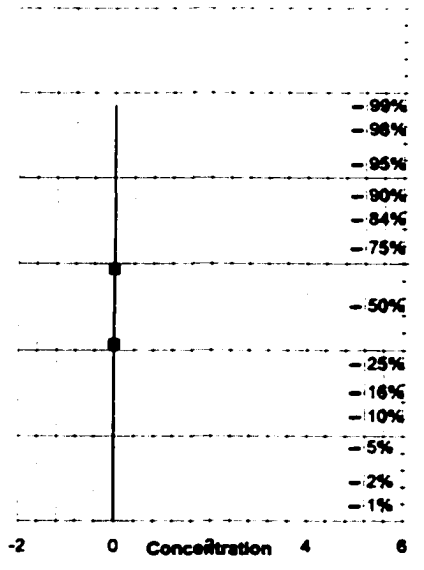
Number of samples (n)	2
Maximum (max)	0.00047
Minimum (min)	0.0002
Range	0.00027
Percent above OEL (%>OEL)	0.000
Mean	0.000
Median	0.000
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-8.090
Std. deviation of logtransformed data (LN)	0.604
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	1.830
W-test of logtransformed data (LN)	1.000
Lognormal (a = 0.05)?	Yes
W-test of data	1.000
Normal (a = 0.05)?	Yes
Estimated Arithmetic Mean - MVUE	0.000
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.001
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	44.032
Mean	0.000
$LCL_{1,95\%}$ - t statistics	-0.001
$UCL_{1,95\%}$ - t statistics	0.001
95th Percentile - Z	0.001
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000



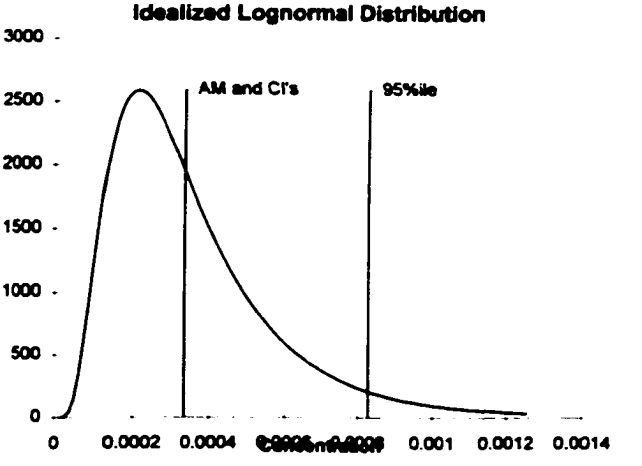
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

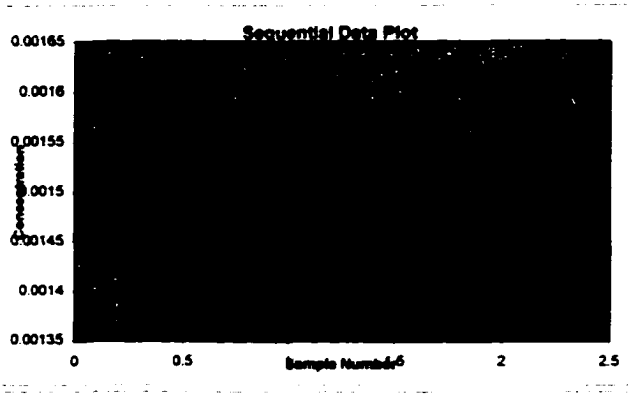
	0.01
	0.0016
	0.0014

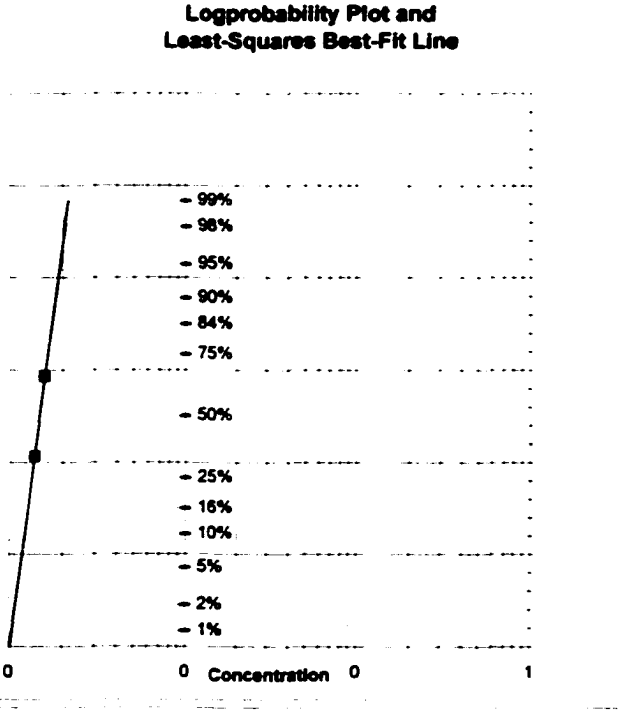
Number of samples (n)	2
Maximum (max)	0.0016
Minimum (min)	0.0014
Range	0.0002
Percent above OEL (%>OEL)	0.000
Mean	0.002
Median	0.002
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.505
Std. deviation of logtransformed data (LN)	0.094
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.099

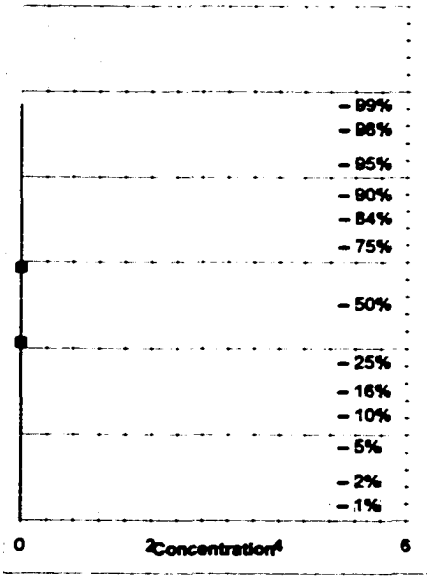
W-test of logtransformed data (LN)	1.000
Lognormal (a = 0.05)?	Yes
W-test of data	1.000
Normal (a = 0.05)?	Yes

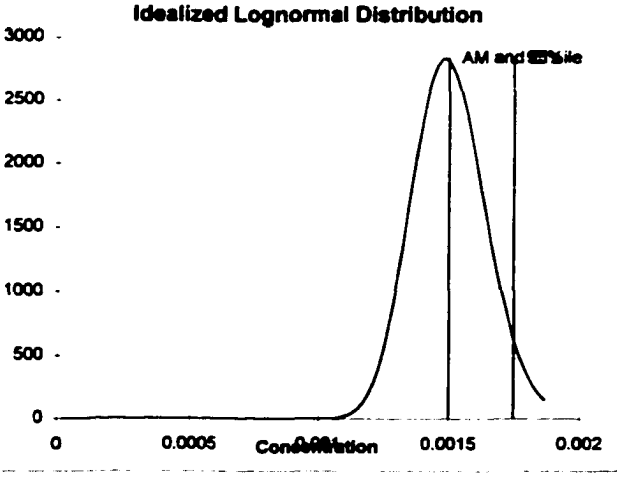
Estimated Arithmetic Mean - MVUE	0.002
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.002
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<43.065

Mean	0.002
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.002
95th Percentile - Z	0.002
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000









Industrial Hygiene Statistics

Data Description:

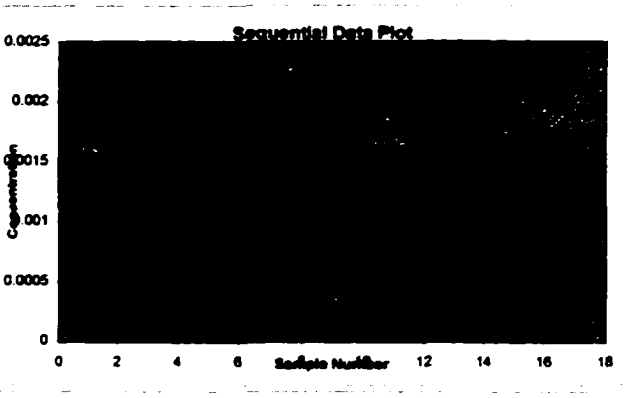
0.01

0.00034
0.00034
0.00034
0.00034
0.0018
0.00099
0.00106
0.00102
0.0018
0.0016
0.0014
0.0015
0.002
0.0017
0.0015
0.0016

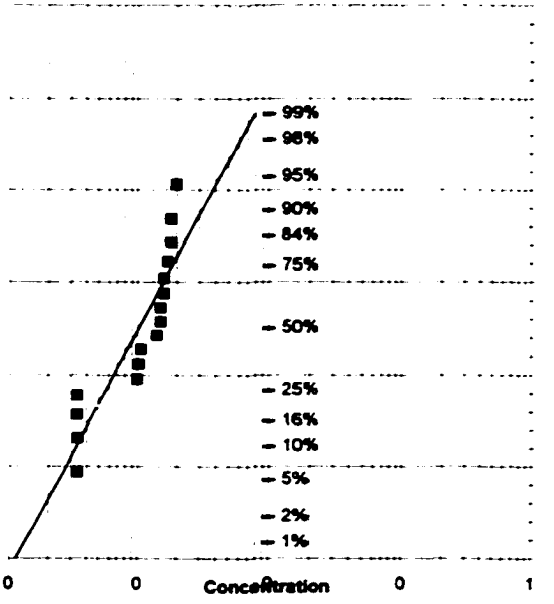
Number of samples (n)	16
Maximum (max)	0.002
Minimum (min)	0.00034
Range	0.00166
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.001
Standard deviation (s)	0.001
Mean of logtransformed data (LN)	-6.893
Std. deviation of logtransformed data (LN)	0.683
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.979
W-test of logtransformed data (LN)	0.765
Lognormal (a = 0.05)?	No
W-test of data	0.869
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.002
95th Percentile	0.003
$UTL_{95\%,95\%}$	0.006
Percent above OEL (%>OEL)	0.040
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	1.206

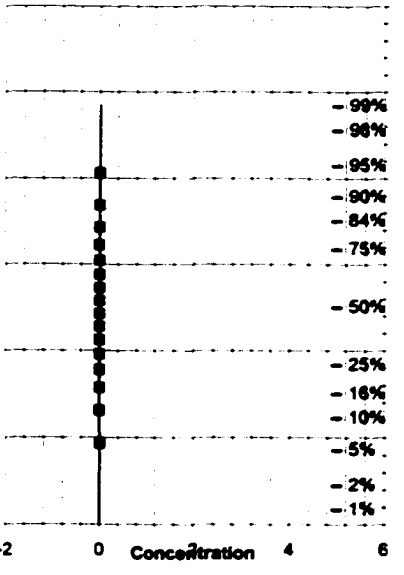
Mean	0.001
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.001
95th Percentile - Z	0.002
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



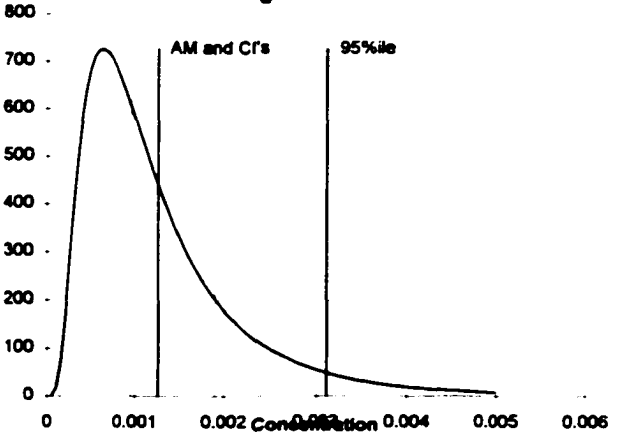
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.01

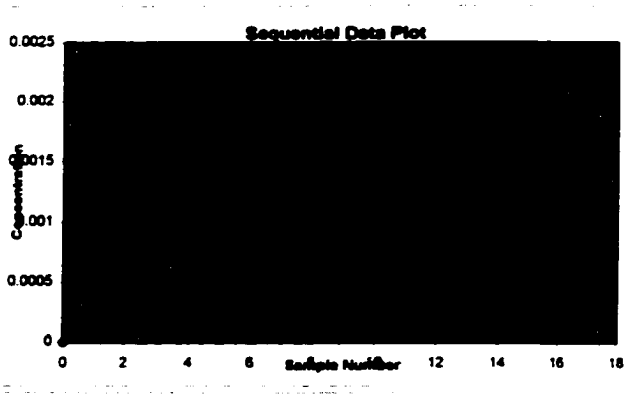
0.0018
0.00099
0.00106
0.00102
0.0018
0.0016
0.0014
0.0015
0.002
0.0017
0.0015
0.0016

Number of samples (n)	12
Maximum (max)	0.002
Minimum (min)	0.00099
Range	0.00101
Percent above OEL (%>OEL)	#REF!
Mean	0.001
Median	0.002
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.526
Std. deviation of logtransformed data (LN)	0.236
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.266

