Industrial Hygiene Sampling

Exposure Assessment

Sept 13, 2007

Objectives

- Introduce “Industrial Hygiene”
- Establish context with respect to Risk Assessment
- Overview of Sampling
  - Purpose
  - Methods
  - Data
- Implications

Industrial Hygiene Definition

- ***Industrial Hygiene:*** *Science and art devoted to the anticipation, recognition, evaluation, prevention, and control of those environmental factors or stresses arising in or from the workplace which may cause sickness, impaired health and well being, or significant discomfort among workers or among citizens of the community.*

Industrial Hygiene

- Sometimes referred to as “occupational “ hygiene (e.g. UK)
- Predates “Risk Assessment” as defined by NAS
- Combines elements of Risk Assessment

Comparison IH and Risk Assessment

Industrial Hygiene	**Risk Assessment**
Anticipation and Recognition	Hazard Identification
Evaluation	Toxicity and Exposure Assessment and Risk Characterization
Control	Risk Management
Hazard Communication	Risk Communication

Industrial Hygiene Exposure

- Industrial Hygiene focus is on exposure assessment
  - Historically the occupational environment
  - Expanded to home and community

Note: As the applications of exposure data grew in various fields, many new “specialties” formed (i.e. environmental engineering, radiation safety, risk assessment etc) and separated from Public Health

Evaluation -
Air Sampling and Analysis

“ The purpose of industrial hygiene sampling is to represent the important components to the physiology of the worker and not to demonstrate the prowess of the chemist”

Paraphrase from Hatch

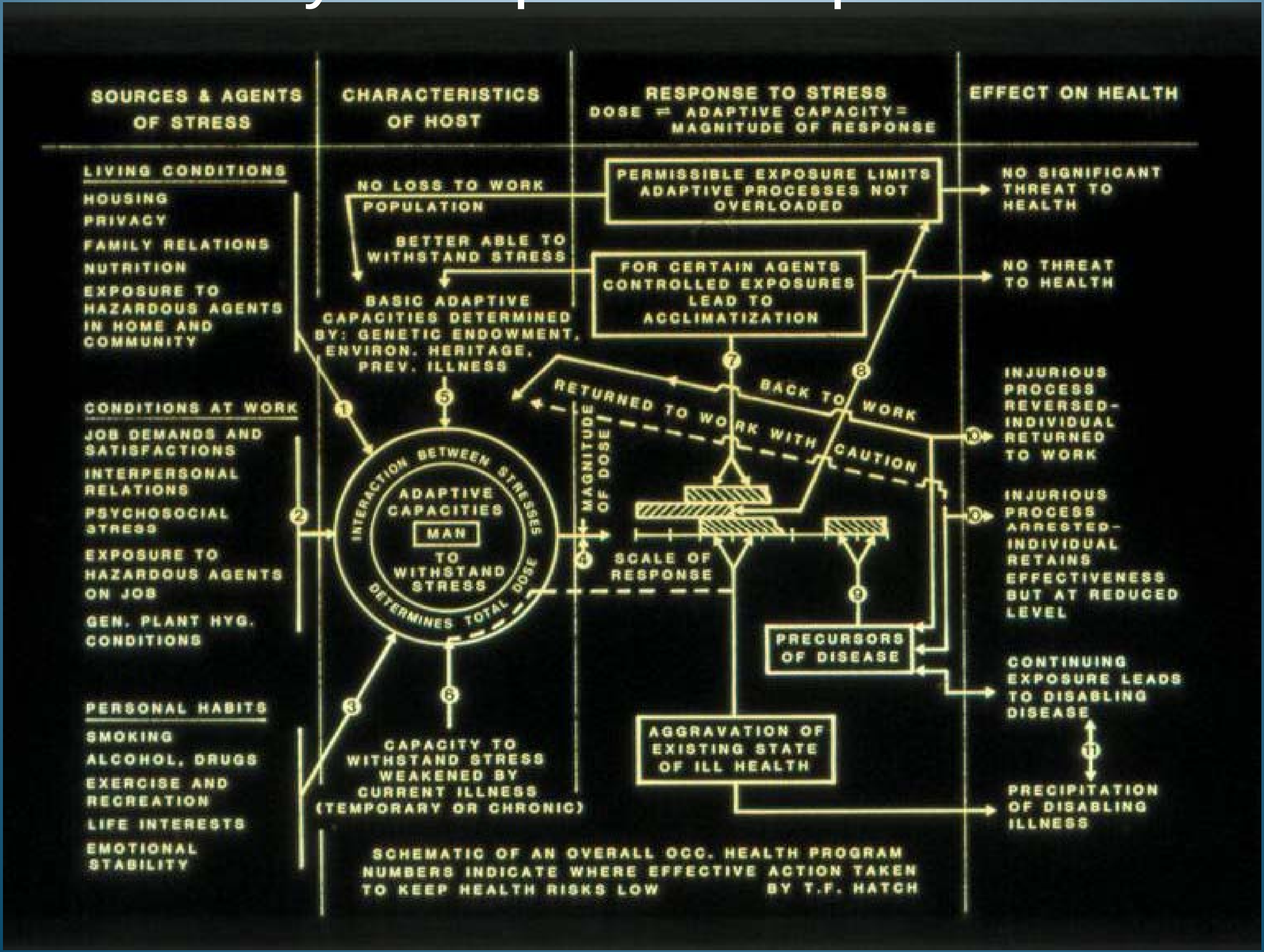
Exposure Assessment Overview

- Exposure Assessment is NOT universally defined by users
- Exposure is not DOSE but seeks to estimate it
- Approaches and examples
  - Exposure Assessment in “Risk Assessment”
  - Occupational settings

Evolution of Exposure Assessment

- 1920's
  - Occupational Exposures began to be quantified and related to workplace health (risk)
  - Result- Exposure limit values
- 1950,60's
  - Environmental concerns, air and water pollution
  - Waste site Clean-up
- 1983
  - NAS "Risk Assessment Paradigm
  - "RAGS"

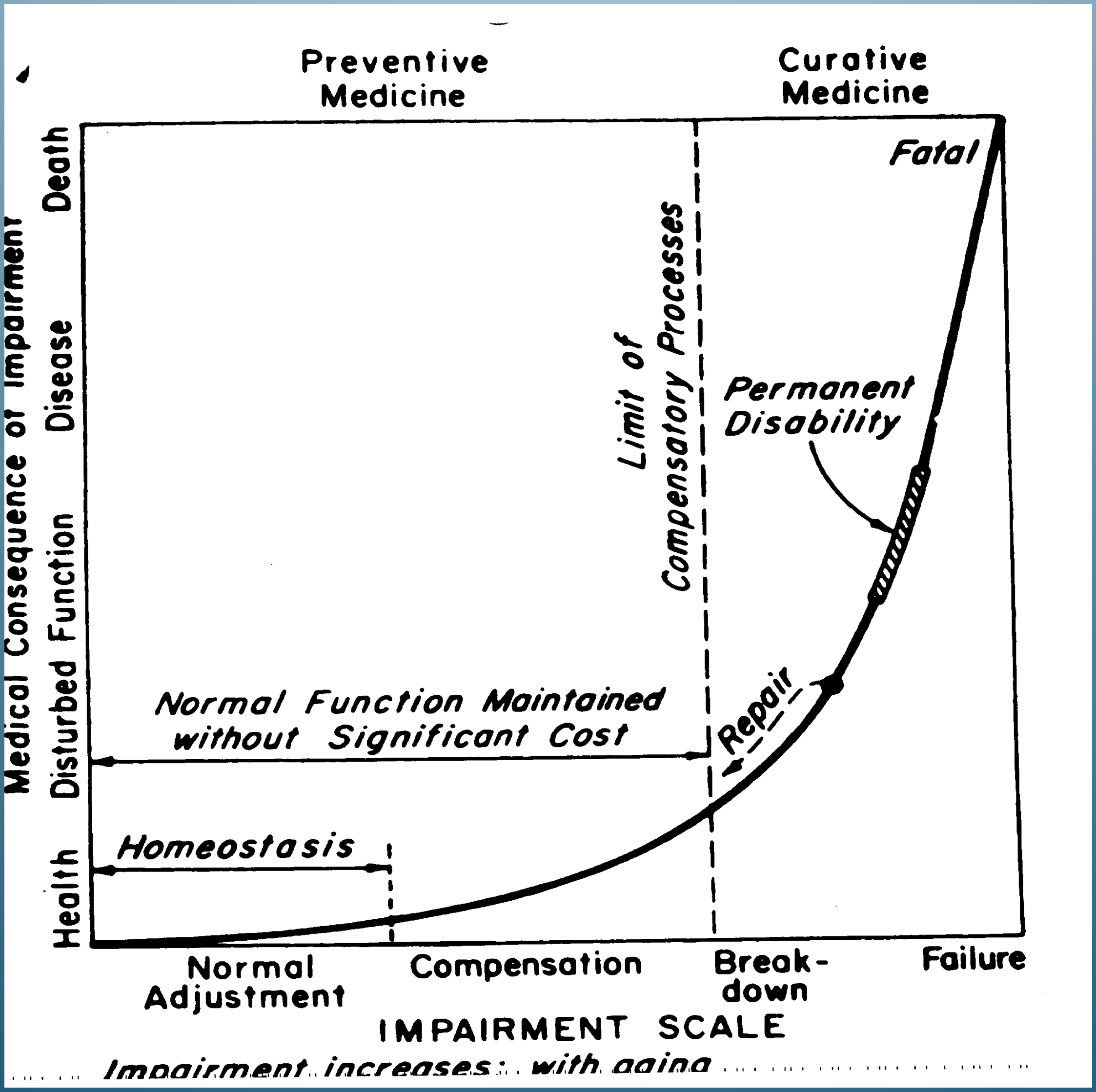
Why is Exposure Important?



SCHEMATIC OF AN OVERALL OCC. HEALTH PROGRAM
NUMBERS INDICATE WHERE EFFECTIVE ACTION TAKEN TO KEEP HEALTH RISKS LOW
BY T.F. HATCH

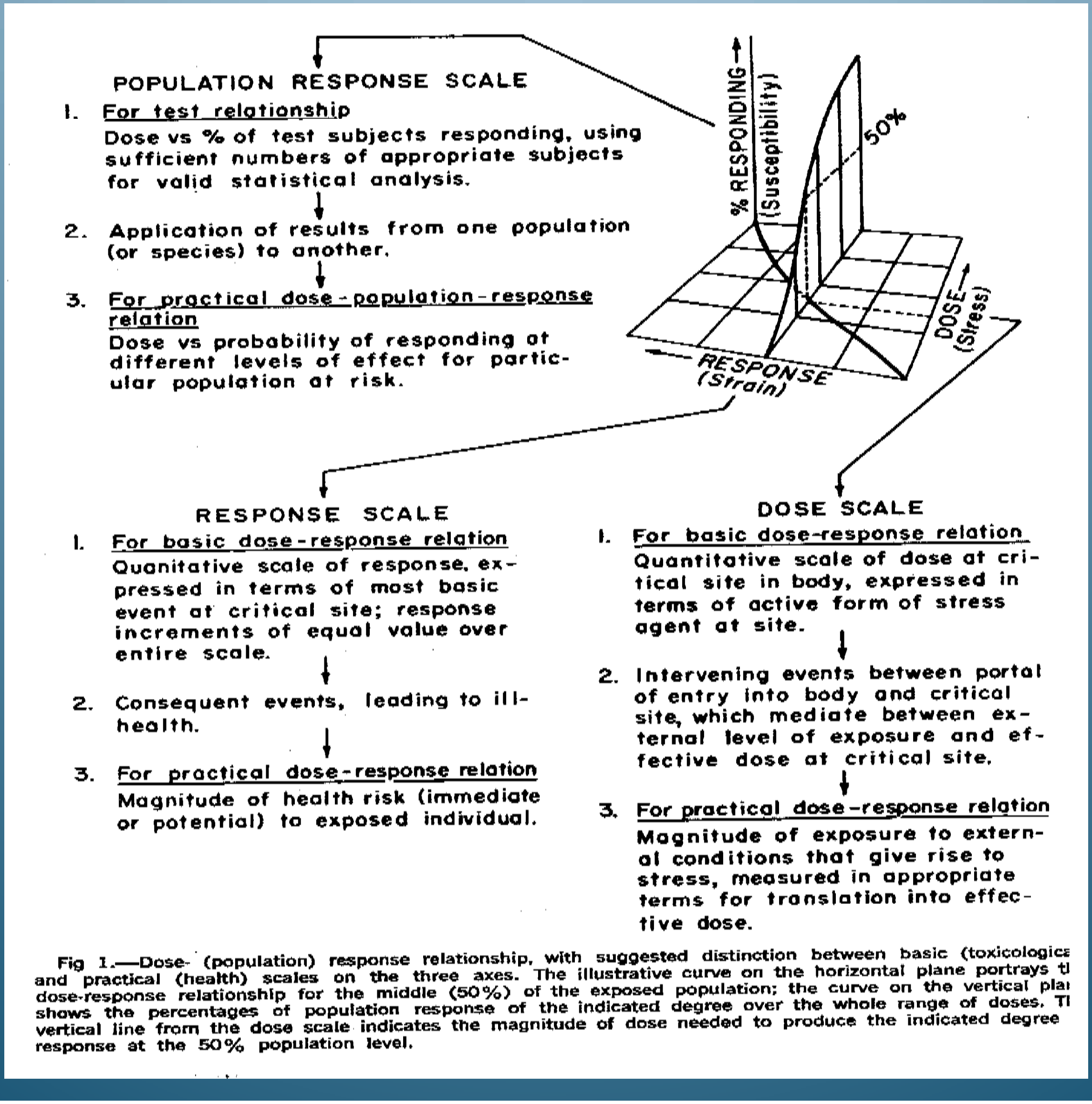
Hatch

Exposure Assessment Goal



We can also consider Impairment as a function of increasing DOSE

Putting It All Together



POPULATION RESPONSE SCALE

1. For test relationship

Dose vs % of test subjects responding, using sufficient numbers of appropriate subjects for valid statistical analysis.

2. Application of results from one population (or species) to another.

3. For practical dose - population - response relation

Dose vs probability of responding at different levels of effect for particular population at risk.

RESPONSE SCALE

1. For basic dose - response relation

Quanitative scale of response, expressed in terms of most basic event at critical site; response increments of equal value over entire scale.

2. Consequent events, leading to ill-health.

3. For practical dose - response relation

Magnitude of health risk (immediate or potential) to exposed individual.

DOSE SCALE

1. For basic dose-response relation

Quantitative scale of dose at critical site in body, expressed in terms of active form of stress agent at site.

2. Intervening events between portal of entry into body and critical site, which mediate between external level of exposure and effective dose at critical site.

3. For practical dose-response relation

Magnitude of exposure to external conditions that give rise to stress, measured in appropriate terms for translation into effective dose.

Fig 1.—Dose- (population) response relationship, with suggested distinction between basic (toxicologic and practical (health) scales on the three axes. The illustrative curve on the horizontal plane portrays t dose-response relationship for the middle (50%) of the exposed population; the curve on the vertical pla shows the percentages of population response of the indicated degree over the whole range of doses. T vertical line from the dose scale indicates the magnitude of dose needed to produce the indicated degree response at the 50% population level.

United States
Environmental Protection
Agency

Exposure Assessments typically include:

- Occupational exposures in the workplace,
- Exposures to the general population from chemicals in the air and drinking water,
- Consumer exposure through the household use of products, and
- Environmental exposure to aquatic life.

An EXPOSURE ASSESSMENT attempts to answer the following questions for a particular substance or chemical:

- WHO or WHAT is exposed (e.g., people, aquatic ecosystems, animals)?
- WHAT IS THE ROUTE of Exposure: Does the exposure occur through breathing air, drinking water, skin contact or any other routes?
- HOW MUCH exposure occurs?
- HOW OFTEN and FOR HOW LONG does exposure occur, that is, what is its frequency and duration ?

An EXPOSURE ASSESSMENT attempts to answer the following questions for a particular substance or chemical:

- WHO or WHAT is exposed?
  - Humans, animals
- WHAT IS THE ROUTE of Exposure?
  - Ingestion, Inhalation, Dermal
- HOW MUCH exposure occurs?
  - Concentration of Chemical [mg/L or mg/kg]
- HOW OFTEN and FOR HOW LONG:
  - Frequency and Duration of Contact [TIME]

Exposure Measurement

- Measurement at the point of contact while exposure occurs
- Estimation from a scenario that evaluates contact variables
- Estimated from biomarkers related to uptake

EPA Exposure Assessment Guideline

Point of Contact Measurements

- Advantages-
  - Direct
  - Accounts for micro environmental variables
  - Specific to activity level
  - Direct relationship to biomarkers
  - Preferred over models
- Disadvantages
  - Subject to analytical prowess
  - Models can be incomplete or highly complex
  - Must be comprehensive or extrapolated to others
  - COST

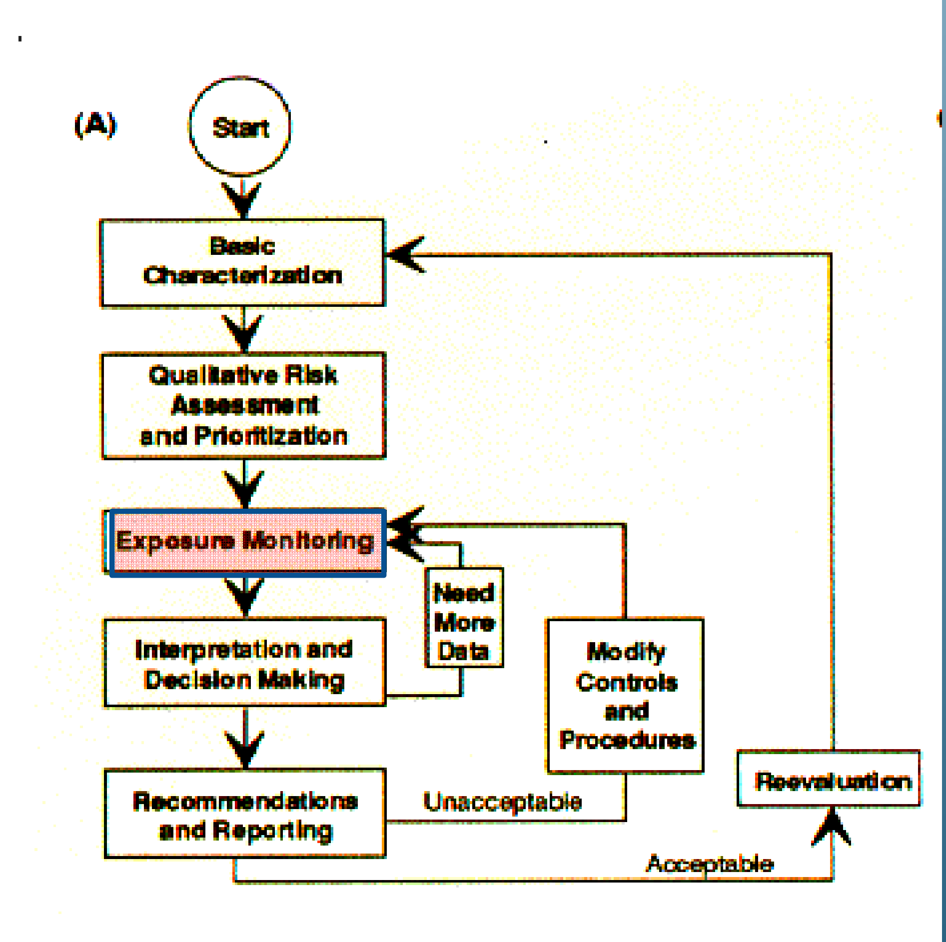
Industrial Hygiene Sampling Unique Value