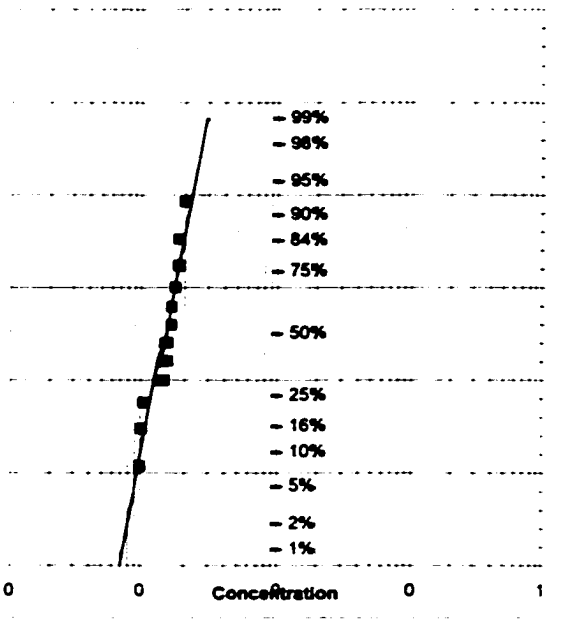
W-test of logtransformed data (LN)	0.887
Lognormal (a = 0.05)?	Yes
W-test of data	0.924
Normal (a = 0.05)?	Yes

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.002
95th Percentile	0.002
$UTL_{95\%,95\%}$	0.003
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<0.000

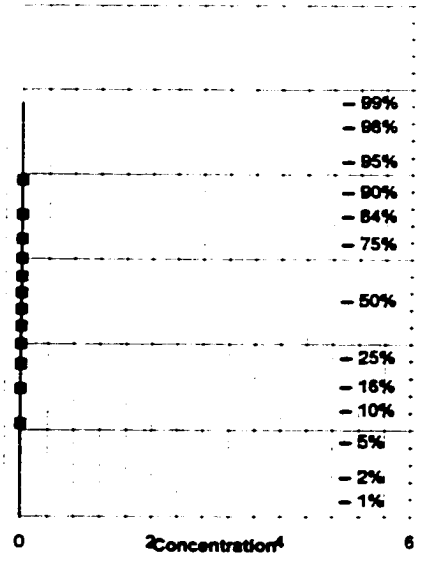
Mean	0.001
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.002
95th Percentile - Z	0.002
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



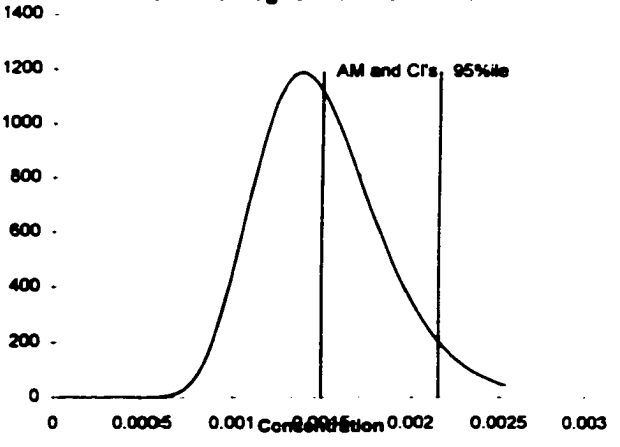
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.01

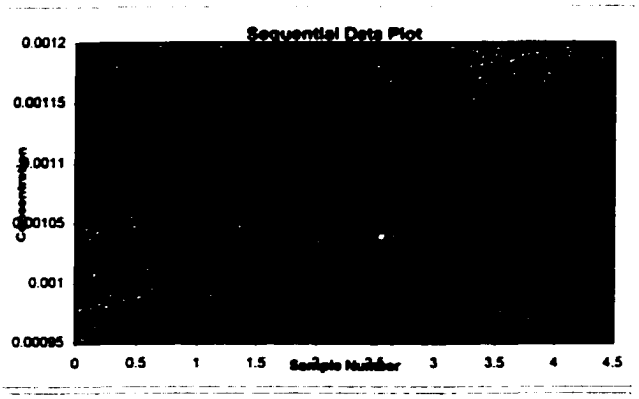
0.00118
0.00099
0.00106
0.00102

Number of samples (n)	4
Maximum (max)	0.00118
Minimum (min)	0.00099
Range	0.00019
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.001
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.849
Std. deviation of logtransformed data (LN)	0.077
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.080

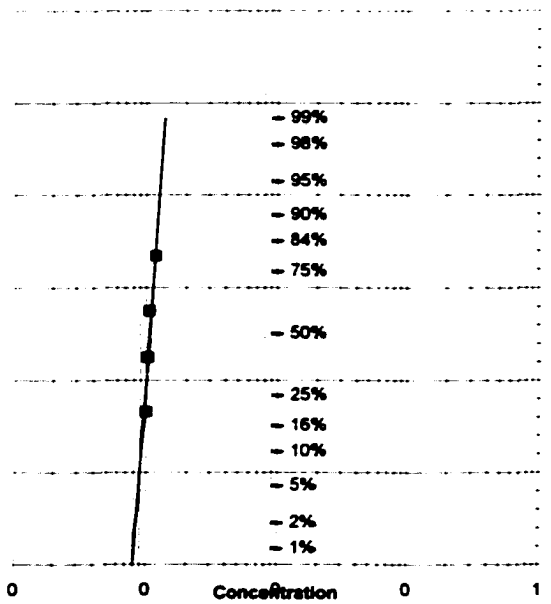
W-test of logtransformed data (LN)	0.915
Lognormal (α = 0.05)?	Yes
W-test of data	0.903
Normal (α = 0.05)?	Yes

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1-95\%}$ - Land's "Exact"	0.001
$UCL_{1-95\%}$ - Land's "Exact"	0.001
95th Percentile	0.001
$UTL_{95\%,95\%}$	0.002
Percent above OEL (%>OEL)	0.000
$LCL_{1-95\%}$ %>OEL	<0.1
$UCL_{1-95\%}$ %>OEL	<2.532

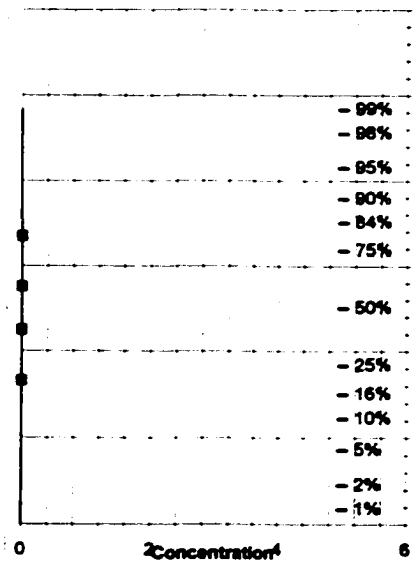
Mean	0.001
$LCL_{1-95\%}$ - t statistics	0.001
$UCL_{1-95\%}$ - t statistics	0.001
95th Percentile - Z	0.001
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



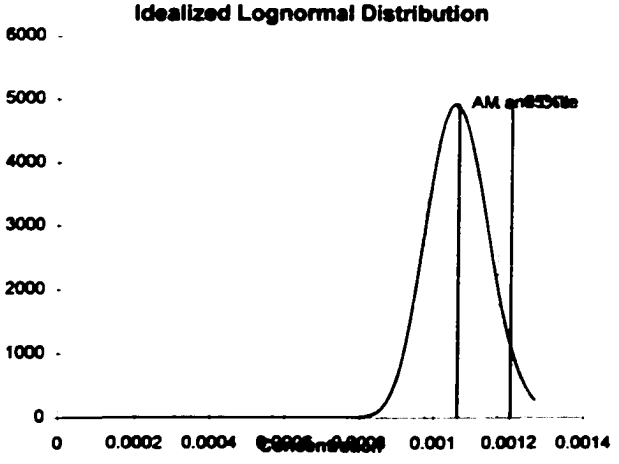
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.01

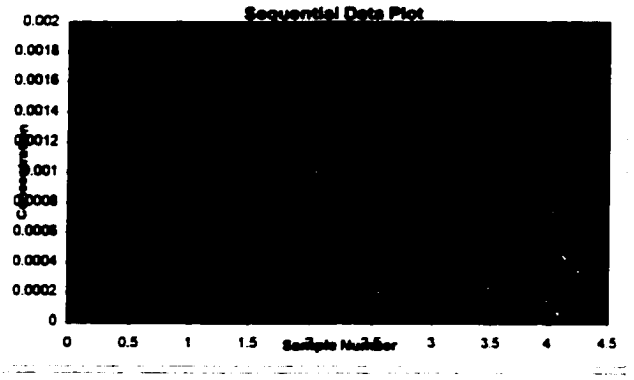
0.0018
0.0015
0.0014
0.0015

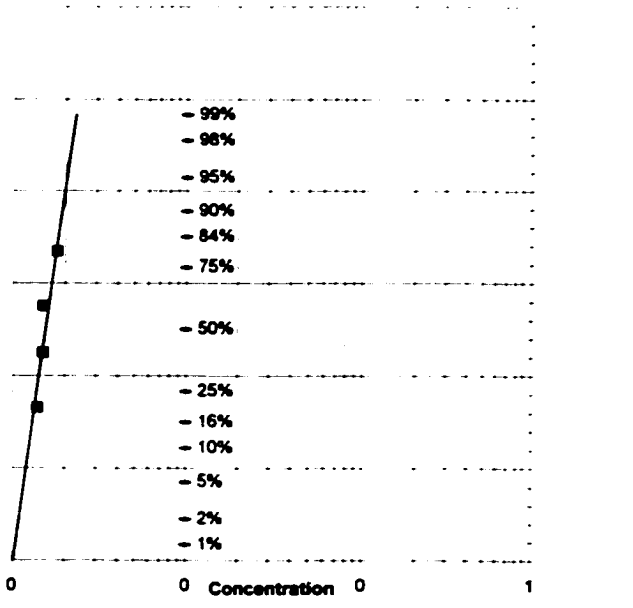
Number of samples (n)	4
Maximum (max)	0.0018
Minimum (min)	0.0014
Range	0.0004
Percent above OEL (%>OEL)	0.000
Mean	0.002
Median	0.002
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.474
Std. deviation of logtransformed data (LN)	0.108
Geometric mean (GM)	0.002
Geometric standard deviation (GSD)	1.114

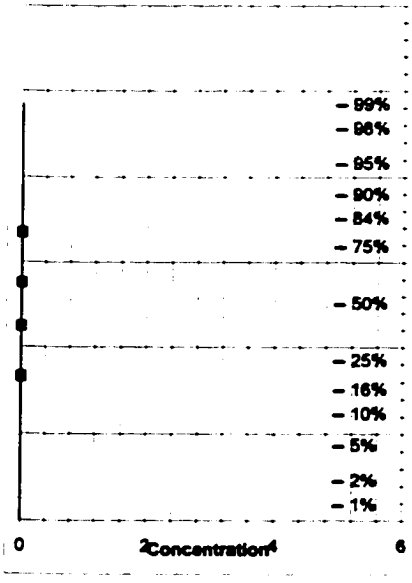
W-test of logtransformed data (LN)	0.857
Lognormal (a = 0.05)?	Yes
W-test of data	0.840
Normal (a = 0.05)?	Yes

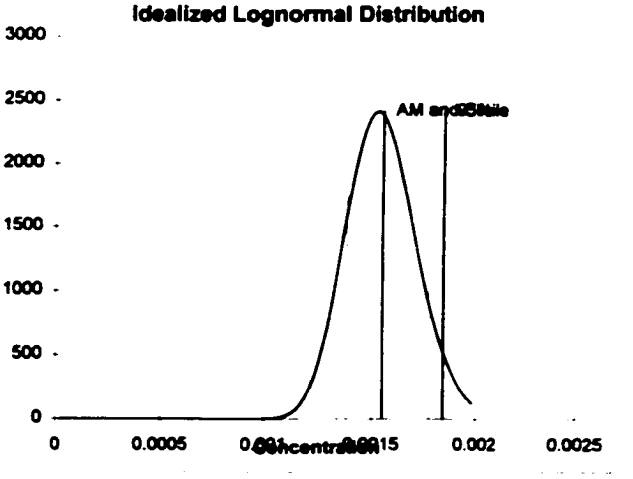
Estimated Arithmetic Mean - MVUE	0.002
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.002
95th Percentile	0.002
$UTL_{95\%,95\%}$	0.003
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<2.532

Mean	0.002
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.002
95th Percentile - Z	0.002
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000









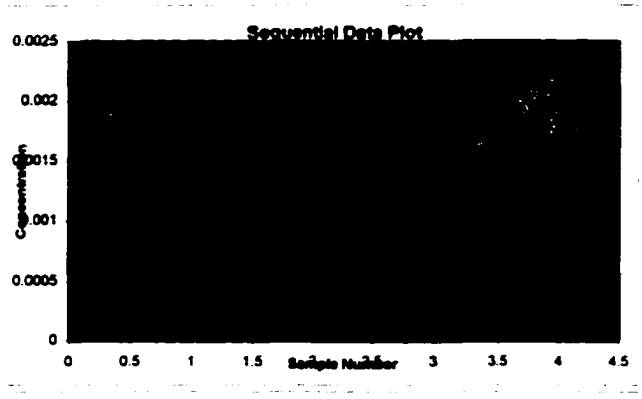
Industrial Hygiene Statistics

Data Description:

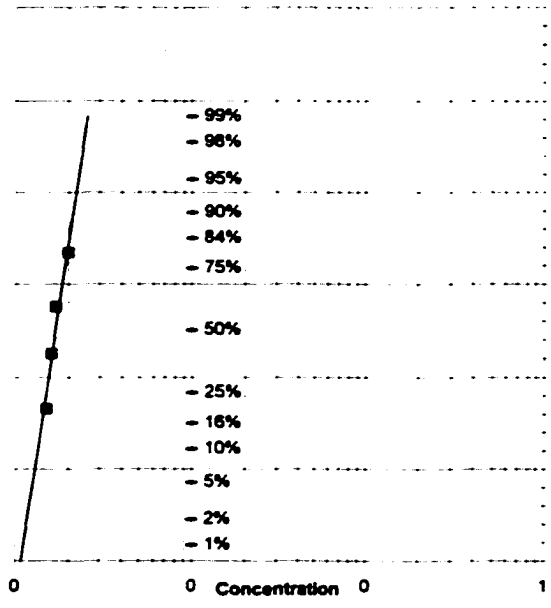
0.01

0.002
0.0017
0.0015
0.0016

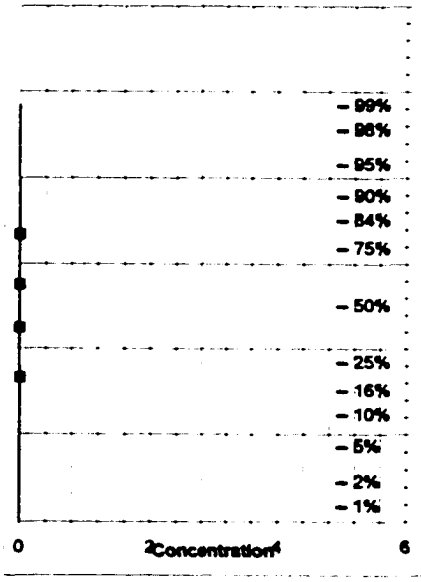
Number of samples (n)	4
Maximum (max)	0.002
Minimum (min)	0.0015
Range	0.0005
Percent above OEL (%>OEL)	0.000
Mean	0.002
Median	0.002
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.383
Std. deviation of logtransformed data (LN)	0.123
Geometric mean (GM)	0.002
Geometric standard deviation (GSD)	1.131
W-test of logtransformed data (LN)	0.947
Lognormal (α = 0.05)?	Yes
W-test of data	0.928
Normal (α = 0.05)?	Yes
Estimated Arithmetic Mean - MVUE	0.002
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.002
95th Percentile	0.002
$UTL_{95\%,95\%}$	0.003
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<2.532
Mean	0.002
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.002
95th Percentile - Z	0.002
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



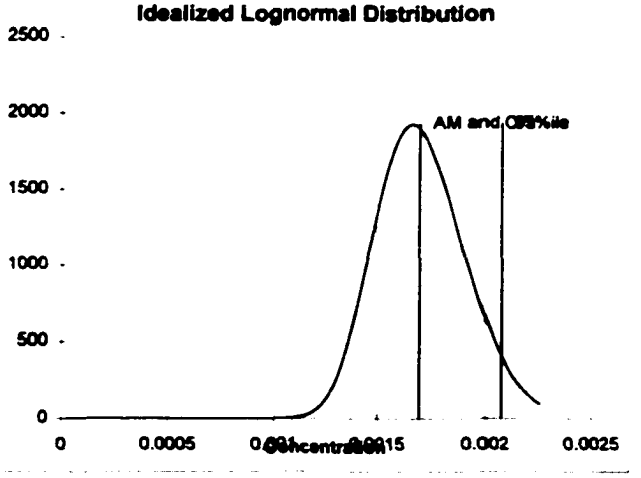
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.04

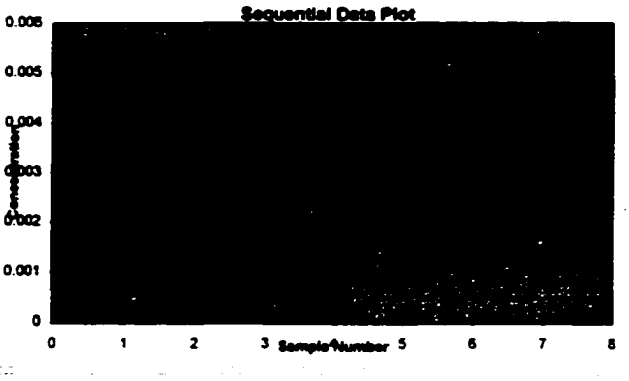
0.0028
0.0011
0.0044
0.0041
0.005
0.0048
0.0041

Number of samples (n)	7
Maximum (max)	0.005
Minimum (min)	0.0011
Range	0.0039
Percent above OEL (%>OEL)	0.000
Mean	0.004
Median	0.004
Standard deviation (s)	0.001
Mean of logtransformed data (LN)	-5.678
Std. deviation of logtransformed data (LN)	0.535
Geometric mean (GM)	0.003
Geometric standard deviation (GSD)	1.707

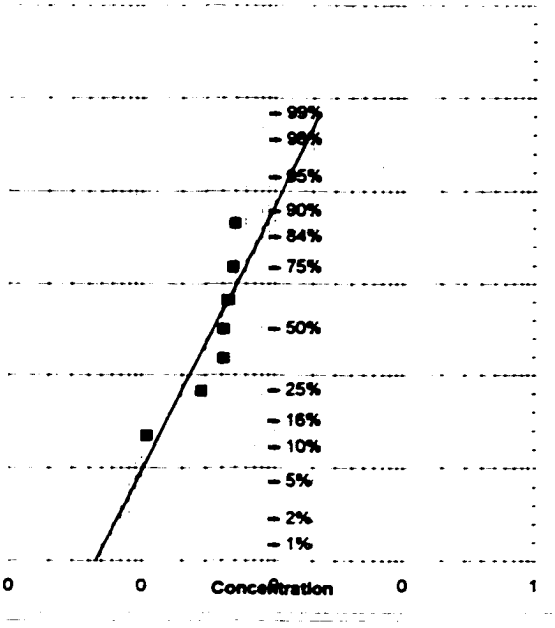
W-test of logtransformed data (LN)	0.727
Lognormal (a = 0.05)?	No
W-test of data	0.842
Normal (a = 0.05)?	Yes

Estimated Arithmetic Mean - MVUE	0.004
$LCL_{1,95\%}$ - Land's "Exact"	0.003
$UCL_{1,95\%}$ - Land's "Exact"	0.007
95th Percentile	0.008
$UTL_{95\%,95\%}$	0.021
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	1.060

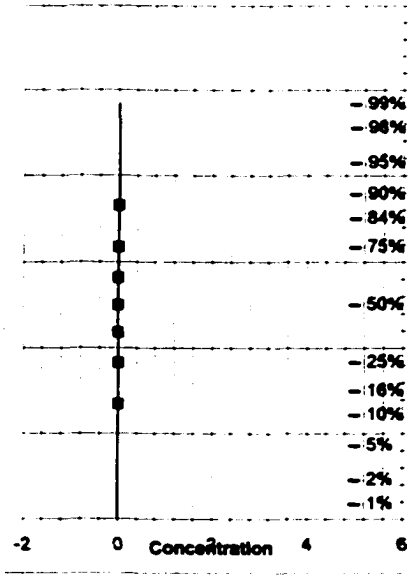
Mean	0.004
$LCL_{1,95\%}$ - t statistics	0.003
$UCL_{1,95\%}$ - t statistics	0.005
95th Percentile - Z	0.006
$UTL_{95\%,95\%}$	0.01
Percent above OEL (%>OEL)	0.000



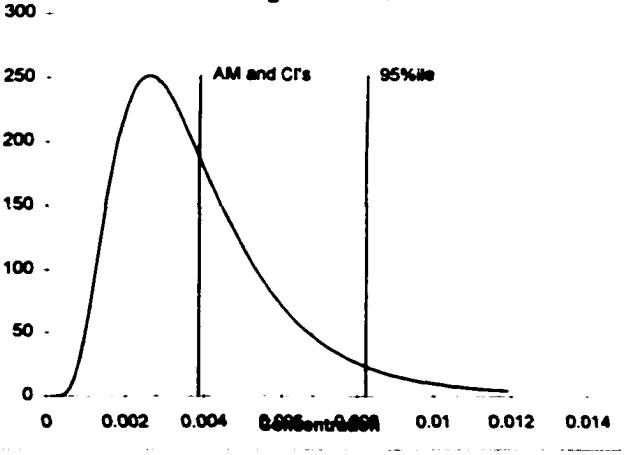
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

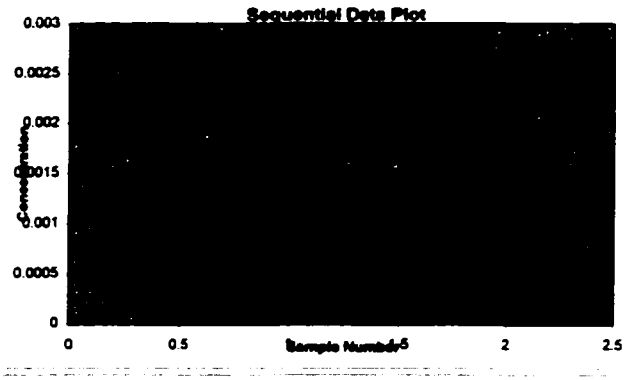
Data Description:

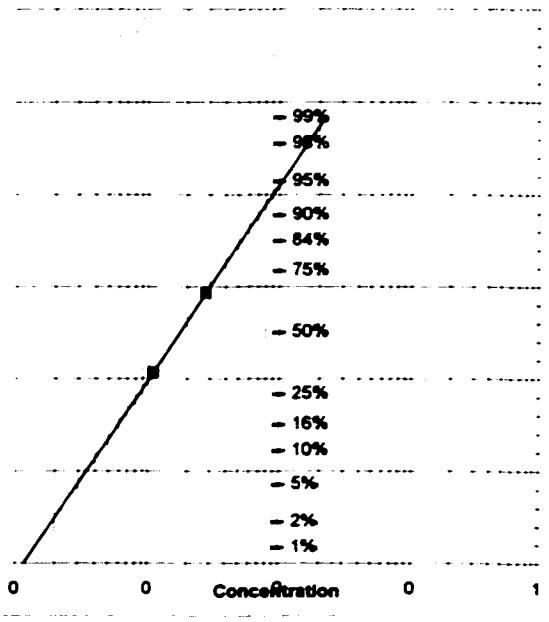
	0.04
	0.0028
	0.0011

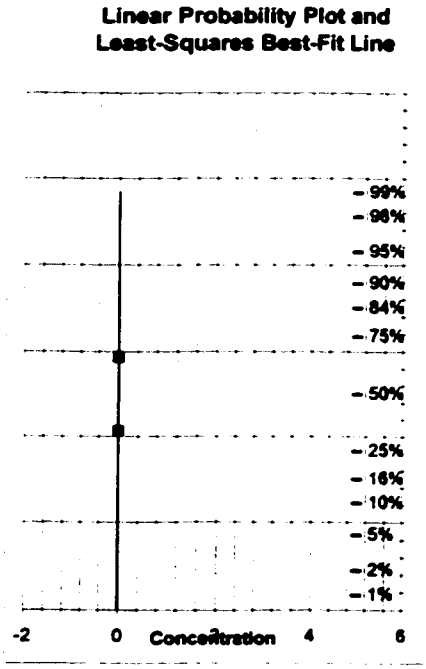
Number of samples (n)	2
Maximum (max)	0.0028
Minimum (min)	0.0011
Range	0.0017
Percent above OEL (%>OEL)	0.000
Mean	0.002
Median	0.002
Standard deviation (s)	0.001
Mean of logtransformed data (LN)	-6.345
Std. deviation of logtransformed data (LN)	0.661
Geometric mean (GM)	0.002
Geometric standard deviation (GSD)	1.936
W-test of logtransformed data (LN)	1.000
Lognormal (a = 0.05)?	Yes
W-test of data	1.000
Normal (a = 0.05)?	Yes

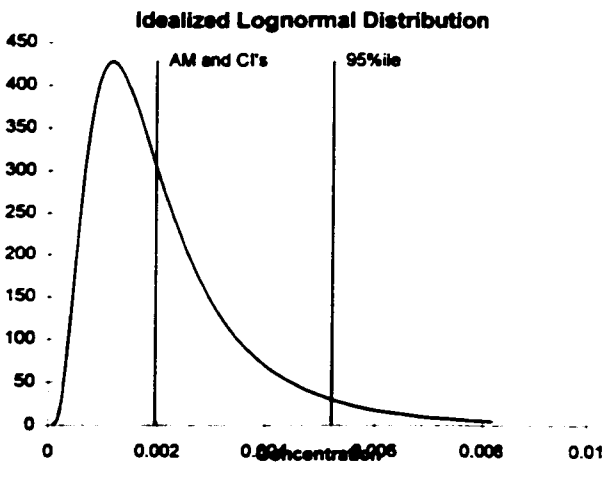
Estimated Arithmetic Mean - MVUE	0.002
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.005
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	48.691

Mean	0.002
$LCL_{1,95\%}$ - t statistics	-0.003
$UCL_{1,95\%}$ - t statistics	0.007
95th Percentile - Z	0.004
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000









Industrial Hygiene Statistics

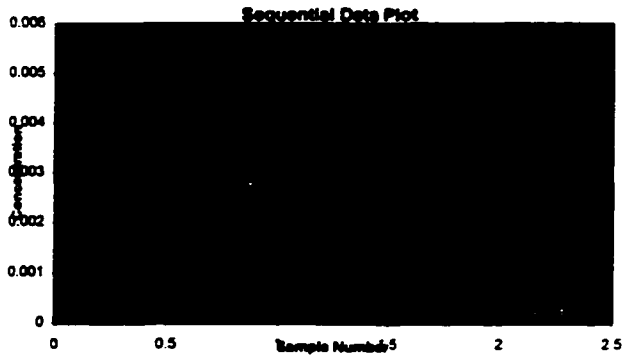
Data Description:

	0.04
	0.0041
	0.005

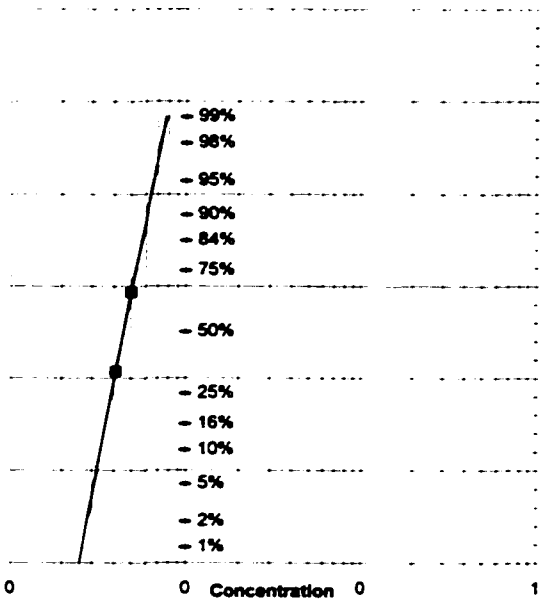
Number of samples (n)	2
Maximum (max)	0.005
Minimum (min)	0.0041
Range	0.0009
Percent above OEL (%>OEL)	0.000
Mean	0.005
Median	0.005
Standard deviation (s)	0.001
Mean of logtransformed data (LN)	-5.398
Std. deviation of logtransformed data (LN)	0.140
Geometric mean (GM)	0.005
Geometric standard deviation (GSD)	1.151
W-test of logtransformed data (LN)	1.000
Lognormal (a = 0.05)?	Yes
W-test of data	1.000
Normal (a = 0.05)?	Yes

Estimated Arithmetic Mean - MVUE	0.005
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.006
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<43.065

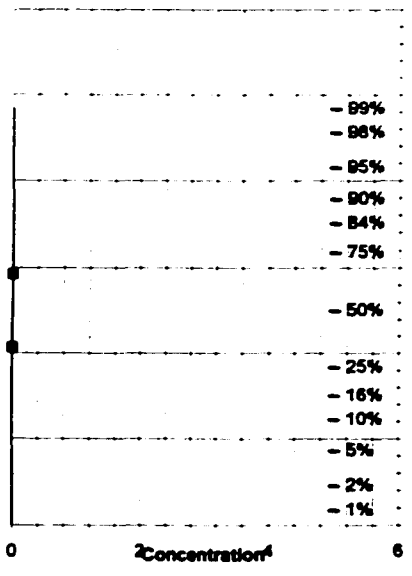
Mean	0.005
$LCL_{1,95\%}$ - t statistics	0.002
$UCL_{1,95\%}$ - t statistics	0.007
95th Percentile - Z	0.006
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000



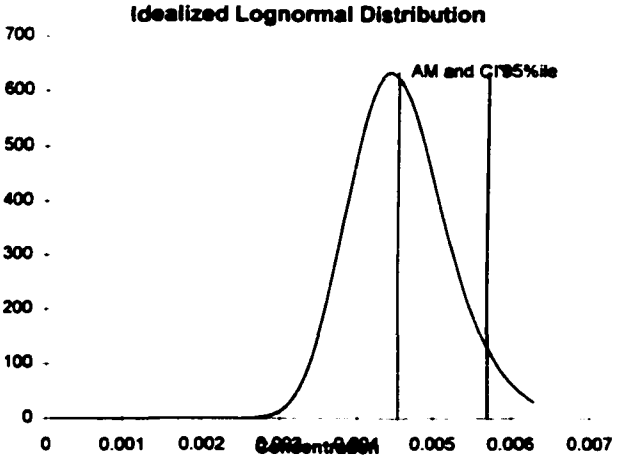
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.04

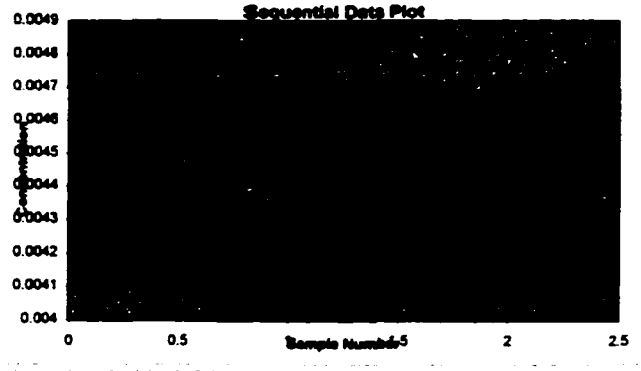
0.0048
0.0041

Number of samples (n)	2
Maximum (max)	0.0048
Minimum (min)	0.0041
Range	0.0007
Percent above OEL (%>OEL)	0.000
Mean	0.004
Median	0.004
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-5.418
Std. deviation of logtransformed data (LN)	0.111
Geometric mean (GM)	0.004
Geometric standard deviation (GSD)	1.118

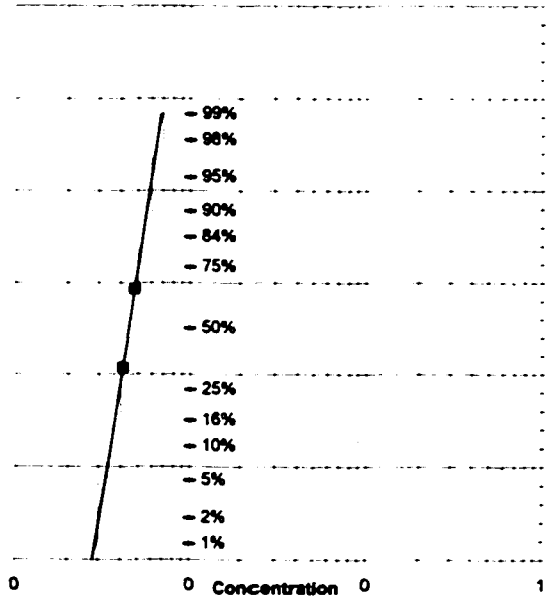
W-test of logtransformed data (LN)	1.000
Lognormal (a = 0.05)?	Yes
W-test of data	1.000
Normal (a = 0.05)?	Yes

Estimated Arithmetic Mean - MVUE	0.004
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.005
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<43.065

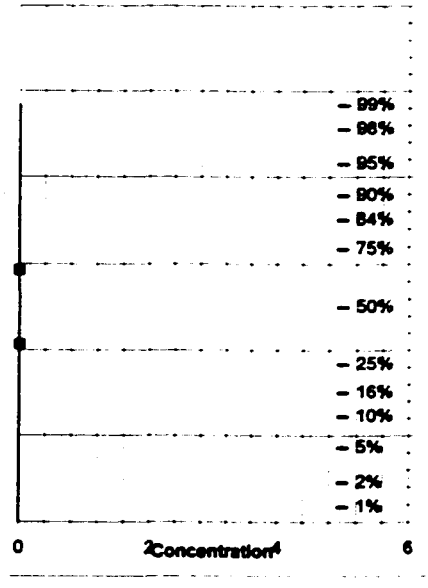
Mean	0.004
$LCL_{1,95\%}$ - t statistics	0.002
$UCL_{1,95\%}$ - t statistics	0.007
95th Percentile - Z	0.005
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000



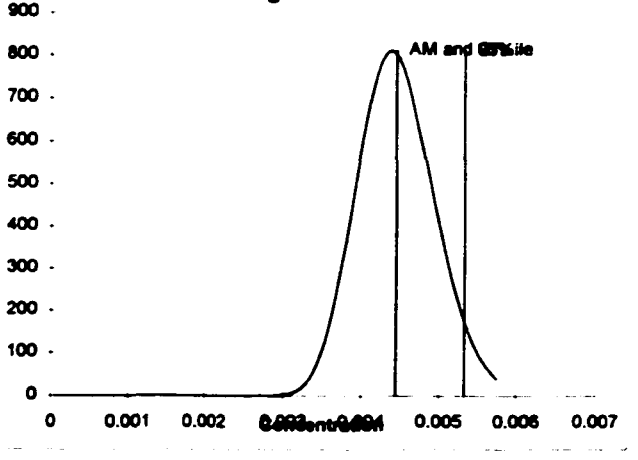
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

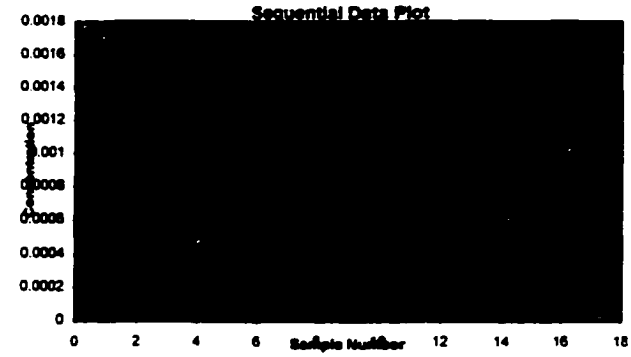
0.04

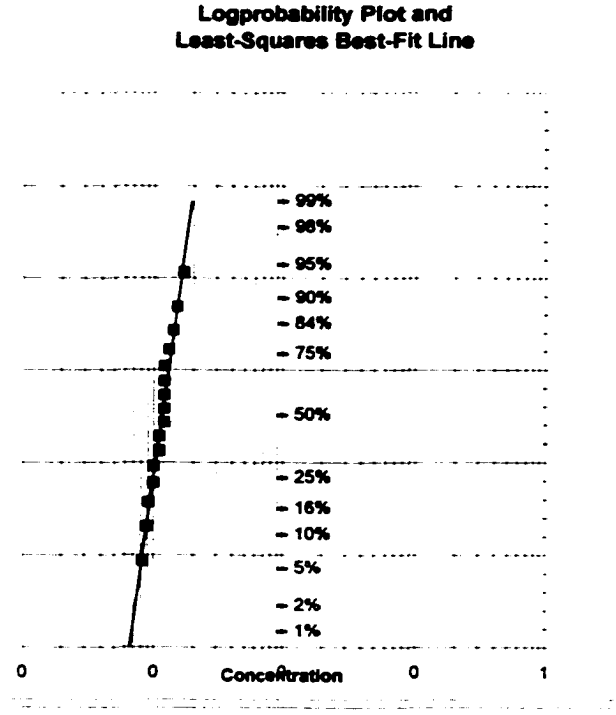
0.001
0.0012
0.0012
0.0012
0.0012
0.0011
0.0011
0.0012
0.0014
0.0013
0.0015
0.0017
0.00089
0.00083
0.00092
0.001

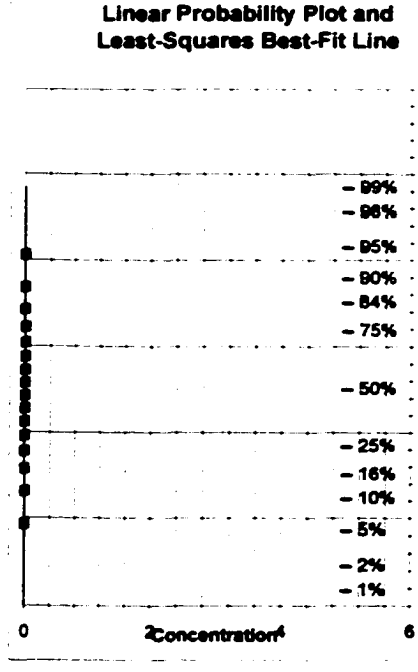
Number of samples (n)	16
Maximum (max)	0.0017
Minimum (min)	0.00083
Range	0.00087
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.001
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.767
Std. deviation of logtransformed data (LN)	0.192
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.211
W-test of logtransformed data (LN)	0.970
Lognormal (α = 0.05)?	Yes
W-test of data	0.949
Normal (α = 0.05)?	Yes

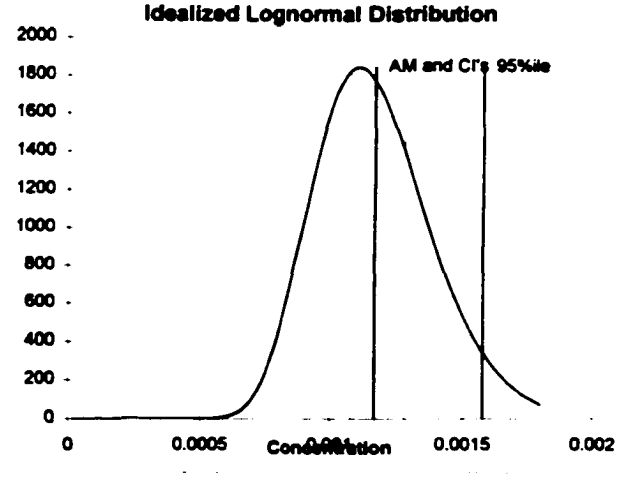
Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.001
95th Percentile	0.002
$UTL_{95\%,95\%}$	0.002
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<0.000

Mean	0.001
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.001
95th Percentile - Z	0.002
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000









Industrial Hygiene Statistics

Data Description:

0.04

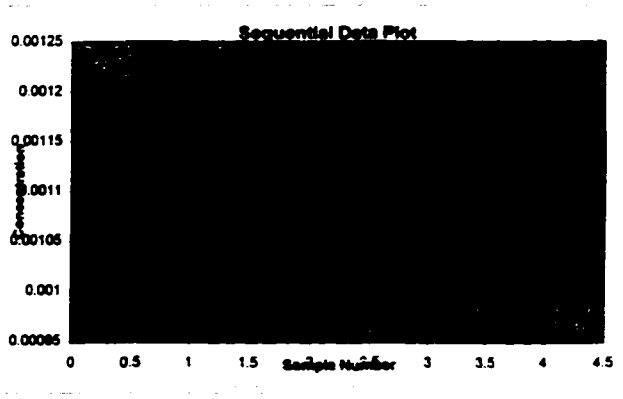
0.001
0.0012
0.0012
0.0012

Number of samples (n)	4
Maximum (max)	0.0012
Minimum (min)	0.001
Range	0.0002
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.001
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.771
Std. deviation of logtransformed data (LN)	0.091
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.095