- Representative monitoring data is preferred over models
- Industrial Hygiene data gathering has a long history and extensive technology
- Relates specifically to “exposure limit values” (TLV, PEL, OEL)
- Relates to historical biomarker information (Biological Exposure Indices – BEI)

IH DATA METRICS

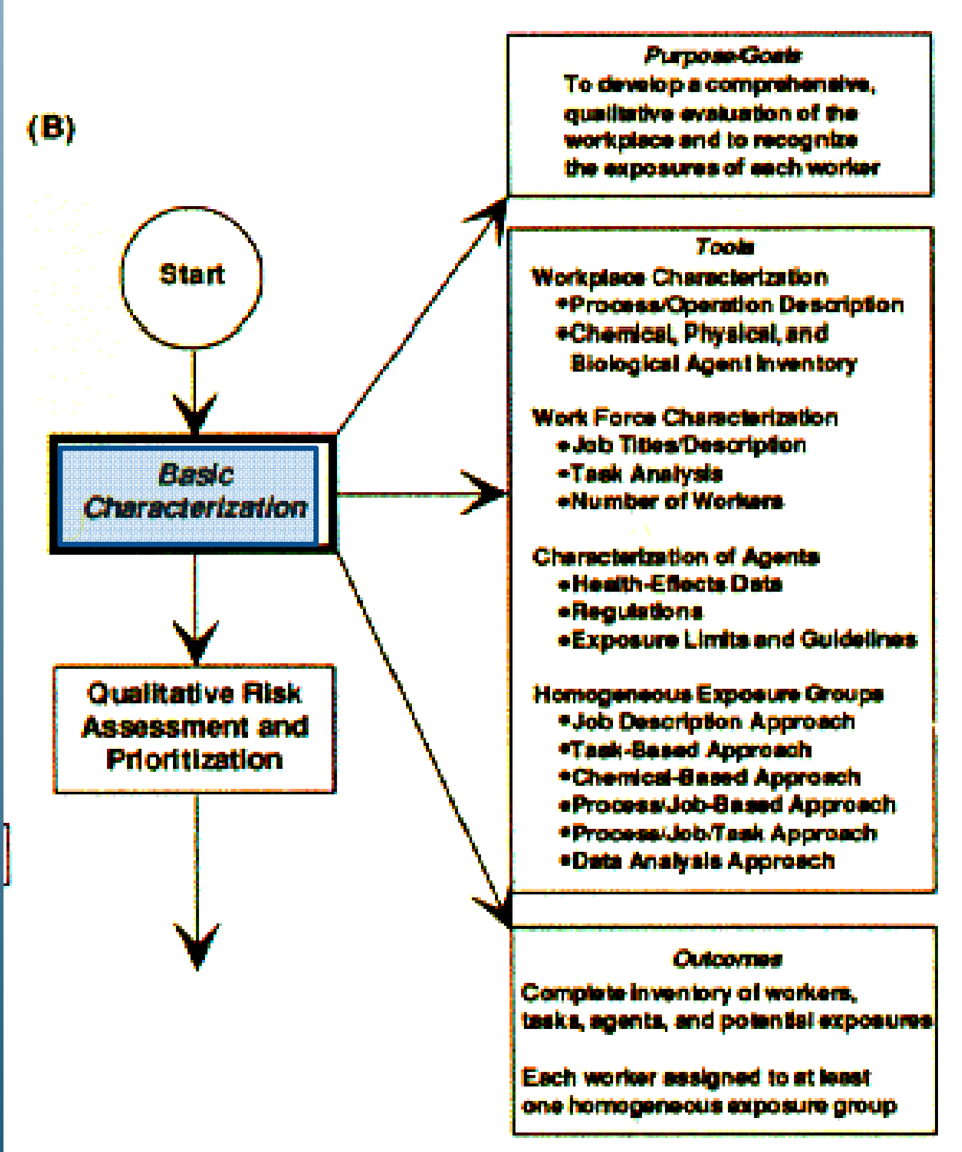
- Time-weighted average
- Peak Exposure
- Short-term exposure
- Units
  - Ppm v/v in air
  - Mg /M3
  - Historical mmpcf

Exposure Assessment Strategy – IH Paradigm



AIHA Guidelines

Exposure Assessment Strategy – IH Paradigm



(B)

Start

Basic Characterization

Qualitative Risk Assessment and Prioritization

Purpose/Goals

To develop a comprehensive, qualitative evaluation of the workplace and to recognize the exposures of each worker

Tools

Workplace Characterization
- Process/Operation Description
- Chemical, Physical, and Biological Agent Inventory

Work Force Characterization
- Job Titles/Description
- Task Analysis
- Number of Workers

Characterization of Agents
- Health-Effects Data
- Regulations
- Exposure Limits and Guidelines

Homogeneous Exposure Groups
- Job Description Approach
- Task-Based Approach
- Chemical-Based Approach
- Process/Job-Based Approach
- Process/Job/Task Approach
- Data Analysis Approach

Outcomes

Complete inventory of workers, tasks, agents, and potential exposures

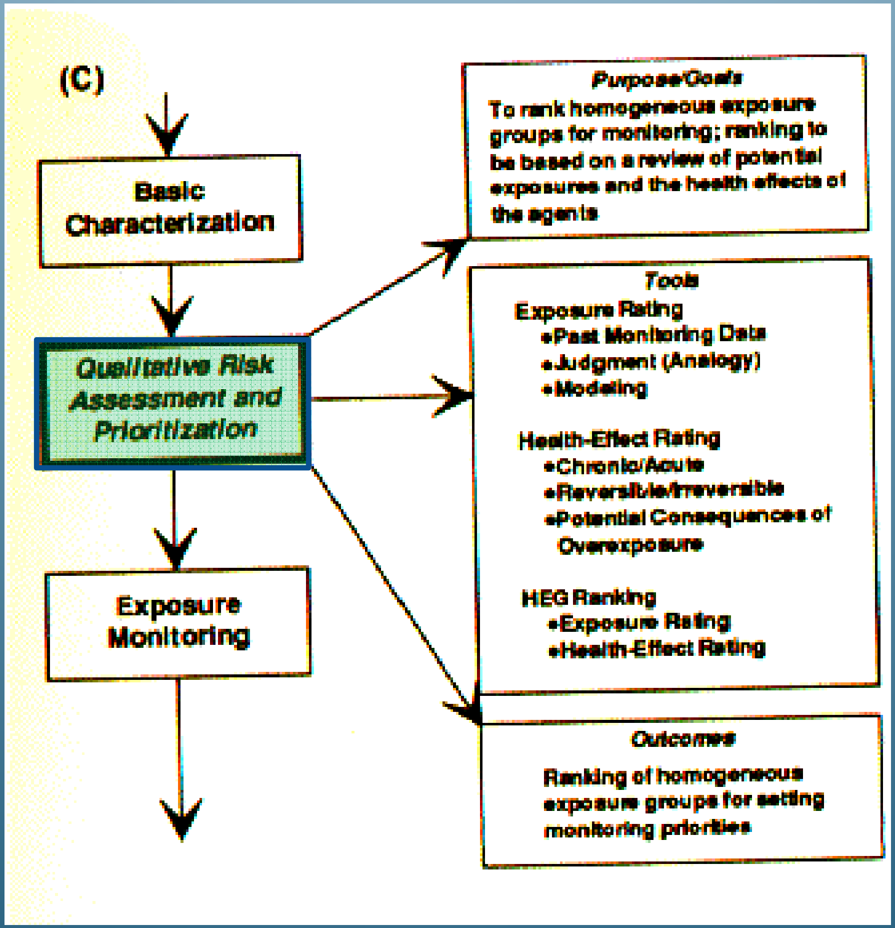
Each worker assigned to at least one homogeneous exposure group

Some Exposure Variables

- Acute Exposure
- Chronic Exposure
- Source of the Agent
- Pathway for Exposure

Exposure Assessment Strategy

Terminology →



Purpose/Goals

To rank homogeneous exposure groups for monitoring; ranking to be based on a review of potential exposures and the health effects of the agents

Tools

Exposure Rating
- Past Monitoring Data
- Judgment (Analogy)
- Modeling

Health-Effect Rating
- Chronic/Acute
- Reversible/Irreversible
- Potential Consequences of Overexposure

HEG Ranking
- Exposure Rating
- Health-Effect Rating

Outcomes

Ranking of homogeneous exposure groups for setting monitoring priorities

Occupational Exposures

- “Often” air mediated – emphasis on “air sampling
- Usually a substantial dermal component that is not readily characterized
- “Skin notation”

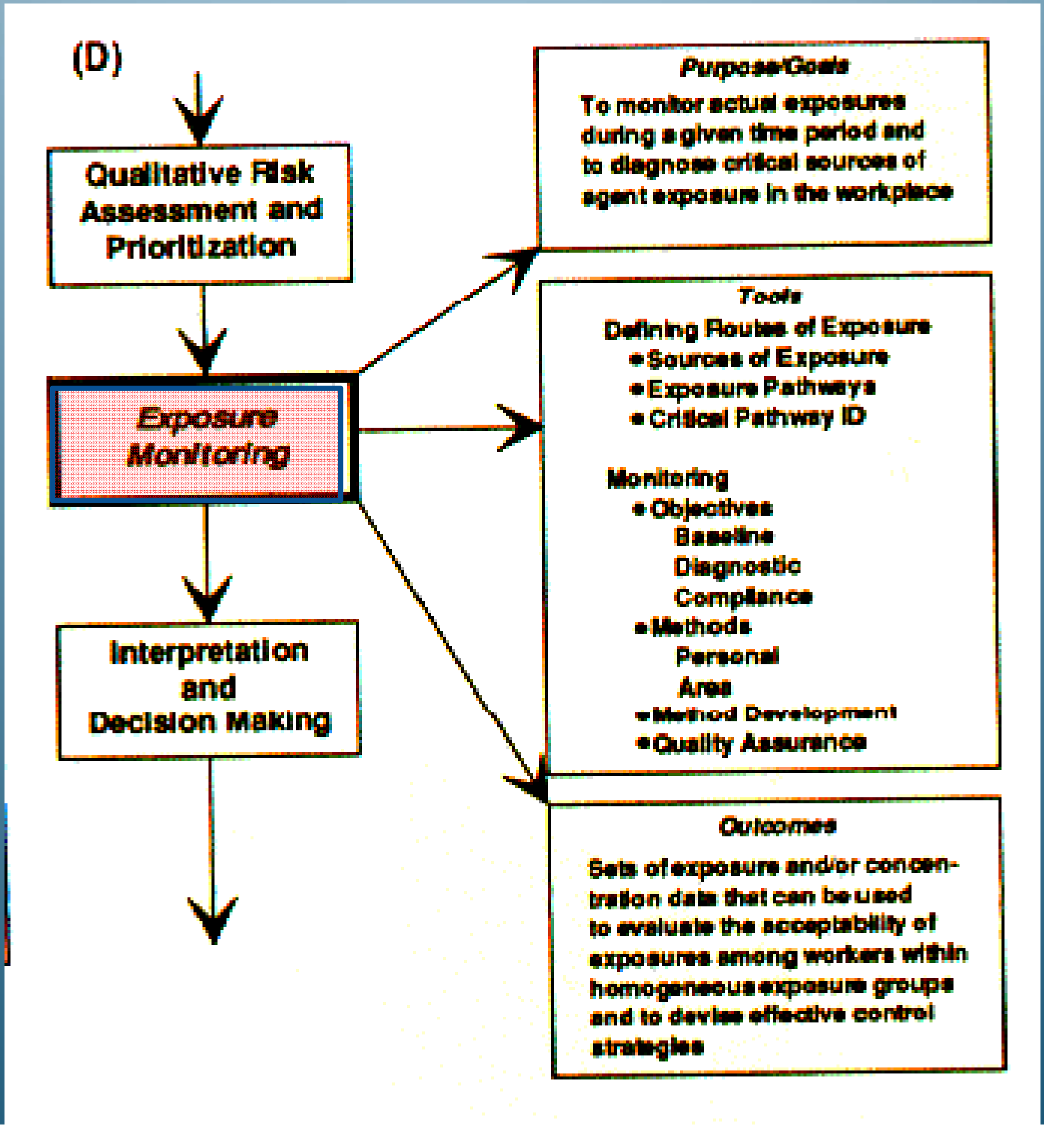
STATES OF MATTER

- Dust
- Fume
- Mist
- Vapor
- Gas
- Aerosol

Walk Through Survey

- Become familiar with plant processes
- ID process chemicals and materials,
- Observe worker activities
- ID and examine existing exposure controls
- Start data collection record

Exposure Assessment Strategy
Industrial Hygiene Monitoring



Qualitative Risk Assessment and Prioritization

Exposure Monitoring

Interpretation and Decision Making

Purpose/Goals

To monitor actual exposures during a given time period and to diagnose critical sources of agent exposure in the workplace

Tools

Defining Routes of Exposure
- Sources of Exposure
- Exposure Pathways
- Critical Pathway ID

Monitoring
- Objectives
  - Baseline
  - Diagnostic
  - Compliance
- Methods
  - Personal
  - Area
- Method Development
- Quality Assurance

Outcomes

Sets of exposure and/or concentration data that can be used to evaluate the acceptability of exposures among workers within homogeneous exposure groups and to devise effective control strategies

SAMPLE ?

- Why sample?
- Who to sample?
- Where to sample?
- What to sample for?
- When to sample?
- How long to sample?

Evaluation of Workplace Hazards – Characterization of the Environment

OBJECTIVES OF AIR SAMPLING (WHY)

- Workplace Characterization
- Investigate employee complaints
- Effectiveness of engineering controls
- Effectiveness of administrative controls
- Maintain a history of worker exposure

Step #2: Selecting Air Sampling Methods

- Inventory Chemicals / Agents to which workers are exposed
- Number of employees to be evaluated
- Frequency of cyclic work process
- Duration of exposure(s)

Step #2: Selecting Air Sampling Methods

- Consistency of exposures
- Mobility of workers in relation to process
- Control measures in effect
- Employee break and lunch habits

Step #3-Determine Relevant Exposure Factors

Acute Effects

Sub-Acute

Chronic

1. 8-hour time-weighted averages (TWAs)
2. Short-Term Exposure Limits (STELs)
3. Ceiling Values
4. Life-Weighted Average

Step #4: Selecting Air Sampling Equipment

- Personal Monitors (preferred)
- Area Samples (Zones)
- Dust ,Fume, Mist, Gas or Vapor
- Direct Reading Instrument
- Detector Tubes
- Diffusion Badges
- Sample Collection Media

Sampling Selection Criteria

COMPREHENSIVE
CONVENIENT
COST EFFECTIVE

SENSITIVE

SELECTIVE

RAPID

Comprehensive

☐ **SENSITIVE TO ALL CONTAMINANTS THAT COULD RESULT IN ADVERSE HEALTH EFFECTS.**

Convenient

- ☐ PORTABLE, RUGGED and QUIET
- ☐ EASILY WORN WITHOUT CHANGES IN NORMAL BEHAVIOUR
- ☐ LOW POWER CONSUMPTION
- ☐ BATTERY OPERATED
- ☐ STABILIZATION TIME < 15 minutes
- ☐ TEMPERATURE RANGE -20^{o} to 40^{o} C
- ☐ HUMIDITY RANGE 0 - 100 %

Cost Effective

☐ NOT PROHIBITIVE TO BUY
☐ INEXPENSIVE TO OPERATE
☐ READILY AVAILABLE COMPONENTS
☐ FEW CONSUMABLE PARTS
☐ LOW MAINTENANCE

Sensitive

- LoD < HEALTH EFFECTS LEVEL
- 0.1 TIMES LEVEL OF INTEREST
- RANGE 0.1 - 10 X LEVEL OF INTEREST
- PRECISION AND ACCURACY +/- 5%
- EASY AND ACCURATE CALIBRATION

Selective

- **LIMITED RESPONSE TO CHEMICALLY SIMILAR COMPOUNDS PRESENT WITH ANALYTE OF INTEREST**

Rapid

- ☐ SHORTER SAMPLING AND ANALYSIS TIMES COMPARED WITH BIOLOGICAL RESPONSE
- ☐ FAST RESPONSE TO CONCENTRATION CHANGES
- ☐ RESPONSE TIME 90% < 30 seconds
- ☐ RS-232 OR EQUIVALENT OUTPUT

Step #5: Establish Sampling Protocol

QUESTIONS TO BE ANSWERED

☐ **Data to be collected (who, what)**
☐ **Location to sample (where)**
☐ **Time to sample (when)**
☐ **Collection technique (how)**
☐ **Analytical technique (how)**
☐ **Number of samples (how many)**
☐ **Data analysis techniques (what kind)**

Personal Monitors

ADVANTAGES

☐ **Measure contaminant at or near breathing zone**

☐ **Worn by an individual during their daily activities**

☐ **Provides an integrated measure of exposure**

☐ **Useful in epidemiological studies**

Personal Monitors

DISADVANTAGES

- Collecting a sufficient mass of specific contaminants
- Specific, detailed sampling and analytical methods must be developed to characterize chemicals
- Time Delay in receiving analytical results from lab
- Sampler size and weight and fragility
- Worker may be reluctant to wear sampler
- Test equipment may alter workers routine

Step #6-Consult With a Qualified Laboratory

A qualified analytical laboratory can assist you in choosing sampling methods most appropriate to the environment being sampled.

Step #7-Choose An Approved Air Sampling Method

US AGENCIES THAT PUBLISH AIR SAMPLING METHODS

- National Institute for Occupational Safety and Health (NIOSH)
- Occupational Safety and Health Administration (OSHA)
- Environmental Protection Agency (EPA)

Step #8-Contact Lab For Additional Assistance

- Lab Catalogs often contains air sampling guides that summarize sampling methods for individual chemicals published by NIOSH, OSHA and EPA.
- All critical parameters such as exposure limits, recommended sampling time, flow rate and air volume are listed.
- Collection media is clearly specified.

Step #9-Choose Your Equipment

An IH utilizes all resources available to determine the best air sampling method. Several methods may be required in the same workplace.

- Active Samplers
  - Air Sampling Pumps
  - Pump Flowmeters (Calibrators)
  - Collection Media
- Passive Samplers
  - Diffusion badges

ACTIVE SAMPLING

…is the collection of airborne hazards by means of a forced movement of air by an air sampling pump through the appropriate sampling media. The pump is used to collect and/or concentrate the chemical of interest onto the sampling media.

THREE KEY ELEMENTS OF ACTIVE SAMPLING

- A sampling pump

Something to pull or push air

- The sampling media

Something to pull or push the air through

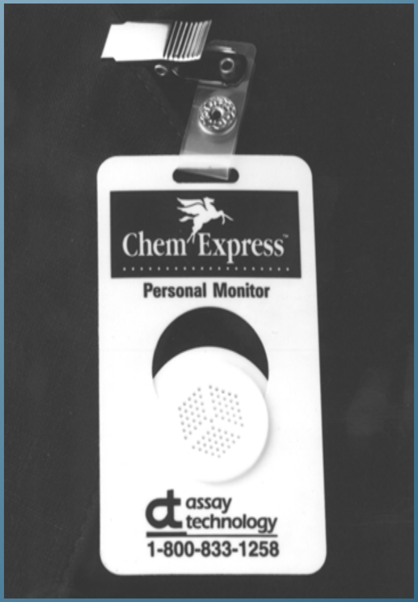
- A calibrator

Something to indicate how much air has been pulled or pushed

PASSIVE SAMPLING

...is defined as the collection of airborne gases and vapors at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane WITHOUT the active movement of air through an air sampling pump.