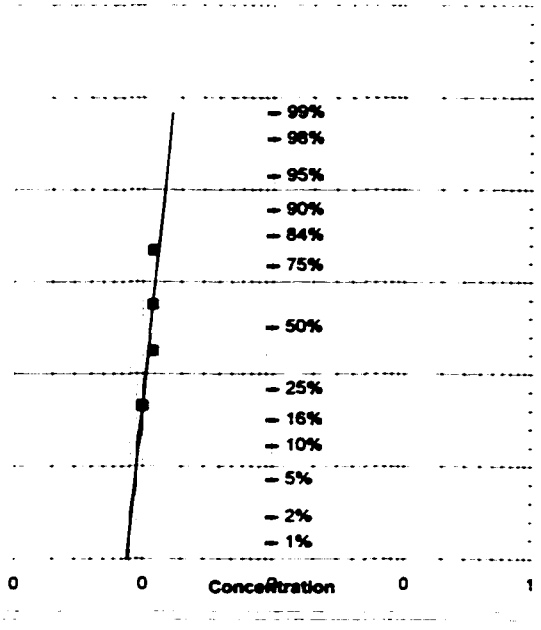
W-test of logtransformed data (LN)	0.630
Lognormal (a = 0.05)?	No
W-test of data	0.630
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.001
95th Percentile	0.001
$UTL_{95\%,95\%}$	0.002
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<2.532

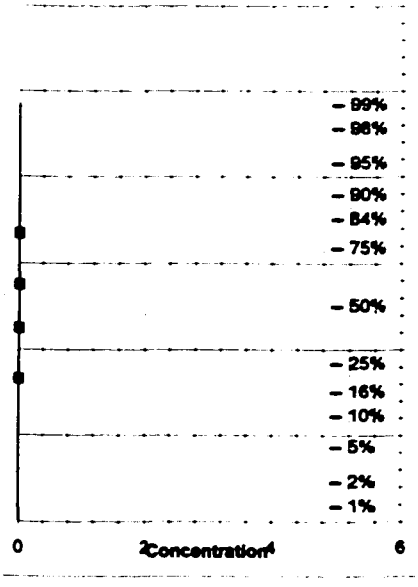
Mean	0.001
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.001
95th Percentile - Z	0.001
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



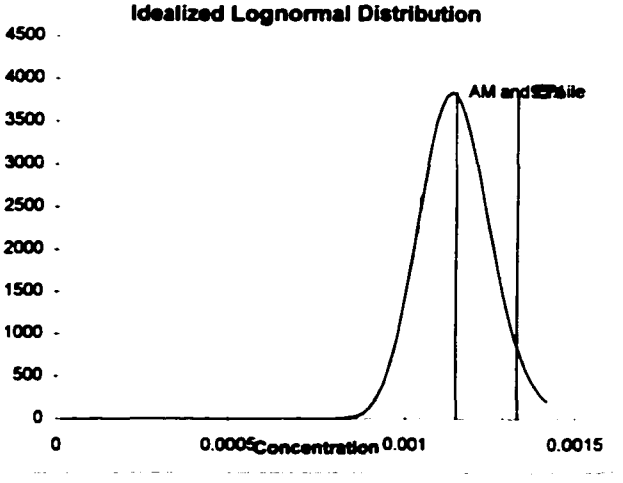
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.04

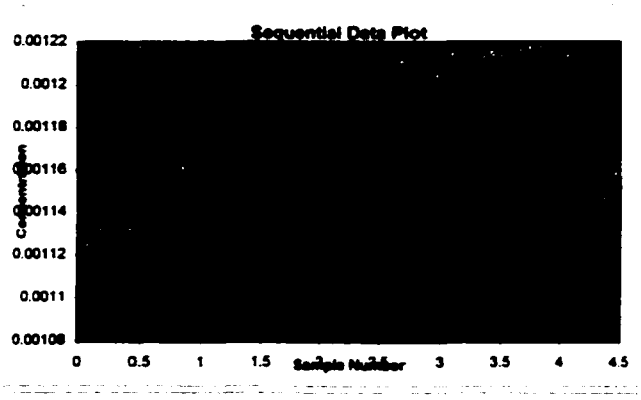
0.0012
0.0011
0.0011
0.0012

Number of samples (n)	4
Maximum (max)	0.0012
Minimum (min)	0.0011
Range	1E-04
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.001
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.769
Std. deviation of logtransformed data (LN)	0.050
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.052

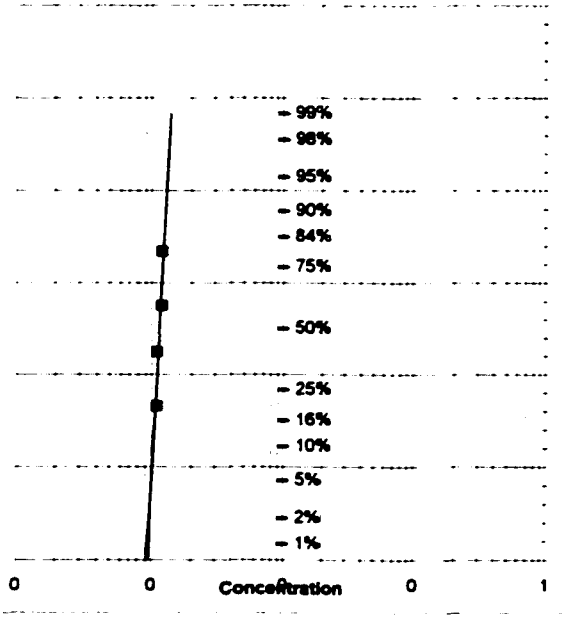
W-test of logtransformed data (LN)	0.731
Lognormal (a = 0.05)?	No
W-test of data	0.731
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.001
95th Percentile	0.001
$UTL_{95\%,95\%}$	0.001
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<2.532

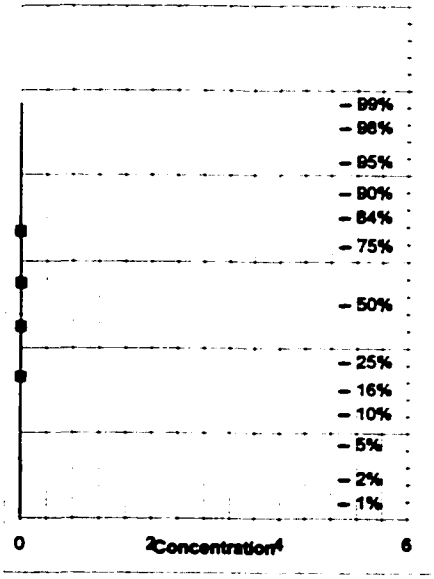
Mean	0.001
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.001
95th Percentile - Z	0.001
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



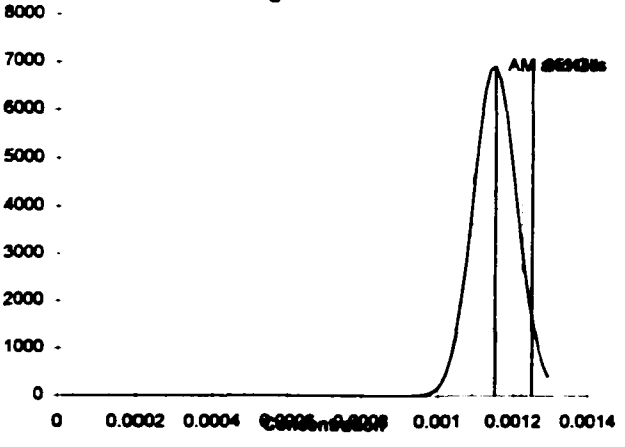
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.04

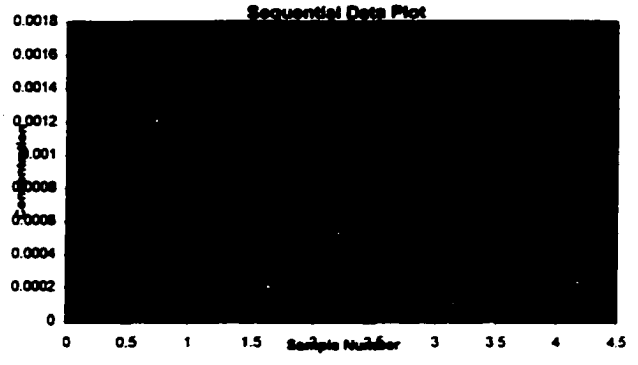
0.0014
0.0013
0.0015
0.0017

Number of samples (n)	4
Maximum (max)	0.0017
Minimum (min)	0.0013
Range	0.0004
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.001
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-6.524
Std. deviation of logtransformed data (LN)	0.114
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.121

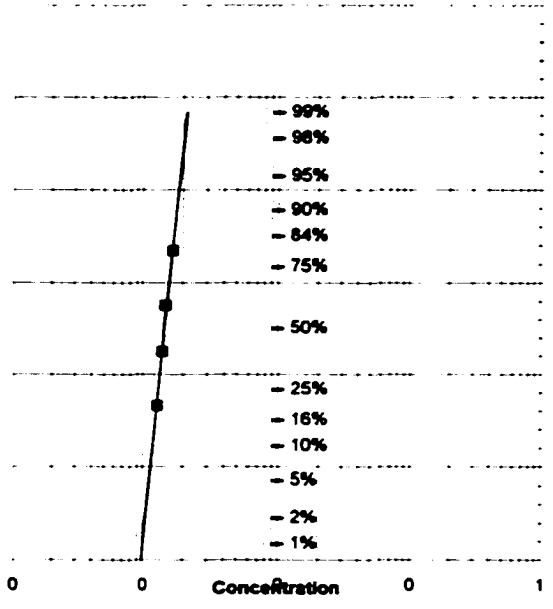
W-test of logtransformed data (LN)	0.984
Lognormal (a = 0.05)?	Yes
W-test of data	0.972
Normal (a = 0.05)?	Yes

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.002
95th Percentile	0.002
$UTL_{95\%,95\%}$	0.003
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<2.532

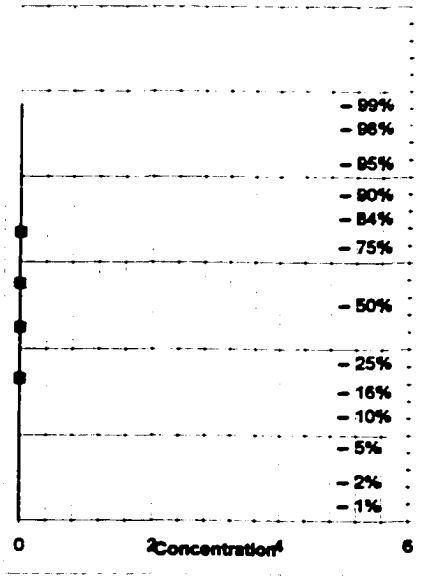
Mean	0.001
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.002
95th Percentile - Z	0.002
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



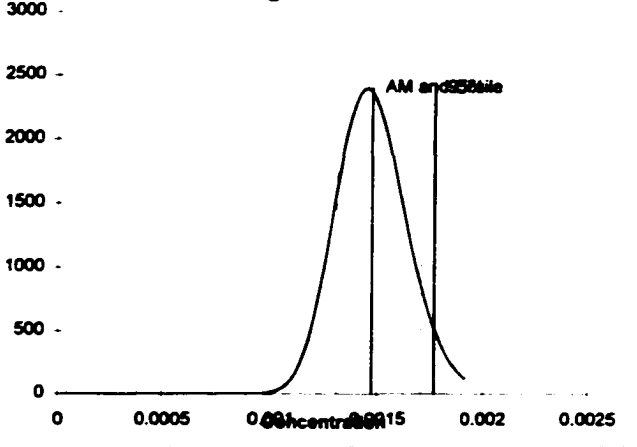
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.04

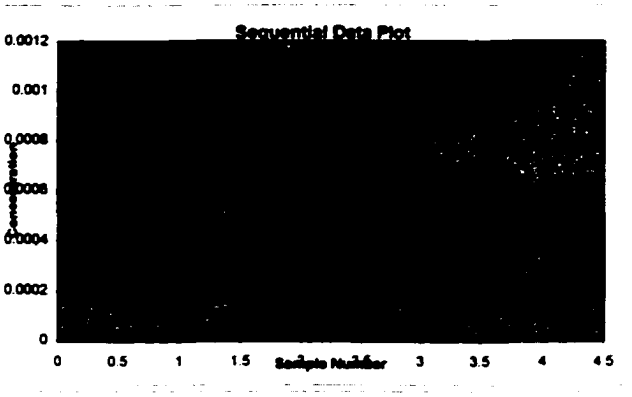
0.00069
0.00083
0.00092
0.001

Number of samples (n)	4
Maximum (max)	0.001
Minimum (min)	0.00083
Range	0.00017
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.001
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-7.004
Std. deviation of logtransformed data (LN)	0.077
Geometric mean (GM)	0.001
Geometric standard deviation (GSD)	1.080

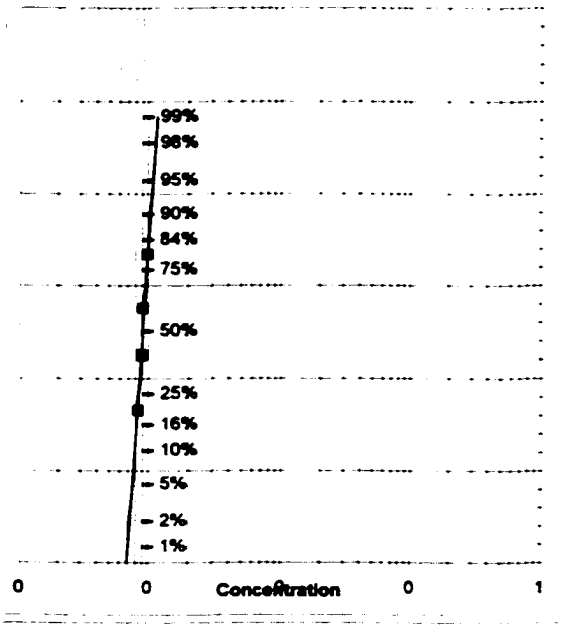
W-test of logtransformed data (LN)	0.994
Lognormal (a = 0.05)?	Yes
W-test of data	0.990
Normal (a = 0.05)?	Yes