Types of Passive Samplers

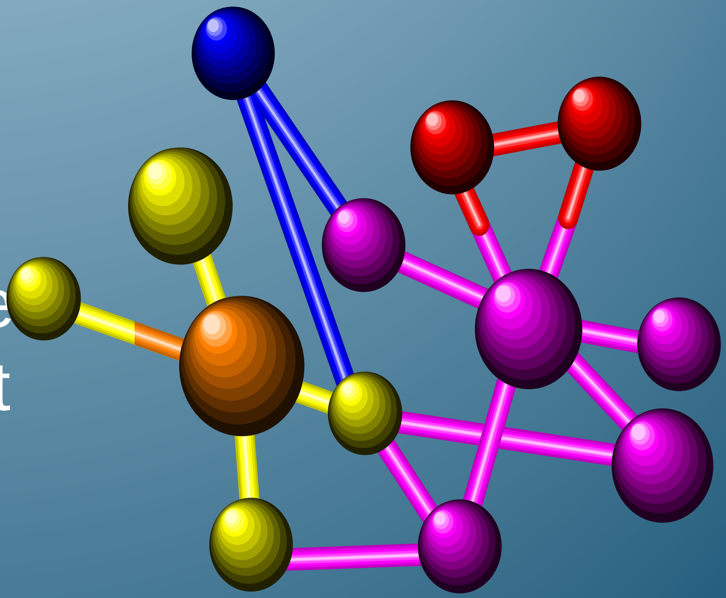


Organic Vapor Sampler
Aldehyde Sampler

Inorganic Mercury Sampler

MOST PASSIVE SAMPLERS OPERATE BY DIFFUSION.

Diffusive samplers rely on the movement of contaminant molecules across a concentration gradient which can be defined by Fick's First Law of Diffusion.



IN OTHER WORDS...

Chemicals will diffuse from an area of high concentration in the air to an area of low concentration on the sampler and the rate of diffusion for individual chemicals can be determined.

WHEN CHOOSING A PASSIVE SAMPLER

- Be sure that it has been tested and verified to work effectively for the chemical of interest. Otherwise, you should use a validated active sampling method for compliance purposes.
- Be sure to note the sampling rate in ml/min given by the supplier along with the minimum and maximum sampling times.

TO COLLECT A PASSIVE SAMPLE

- Simply open the sampler at the sampling site and attach it to the worker in the breathing zone or hang in an area.
- It is important that there be some degree of air movement at the sampling site. Placement of the sampler in stagnant air will cause “starvation” and will cause low results to occur.

Read On for Further Information

The following sections describe sampling using a variety of sampling media:

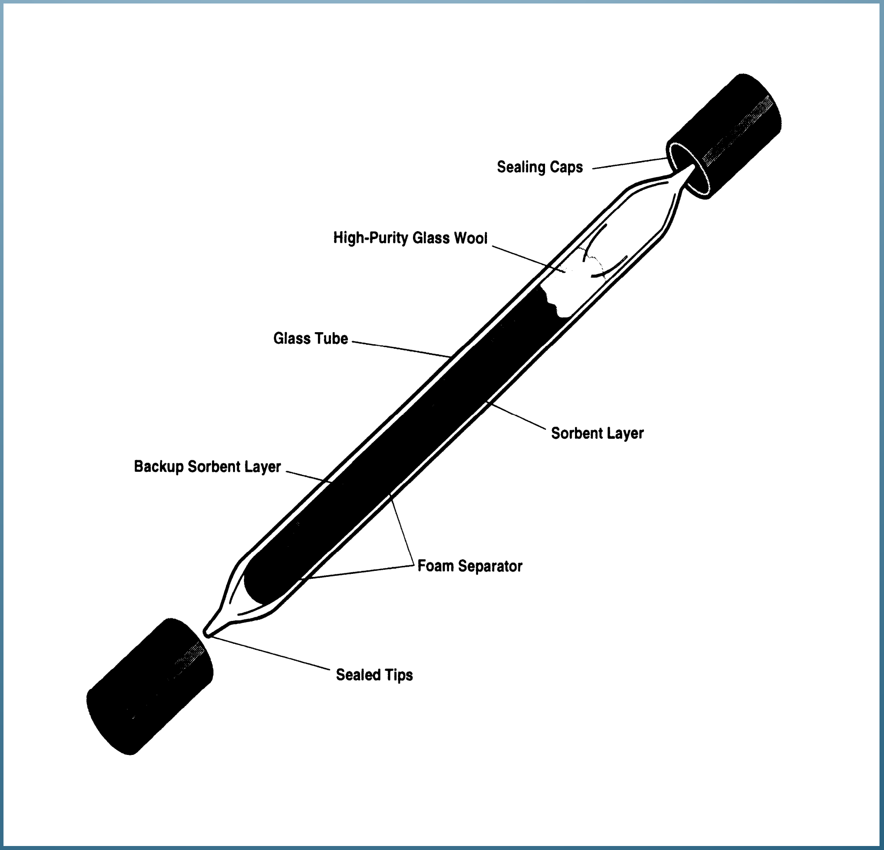
- Sorbent Tube
- Filters
- Impingers
- Sampling Bags
- Passive Samplers

ACTIVE SAMPLING OF GASES AND VAPORS

Many sampling methods require the use of sorbent tubes for sampling gases and vapors.

A sorbent tube is a small glass tube normally filled with two layers of a solid sorbent material.

Sorbent Sample Tube With Backup Sorbent Layer



COMMON SORBENT MATERIALS

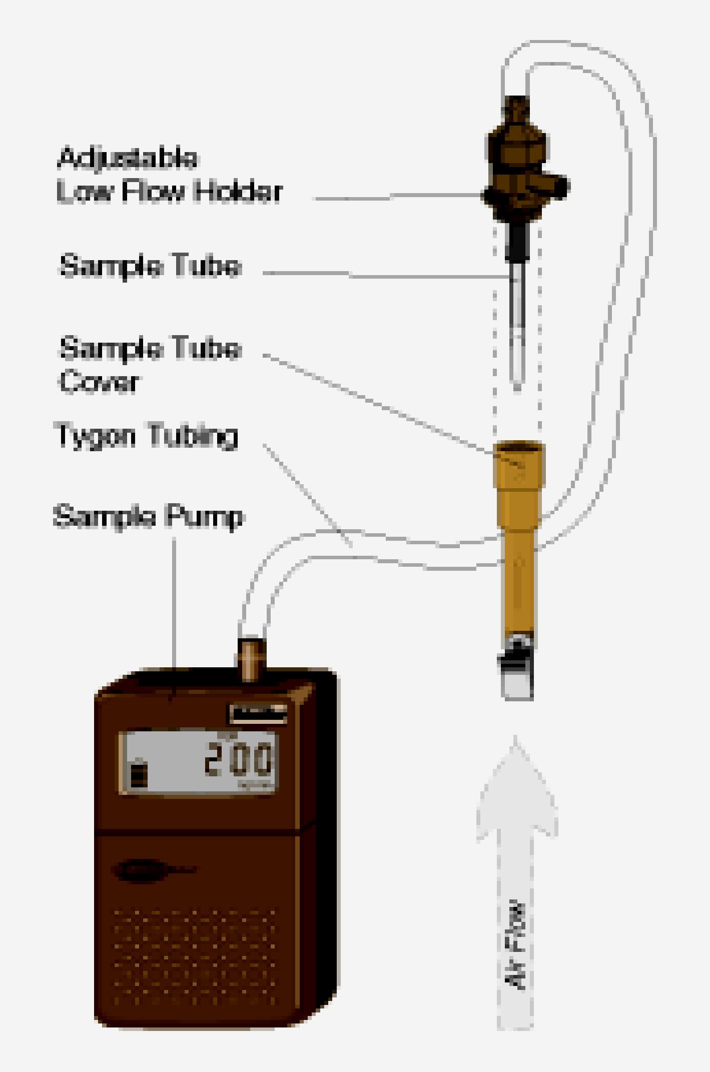
- Activated Charcoal
- Silica Gel
- Tenax
- XAD-2
- Chromosorbs

The sorbent used to collect specific chemicals will be specified in the sampling method.

TO COLLECT A SAMPLE WITH SORBENT TUBES

- The end tips of the tube are broken and a known volume of air is drawn through the tube using an air sampling pump that has been calibrated to the flow rate specified in the sampling method.
- Airborne chemicals are trapped by the first layer with the back-up layer assuring complete removal of chemicals from the air.

SORBENT TUBE SAMPLING TRAIN



OSHA Versatile Samplers

A Breakthrough for Multi-Phase Sampling

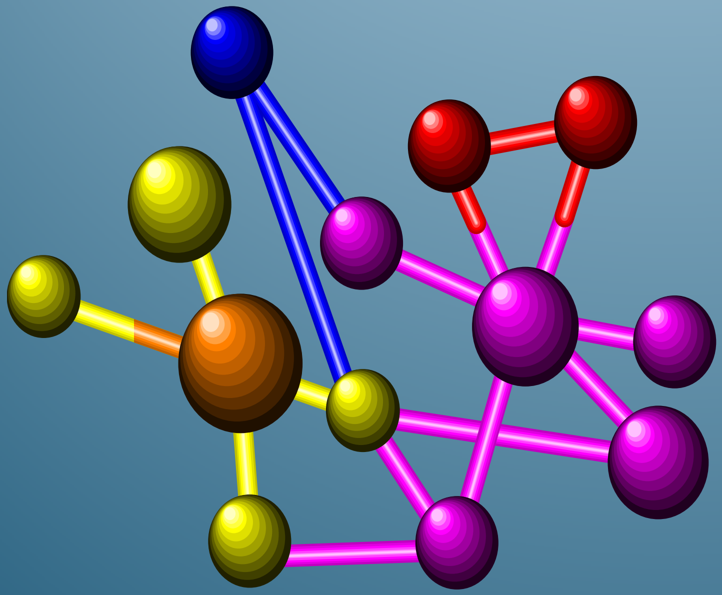
- Sorbent and Filter combined in one tube
- Collects vapors and aerosols
- Available with a variety of sorbents
- For pesticides, TNT, DNT, and phthalates

Multiple Bed Tubes

An Advancement for Environmental Sampling

- Tubes contain multiple layers of different types of sorbent
- Different classes of chemicals can be trapped in different layers of sorbent
- Tubes available for solvent or thermal desorption
- Custom tubes are available from SKC with almost any sorbent

THERMAL DESORPTION



- Allows for improved sensitivity--down to sub-ppb
- Nearly 100% recovery from media
- Suitable for ambient, indoor air and environmental studies

Precautions When Using Thermal Desorption

- Make sure size of tubes is compatible with thermal desorber being used
- Remember that tubes must be heat purged before use
- Do not use solvent desorption tubes for thermal desorption applications

SKC VOST SAMPLERS

For Sampling Stationary Sources

Volatile
Organic
Sampling
Trains

For For EPA Methods 0030 and 0031
EPA Method 0031

POLYURETHANE FOAM

A Novel New Sorbent

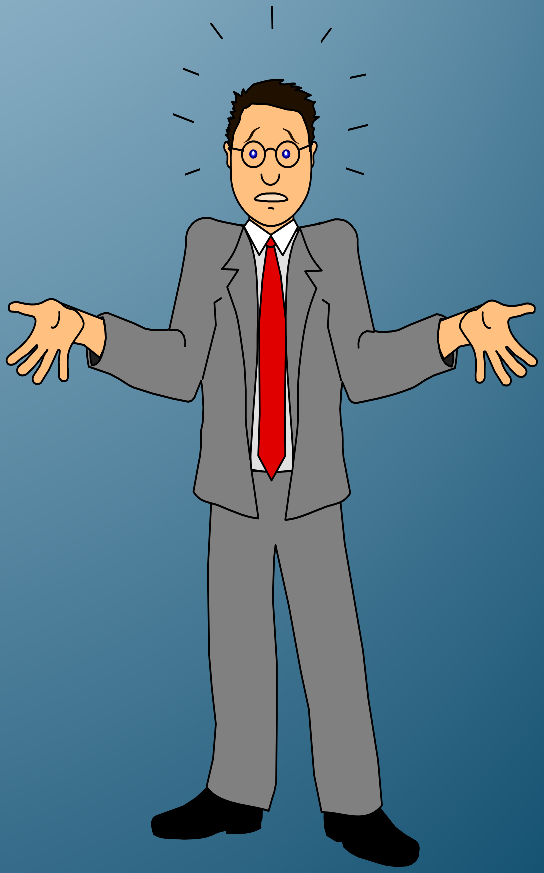
- Specified in EPA Methods for Organochlorine Pesticides , PCBs , PNAs and PCDDs
- PUF/Sorbent Combinations Available with Tenax, XAD-2 or other sorbents
- High Volume and Low Volume Tubes Available from SKC
- SKC PUF Sorbent Refilling Service Saves You Money

POLYURETHANE FOAM (PUF) TUBE

PUF “SANDWICHES”

Combine PUF and Sorbent

- Extends applications to more volatile compounds
- Standard sorbents are Tenax or XAD-2
- Low volume tubes used with personal pumps
- High volume tubes used with GMW Sampler

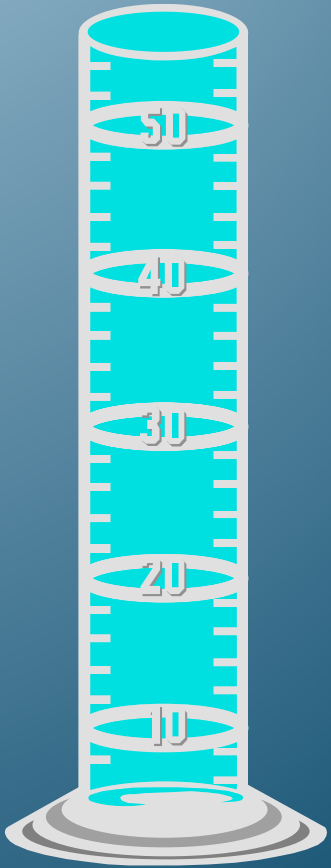


COATED FILTERS

A Great Media to Trap Unstable Compounds

Liquid mediums on filters derivatize the chemical of interest

This produces a more stable compound for storage and analysis



COATED FILTERS AVAILABLE FROM SKC

To Sample for a Variety of Chemicals

- Fluorides
- Diisocyanates
- Methylene Bisphenyl Isocyanate
- Glutaraldehyde
- Organic Amines
- Mercaptans
- Hydrogen Sulfide
- Acetic Anhydride
- Chlorine
- Bromine
- Sulfur Dioxide

AFTER SAMPLE COLLECTION

The tube is capped and sent to a qualified laboratory for analysis.

There the sorbent is removed and the trapped chemicals are extracted using either solvents or heat and identified and quantified using gas chromatography or other laboratory equipment.

ACTIVE SAMPLING OF GASES AND VAPORS (GAS BAGS)

In some cases, it may be desirable to collect the entire air sample in a special bag designed for that purpose.

This type of sample is termed a grab or instantaneous sample.

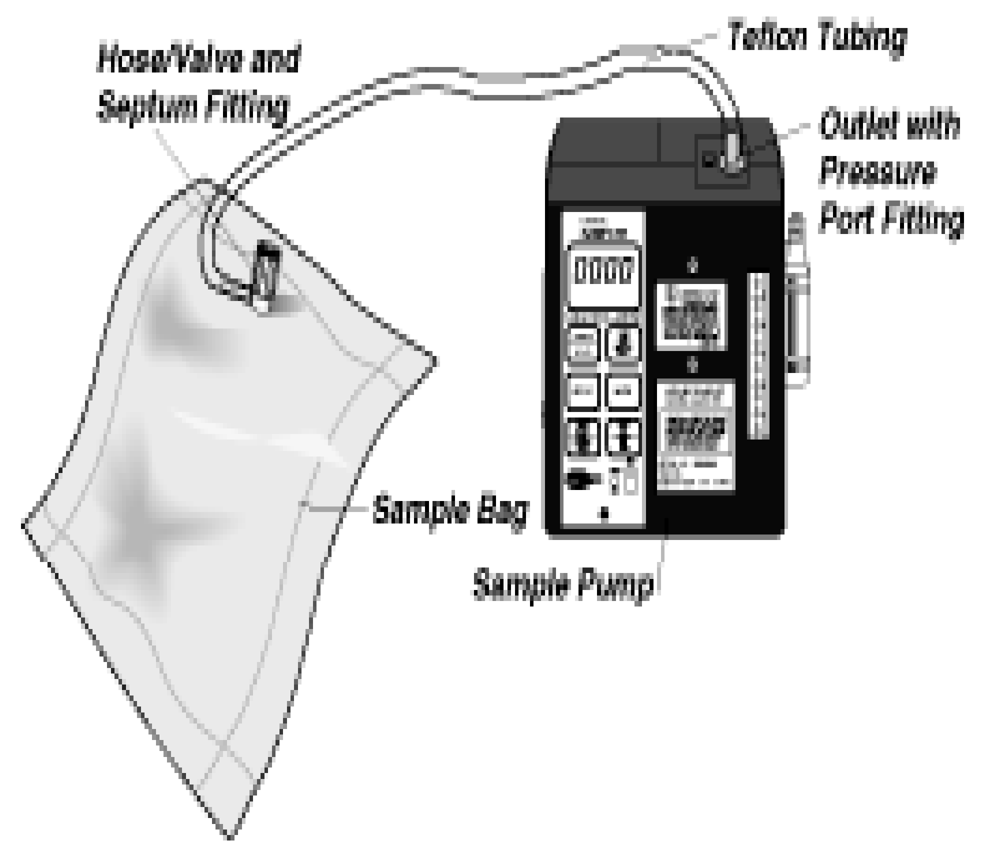
GRAB SAMPLES

- Are usually taken for short periods of time to indicate peak airborne concentrations
- Can be used to determine TWA exposures in areas where chemical levels remain constant

TO COLLECT A SAMPLE WITH SAMPLE BAGS

- Pumps with an exhaust or pressure port can be used to push air into a sampling bag that is connected to the pump with teflon tubing.
- Alternatively, bags can be placed into a chamber which is evacuated using a pump to fill the bag by negative pressure.

FILLING A BAG BY POSITIVE PRESSURE



FILLING A BAG BY NEGATIVE PRESSURE

AFTER SAMPLE COLLECTION

- Bags containing the sample can be analyzed in the field using direct reading instruments.

- Bags can also be shipped to the laboratory where they can be analyzed by gas chromatography or other laboratory equipment.

ACTIVE SAMPLING OF GASES AND VAPOR S (IMPINGERS)

Some chemical hazards such as acids, ozone, chlorine and formaldehyde can be sampled using impingers.

Impingers are specially designed glass bottles that are filled with a collection liquid specified in the sampling method for specific chemicals.