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.001
$UCL_{1,95\%}$ - Land's "Exact"	0.001
95th Percentile	0.001
$UTL_{95\%,95\%}$	0.001
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<2.532

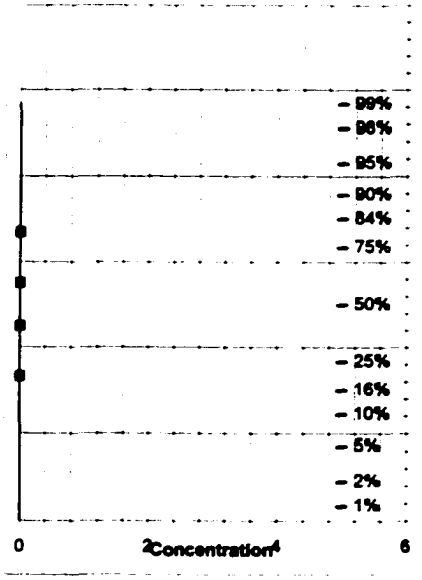
Mean	0.001
$LCL_{1,95\%}$ - t statistics	0.001
$UCL_{1,95\%}$ - t statistics	0.001
95th Percentile - Z	0.001
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



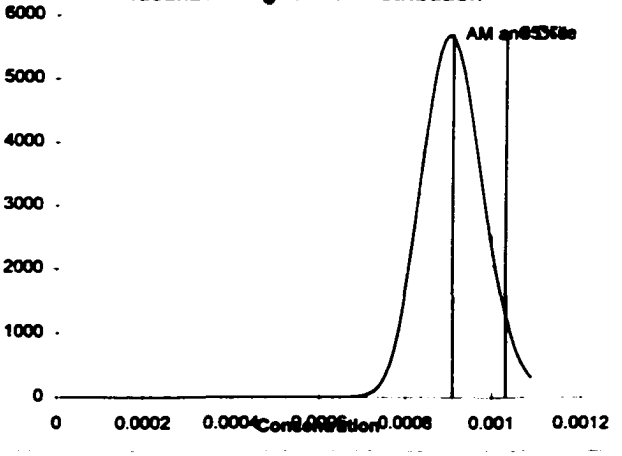
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.02

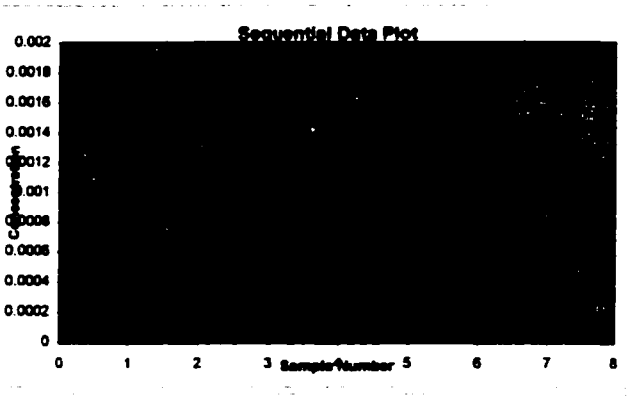
0.00026
0.00025
0.00004
0.000036
0.00012
0.0018
0.000057

Number of samples (n)	7
Maximum (max)	0.0018
Minimum (min)	0.000036
Range	0.001764
Percent above OEL (%>OEL)	0.000
Mean	0.000
Median	0.000
Standard deviation (s)	0.001
Mean of logtransformed data (LN)	-8.861
Std. deviation of logtransformed data (LN)	1.384
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	3.989

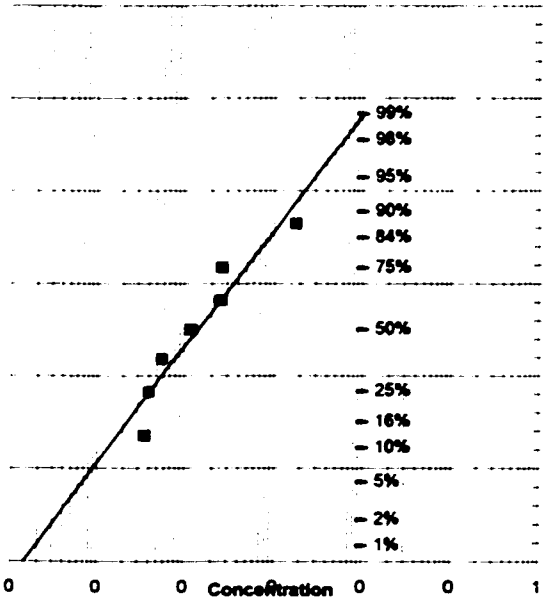
W-test of logtransformed data (LN)	0.899
Lognormal (a = 0.05)?	Yes
W-test of data	0.581
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.000
$LCL_{1,95\%}$ - Land's "Exact"	0.000
$UCL_{1,95\%}$ - Land's "Exact"	0.006
95th Percentile	0.001
$UTL_{95\%,95\%}$	0.016
Percent above OEL (%>OEL)	0.017
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	4.066

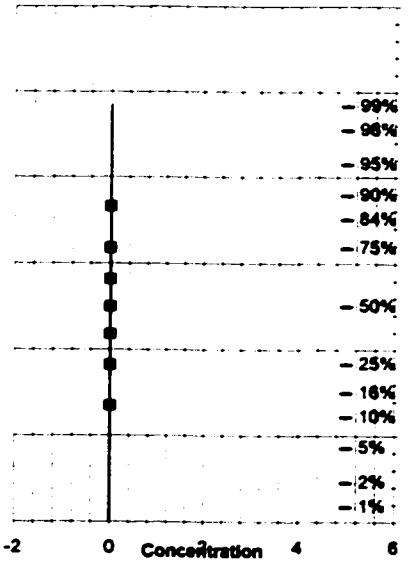
Mean	0.000
$LCL_{1,95\%}$ - t statistics	0.000
$UCL_{1,95\%}$ - t statistics	0.001
95th Percentile - Z	0.001
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



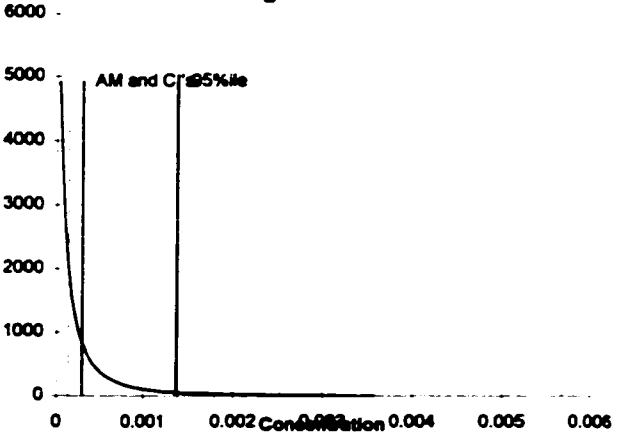
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution

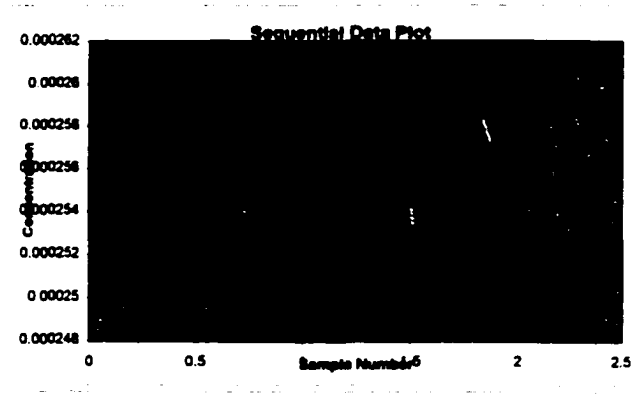


Industrial Hygiene Statistics

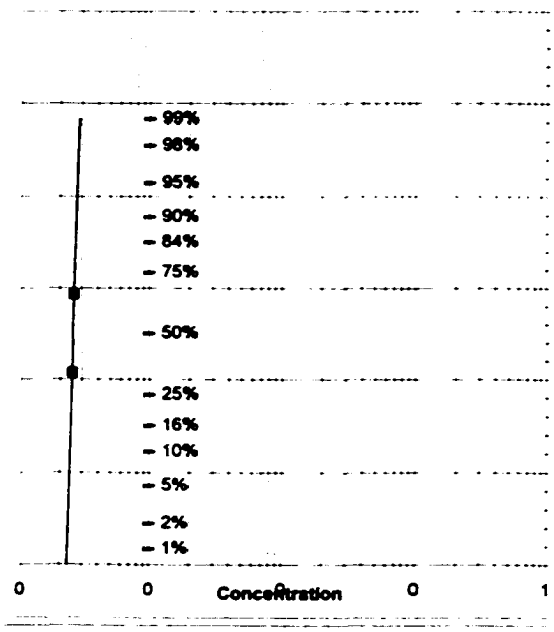
Data Description:

	0.02
	0.00026
	0.00025

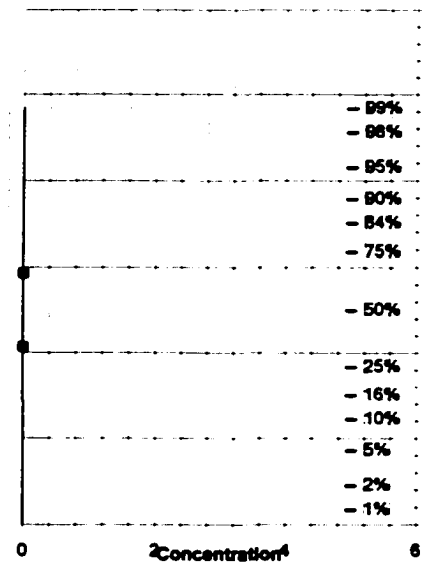
Number of samples (n)	2
Maximum (max)	0.00026
Minimum (min)	0.00025
Range	1E-05
Percent above OEL (%>OEL)	0.000
Mean	0.000
Median	0.000
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-8.274
Std. deviation of logtransformed data (LN)	0.028
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	1.028
W-test of logtransformed data (LN)	1.000
Lognormal (α = 0.05)?	Yes
W-test of data	1.000
Normal (α = 0.05)?	Yes
Estimated Arithmetic Mean - MVUE	0.000
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.000
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<43.065
Mean	0.000
$LCL_{1,95\%}$ - t statistics	0.000
$UCL_{1,95\%}$ - t statistics	0.000
95th Percentile - Z	0.000
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000



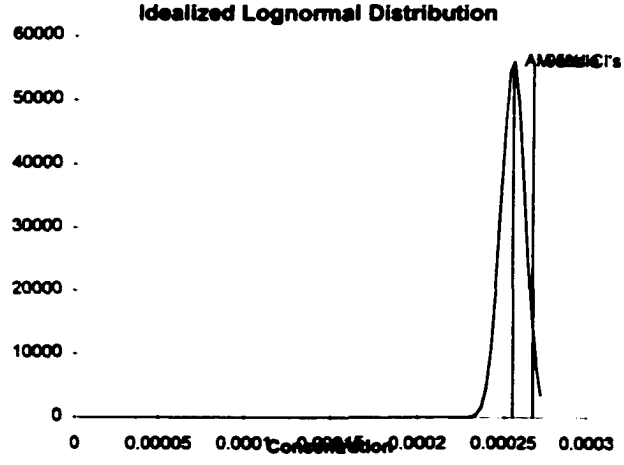
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

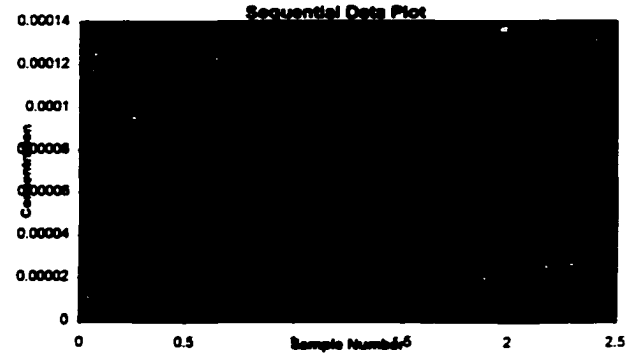
	0.02
	0.000036
	0.00012

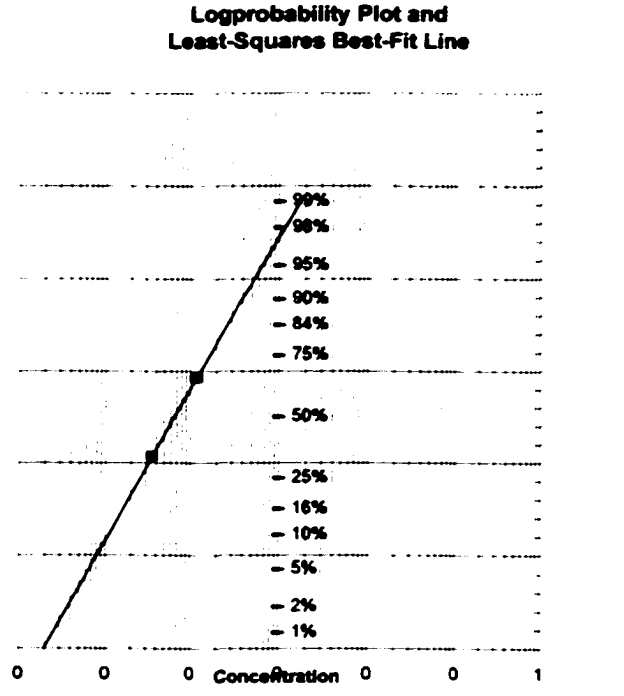
Number of samples (n)	2
Maximum (max)	0.00012
Minimum (min)	0.000036
Range	0.000084
Percent above OEL (%>OEL)	0.000
Mean	0.000
Median	0.000
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-9.630
Std. deviation of logtransformed data (LN)	0.851
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	2.343