IMPINGERS

NOTES ABOUT IMPINGERS

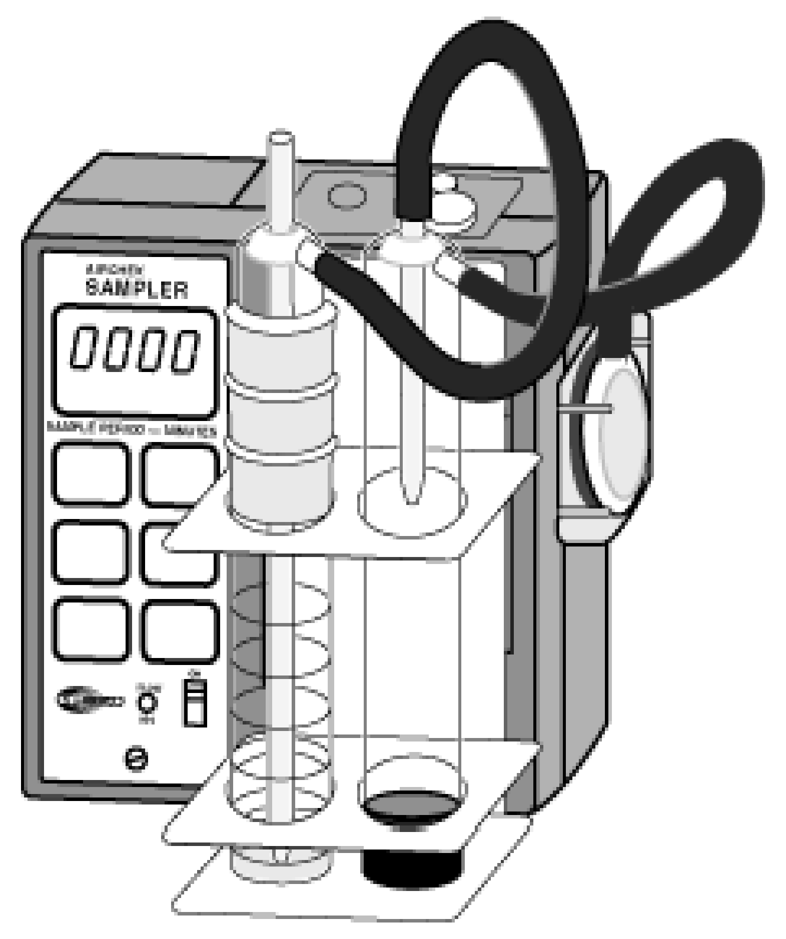
In some cases, the impinger nozzle is fritted or modified with thousands of small holes. This disperses the air and allows for better contact between the air sample and the impinger liquid.

TO COLLECT A SAMPLE WITH IMPINGERS

A sample pump is used to bubble air through the impinger which contains a liquid medium that has been specified in the method.

The liquid will physically dissolve or chemically react with the chemical of interest.

IMPINGER SAMPLING TRAIN



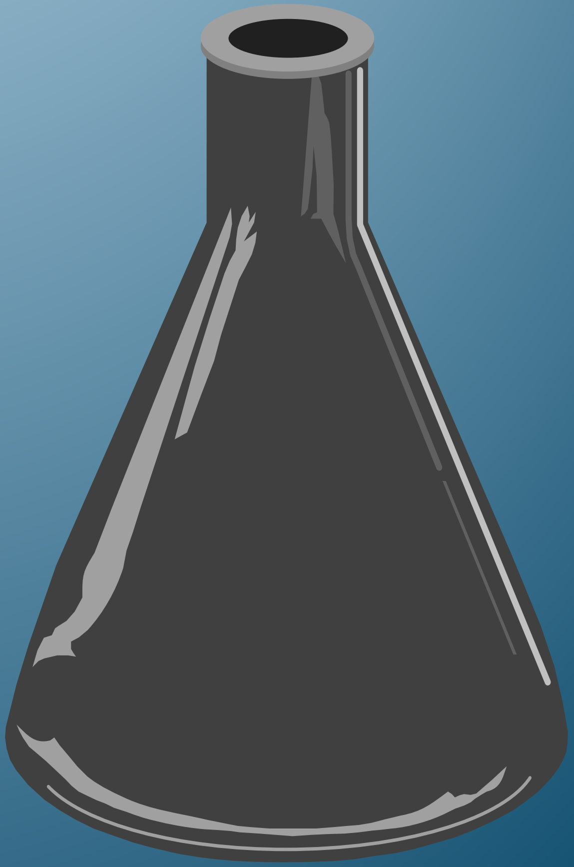
AFTER SAMPLE COLLECTION

- The liquid is removed from the impinger and sent to the laboratory for analysis.

- The impinger can then be cleaned and reused for future samples.

AFTER SAMPLE COLLECTION

- Cover the sample opening to stop sample collection.
- Properly label the sample.
- Ship to the laboratory for chemical analysis.



List of Analytical Methods and Examples of Common Analytes

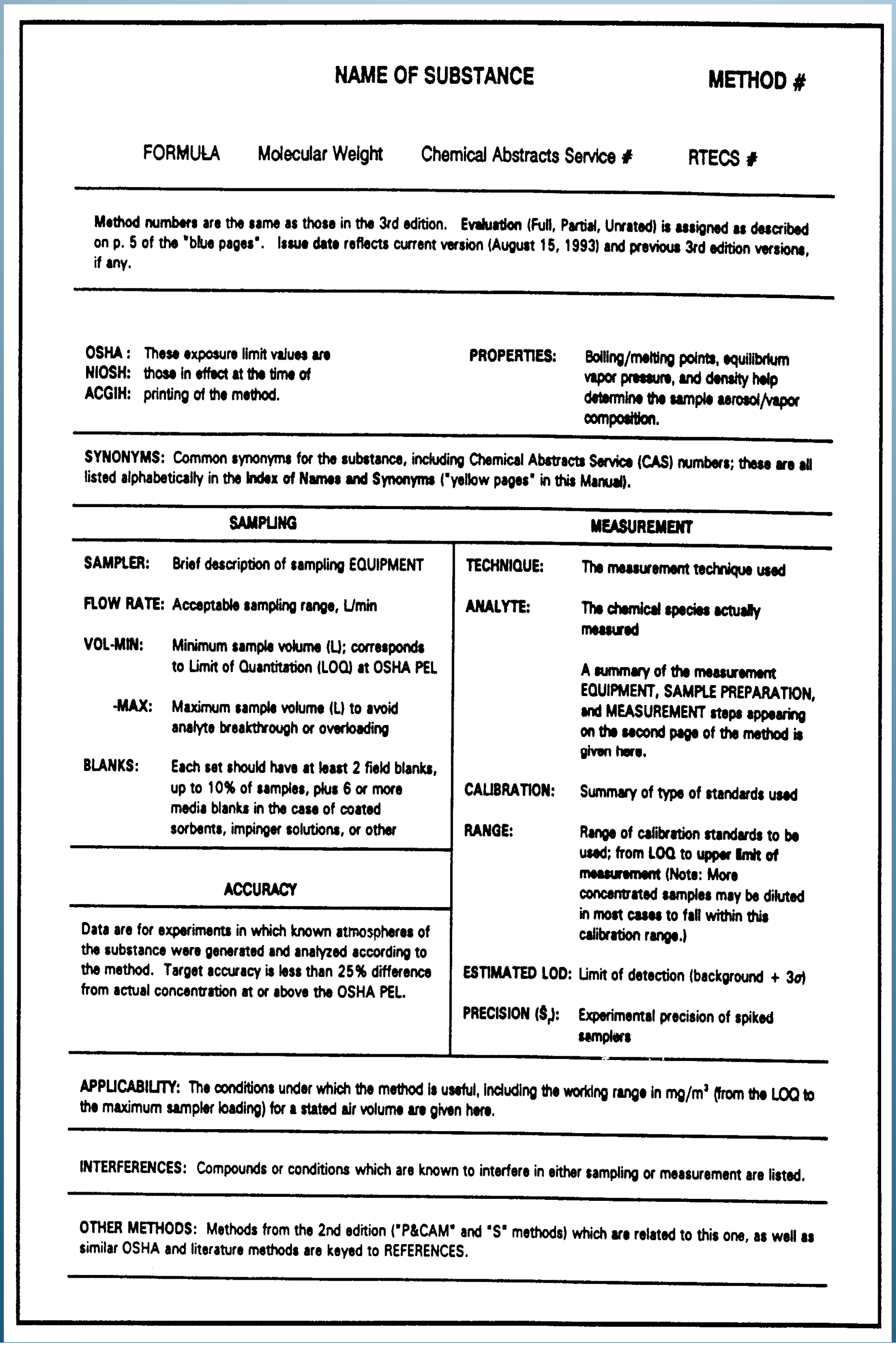
Analytical Method	*Examples of Analyte Compounds*
GC/ flame ionization detector	PAHs, ketones, halogenated hydrocarbons, alcohols, ethers, aromatic hydrocarbons
GC/ photoionization detector	ethylene oxide, tetraethyl lead, tetramethyl lead
GC/ nitrogen phosphorus detector	acrolein, nicotine, acetone cyanohydrin, organophosphate pesticides
GC/ electron capture detector	butadienes, pentadienes, chlordane, polychorinated benzenes, PCBs
GC/ flame photometric detector	mercaptans, carbon disulfide, nitromethane, tributylphosphate
GC/ thermal conductivity detector	carbon dioxide

Analytical Approach Diversity

Analytical Method	***Examples of Analyte Compounds***
GC/ mass spectrometry	aldehyde screening
HPLC/ ultraviolet detector	acetaldehyde, anisidine, p-chlorophenol, diethylenetriamine, ethylenediamine, maleic anhydride, p-nitroanaline
HPLC/ electrochemical detector	isocyanates
Visible absorption spectrophotometry	acetic anhydride, ammonia, formaldehyde, hydrazine, nitrogen dioxide, phosphine
Ion chromatography	aminoethanol compounds, chloroacetic acid, inorganic acids, iodine, chlorine, hydrogen sulfide, sulfur dioxide

Source: **National Institute for Occupational Safety and Health (NIOSH):** *NIOSH Manual of Analytical Methods*, 4th Ed. (DHHS [NIOSH] Pub. No. 94–113). Cincinnati: NIOSH, 1994.

A clear and complete “chain of custody must be observed



NAME OF SUBSTANCE **METHOD #**

FORMULA Molecular Weight Chemical Abstracts Service # RTECS #

Method numbers are the same as those in the 3rd edition. Evaluation (Full, Partial, Unrated) is assigned as described on p. 5 of the "blue pages". Issue date reflects current version (August 15, 1993) and previous 3rd edition versions, if any.

OSHA : These exposure limit values are
NIOSH: those in effect at the time of
ACGIH: printing of the method.

PROPERTIES: Boiling/melting points, equilibrium vapor pressure, and density help determine the sample aerosol/vapor composition.

SYNONYMS: Common synonyms for the substance, including Chemical Abstracts Service (CAS) numbers; these are all listed alphabetically in the Index of Names and Synonyms ("yellow pages" in this Manual).