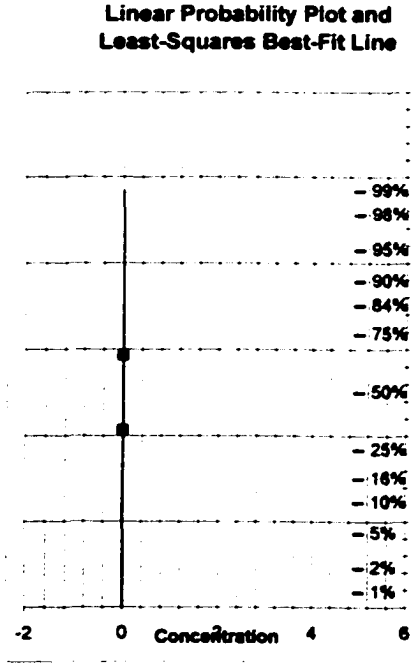
W-test of logtransformed data (LN)	1.000
Lognormal (a = 0.05)?	Yes
W-test of data	1.000
Normal (a = 0.05)?	Yes

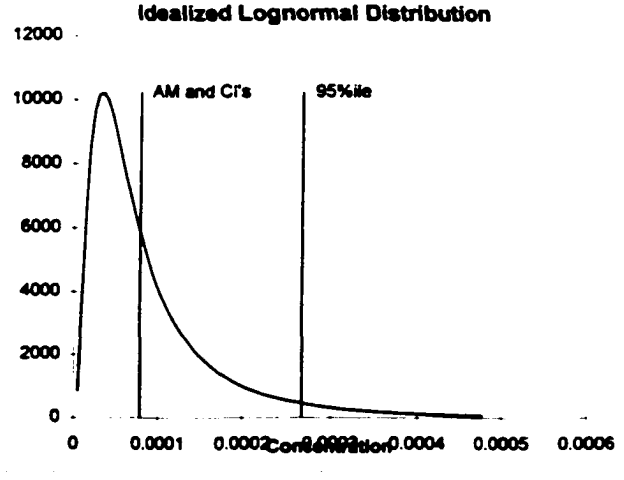
Estimated Arithmetic Mean - MVUE	0.000
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.000
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<43.065

Mean	0.000
$LCL_{1,95\%}$ - t statistics	0.000
$UCL_{1,95\%}$ - t statistics	0.000
95th Percentile - Z	0.000
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000









Industrial Hygiene Statistics

Data Description:

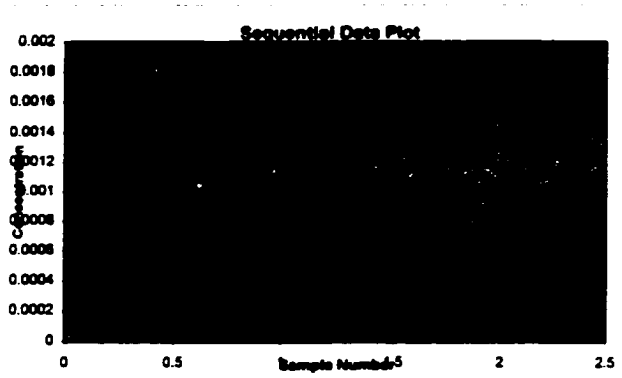
	0.02
	0.0018
	0.000057

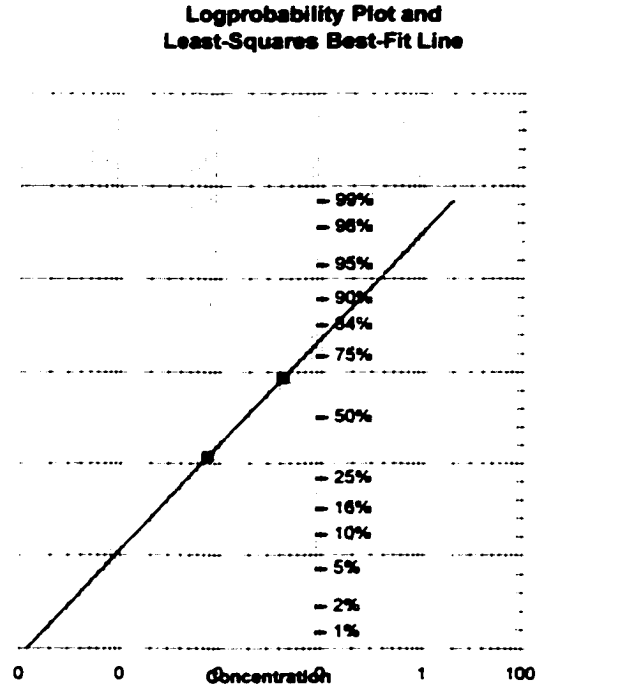
Number of samples (n)	2
Maximum (max)	0.0018
Minimum (min)	0.000057
Range	0.001743
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.001
Standard deviation (s)	0.001
Mean of logtransformed data (LN)	-8.046
Std. deviation of logtransformed data (LN)	2.441
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	11.486

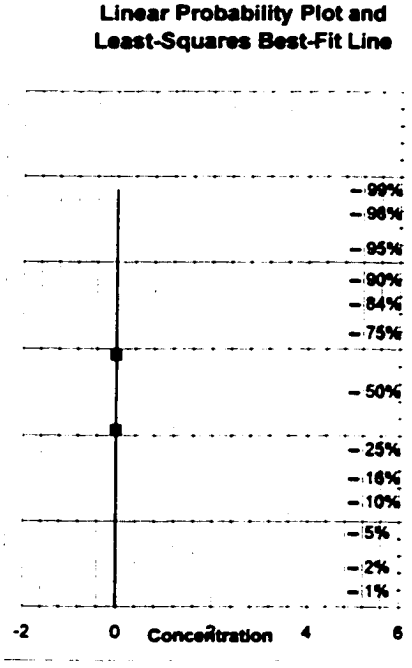
W-test of logtransformed data (LN)	1.000
Lognormal (α = 0.05)?	Yes
W-test of data	1.000
Normal (α = 0.05)?	Yes

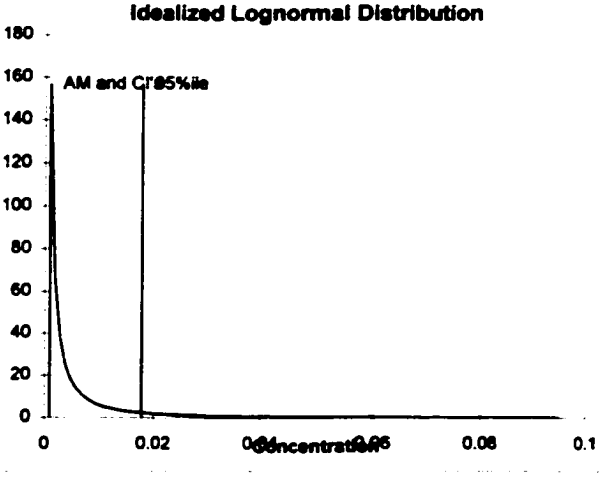
Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	#VALUE!
$UCL_{1,95\%}$ - Land's "Exact"	#VALUE!
95th Percentile	0.018
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	4.518
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	67.672

Mean	0.001
$LCL_{1,95\%}$ - t statistics	-0.005
$UCL_{1,95\%}$ - t statistics	0.006
95th Percentile - Z	0.003
$UTL_{95\%,95\%}$	#N/A
Percent above OEL (%>OEL)	0.000









Industrial Hygiene Statistics

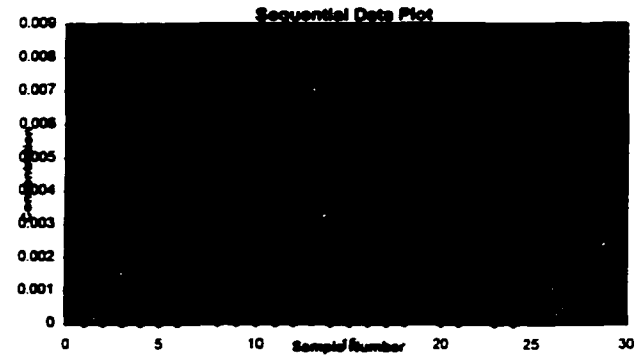
Data Description:

0.02
0.00005
0.00005
0.00005
0.00005
0.00005
0.00005
0.0078
0.00006
0.00006
0.00006
0.00006
0.00006
0.000098
0.000049
0.000049
0.000049
0.000049
0.000049
0.0012
0.000047
0.000047
0.0024
0.000047
0.000047

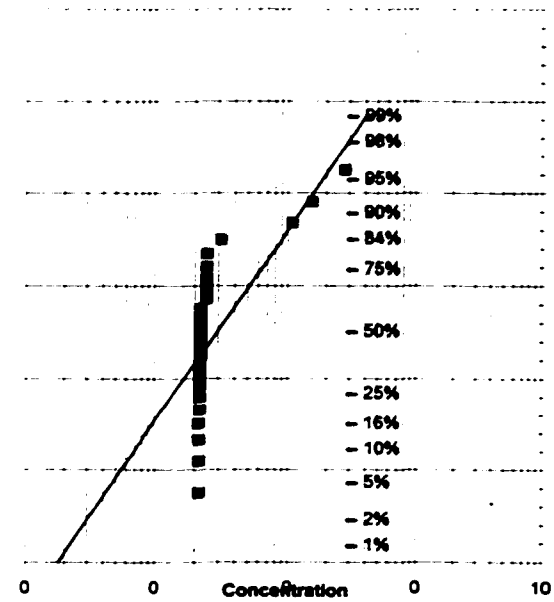
Number of samples (n)	24
Maximum (max)	0.0078
Minimum (min)	0.000047
Range	0.007753
Percent above OEL (%>OEL)	0.000
Mean	0.001
Median	0.000
Standard deviation (s)	0.002
Mean of logtransformed data (LN)	-9.348
Std. deviation of logtransformed data (LN)	1.380
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	3.976
W-test of logtransformed data (LN)	0.489
Lognormal (a = 0.05)?	No
W-test of data	0.333
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.000
$LCL_{1-95\%}$ - Land's "Exact"	0.000
$UCL_{1-95\%}$ - Land's "Exact"	0.001
95th Percentile	0.001
$UTL_{95\%,95\%}$	0.002
Percent above OEL (%>OEL)	0.004
$LCL_{1-95\%}$ %>OEL	<0.1
$UCL_{1-95\%}$ %>OEL	0.157

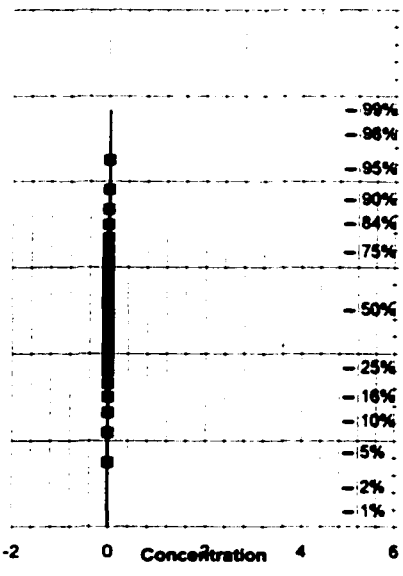
Mean	0.001
$LCL_{1-95\%}$ - t statistics	0.000
$UCL_{1-95\%}$ - t statistics	0.001
95th Percentile - Z	0.003
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



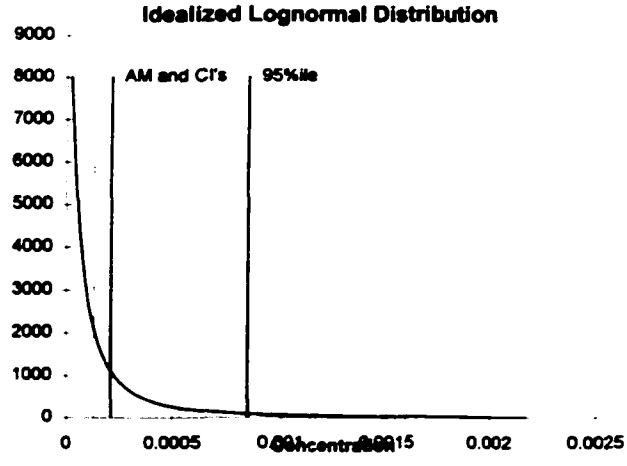
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.02	

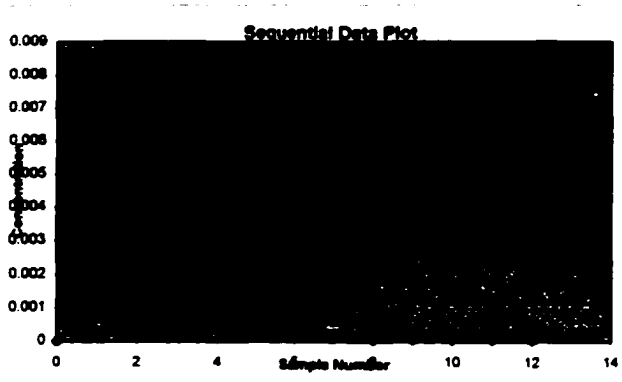
0.0078	
0.00006	
0.00006	
0.00006	
0.00006	
0.00006	

Number of samples (n)	6
Maximum (max)	0.0078
Minimum (min)	0.00006
Range	0.00774
Percent above OEL (%>OEL)	#REF!
Mean	0.001
Median	0.000
Standard deviation (s)	0.003
Mean of logtransformed data (LN)	-8.910
Std. deviation of logtransformed data (LN)	1.987
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	7.295

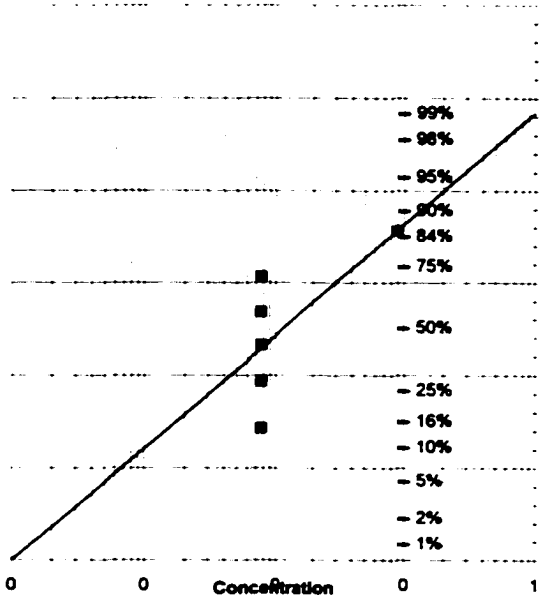
W-test of logtransformed data (LN)	0.496
Lognormal (a = 0.05)?	No
W-test of data	0.496
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.000
$UCL_{1,95\%}$ - Land's "Exact"	0.926
95th Percentile	0.004
$UTL_{95\%,95\%}$	0.214
Percent above OEL (%>OEL)	0.595
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	15.392

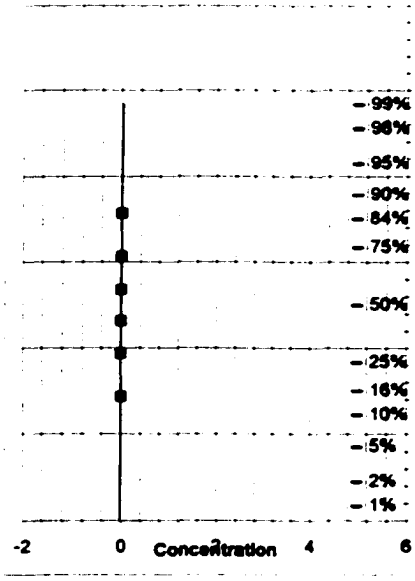
Mean	0.001
$LCL_{1,95\%}$ - t statistics	-0.001
$UCL_{1,95\%}$ - t statistics	0.004
95th Percentile - Z	0.007
$UTL_{95\%,95\%}$	0.01
Percent above OEL (%>OEL)	0.000



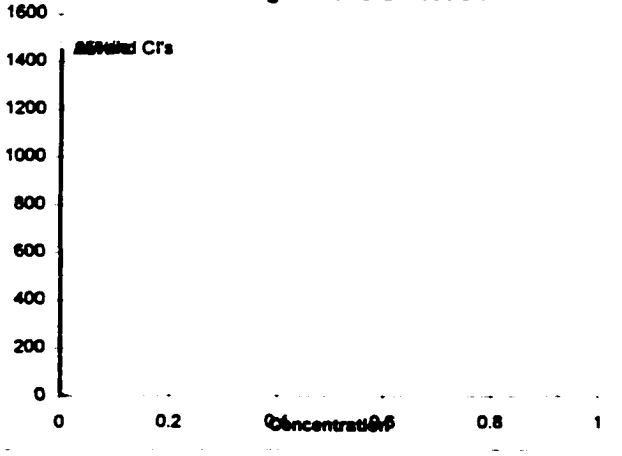
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.02

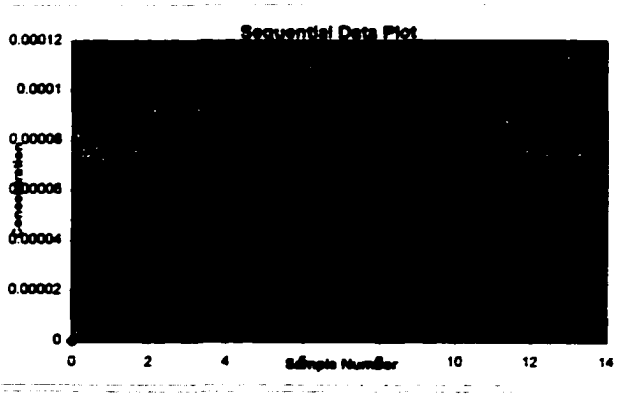
0.000098
0.000049
0.000049
0.000049
0.000049
0.000049

Number of samples (n)	6
Maximum (max)	0.000098
Minimum (min)	0.000049
Range	0.000049
Percent above OEL (%>OEL)	#REF!
Mean	0.000
Median	0.000
Standard deviation (s)	0.000
Mean of logtransformed data (LN)	-9.808
Std. deviation of logtransformed data (LN)	0.283
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	1.327

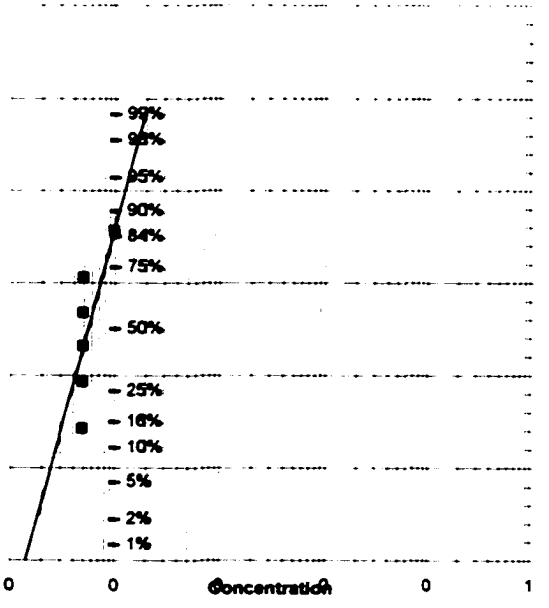
W-test of logtransformed data (LN)	0.496
Lognormal (a = 0.05)?	No
W-test of data	0.496
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.000
$LCL_{1,95\%}$ - Land's "Exact"	0.000
$UCL_{1,95\%}$ - Land's "Exact"	0.000
95th Percentile	0.000
$UTL_{95\%,95\%}$	0.000
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<0.263

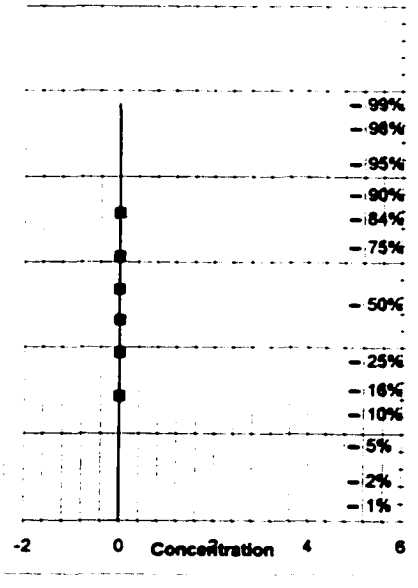
Mean	0.000
$LCL_{1,95\%}$ - t statistics	0.000
$UCL_{1,95\%}$ - t statistics	0.000
95th Percentile - Z	0.000
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



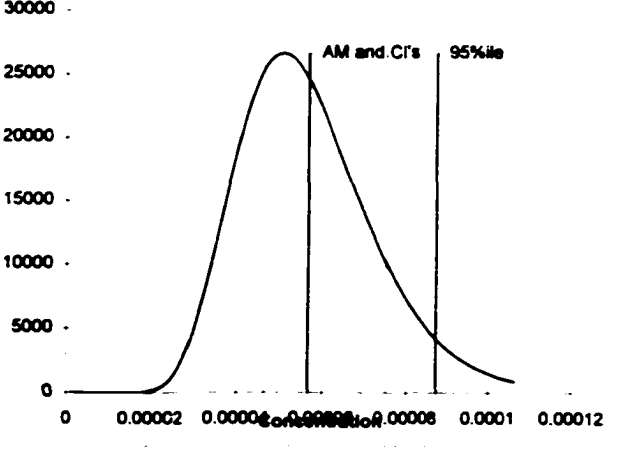
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



Industrial Hygiene Statistics

Data Description:

0.02

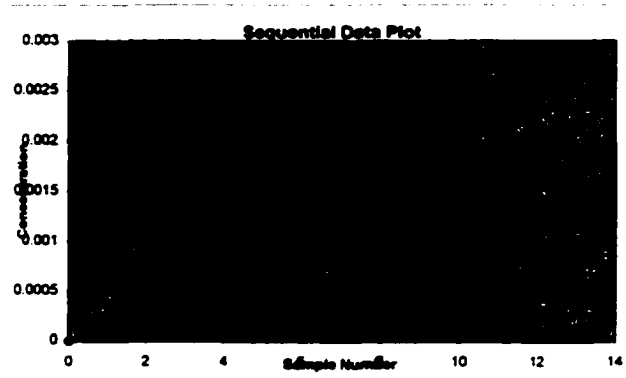
0.0012
0.000047
0.000047
0.0024
0.000047
0.000047

Number of samples (n)	6
Maximum (max)	0.0024
Minimum (min)	0.000047
Range	0.002353
Percent above OEL (%>OEL)	#REF!
Mean	0.001
Median	0.000
Standard deviation (s)	0.001
Mean of logtransformed data (LN)	-6.770
Std. deviation of logtransformed data (LN)	1.865
Geometric mean (GM)	0.000
Geometric standard deviation (GSD)	6.456

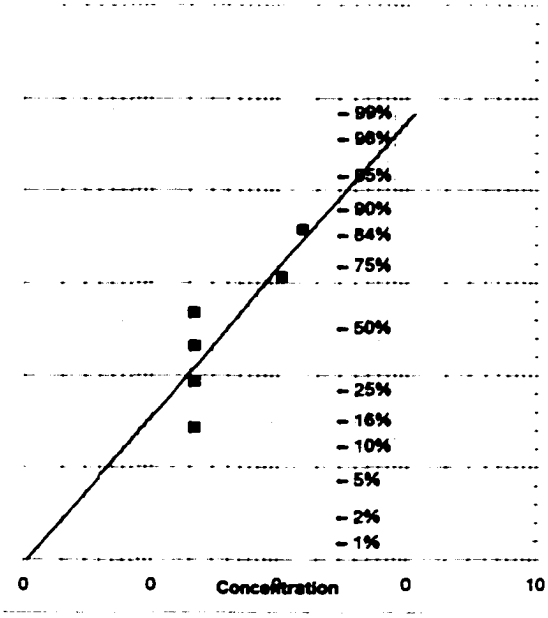
W-test of logtransformed data (LN)	0.691
Lognormal (a = 0.05)?	No
W-test of data	0.708
Normal (a = 0.05)?	No

Estimated Arithmetic Mean - MVUE	0.001
$LCL_{1,95\%}$ - Land's "Exact"	0.000
$UCL_{1,95\%}$ - Land's "Exact"	0.377
95th Percentile	0.003
$UTL_{95\%,95\%}$	0.156
Percent above OEL (%>OEL)	0.460
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	14.271

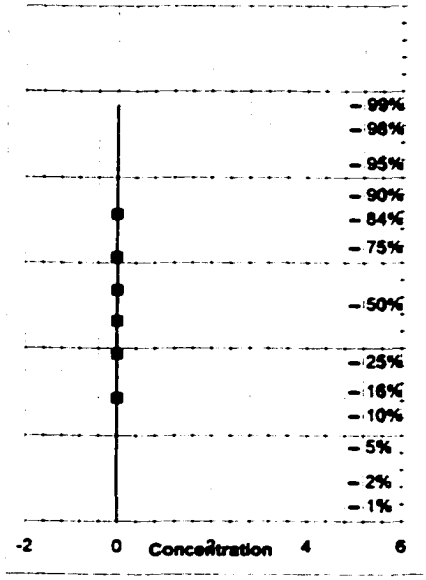
Mean	0.001
$LCL_{1,95\%}$ - t statistics	0.000
$UCL_{1,95\%}$ - t statistics	0.001
95th Percentile - Z	0.002
$UTL_{95\%,95\%}$	0.00
Percent above OEL (%>OEL)	0.000



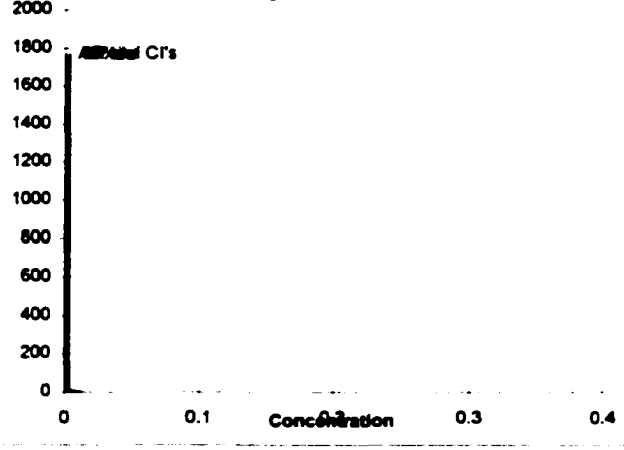
Logprobability Plot and Least-Squares Best-Fit Line



Linear Probability Plot and Least-Squares Best-Fit Line



Idealized Lognormal Distribution



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