SAMPLING

SAMPLER: Brief description of sampling EQUIPMENT

FLOW RATE: Acceptable sampling range, L/min

VOL-MIN: Minimum sample volume (L); corresponds to Limit of Quantitation (LOQ) at OSHA PEL

-MAX: Maximum sample volume (L) to avoid analyte breakthrough or overloading

BLANKS: Each set should have at least 2 field blanks, up to 10% of samples, plus 6 or more media blanks in the case of coated sorbents, impinger solutions, or other

ACCURACY

Data are for experiments in which known atmospheres of the substance were generated and analyzed according to the method. Target accuracy is less than 25% difference from actual concentration at or above the OSHA PEL.

MEASUREMENT

TECHNIQUE: The measurement technique used

ANALYTE: The chemical species actually measured

A summary of the measurement EQUIPMENT, SAMPLE PREPARATION, and MEASUREMENT steps appearing on the second page of the method is given here.

CALIBRATION: Summary of type of standards used

RANGE: Range of calibration standards to be used; from LOQ to upper limit of measurement (Note: More concentrated samples may be diluted in most cases to fall within this calibration range.)

ESTIMATED LOD: Limit of detection (background + 3σ)

PRECISION ($\bar{S}_r$): Experimental precision of spiked samplers

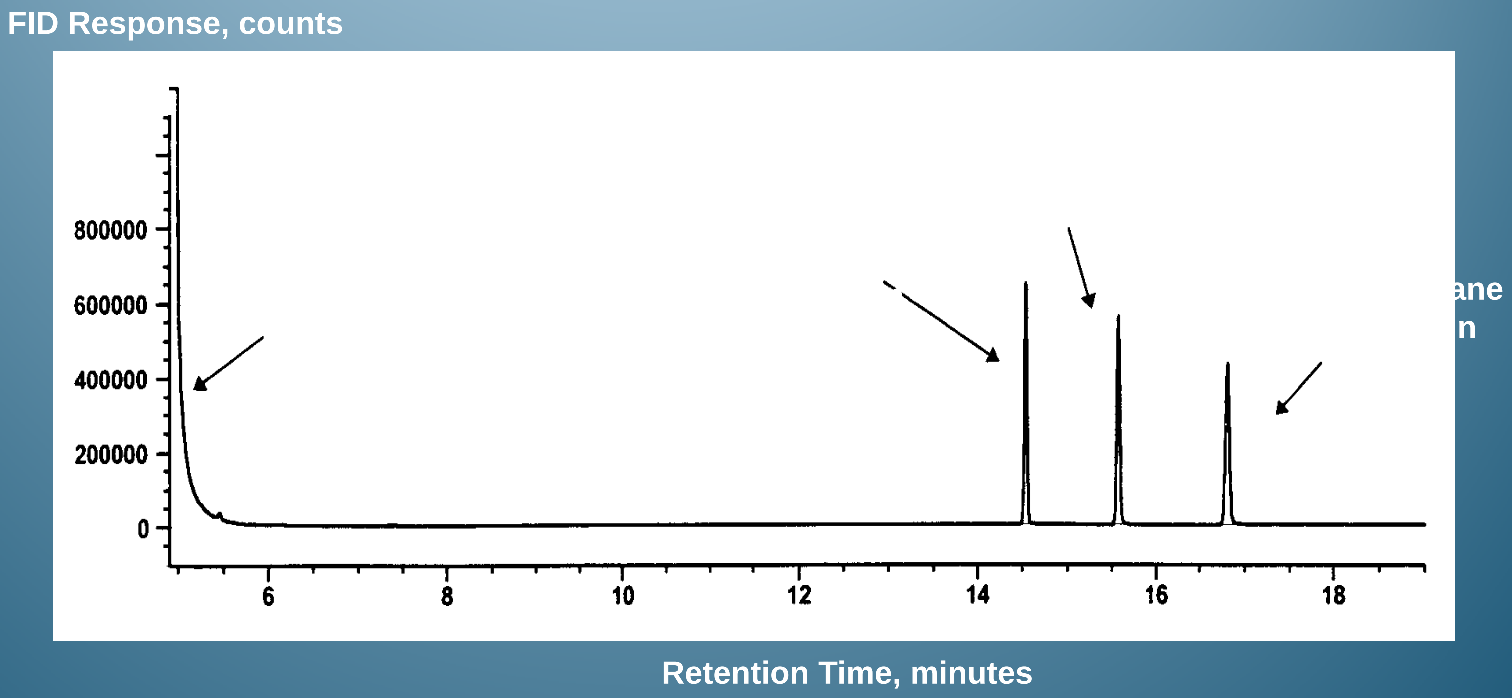
APPLICABILITY: The conditions under which the method is useful, including the working range in mg/m³ (from the LOQ to the maximum sampler loading) for a stated air volume are given here.

INTERFERENCES: Compounds or conditions which are known to interfere in either sampling or measurement are listed.

OTHER METHODS: Methods from the 2nd edition ("P&CAM" and "S" methods) which are related to this one, as well as similar OSHA and literature methods are keyed to REFERENCES.

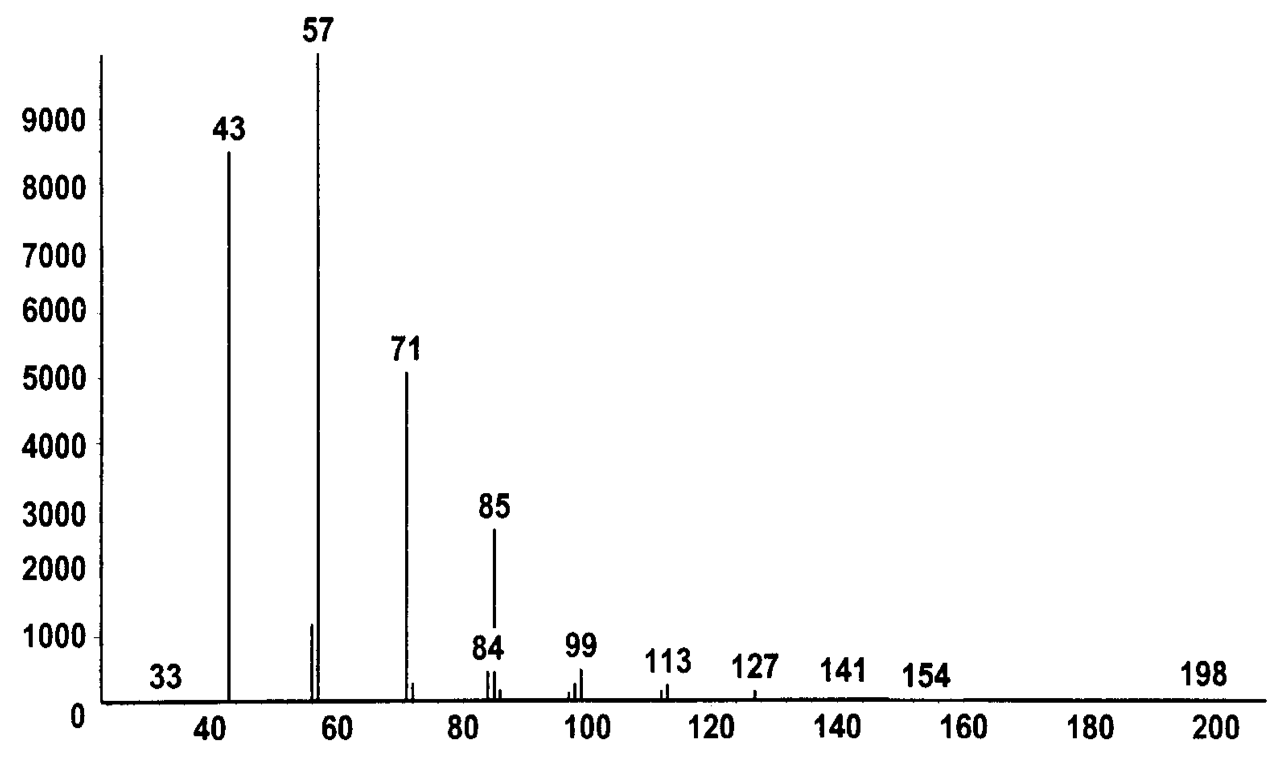
Layout of cover page for NIOSH sampling and analytical methods.

Typical Chromatogram Produced Using a FID



Typical chromatogram produced using a FID and showing separation of n-tetradecane (retention time 14.540 min), n-pentadecane (retention time 15.573 min), and n-hexadecane (retention time 16.802 min).

Typical Mass Spectrum for Tetradecane Showing the Relative Abundance of Each Mass Fragment



Mass/Charge Ratio

Commonly Used Direct-Reading Instruments for Gases and Vapors

Instrument ***Common Analytes*** ***Principle of Operation*** ***Range***

Combustible Combustible gases and vapors Hot
wire—test gas is passed over a heated Usually measured in
gas detectors (nonspecific) wire (sometimes in the presence of a catalyst).
percentage of the
The test gas burns, changing the temperature
lower explosive limit.
of the filament, and the electrical resistance of
Some models
the filament is measured. measure
down to
1 ppm.

Colorimetric Various vapors including formalde- Reaction
of the test gas with a chemical Variable
detectors hyde, hydrogen sulfide, sulfur diox- reagent
(either as a liquid or in some cases an
ide, toluene diisocyanate (specific)
impregnated paper or tape) and measurement
of the color produced

Electrochemical Carbon monoxide, nitric oxide, nitro-
Chemical oxidation of test gas 1 to 3000 ppm
sensors gen dioxide, hydrogen sulfide, sulfur

Commonly Used Direct-Reading Instruments for Gases and Vapors (continued)

Instrument	*Common Analytes*	*Principle of Operation*	*Range*
Infrared gas	Organic and inorganic gases and		
	Measures infrared absorbance of test gas		Sub-ppm
to low			
analyzers	vapors (specific)		percent
levels			
Metal oxide	Hydrogen sulfide, nitro, amine,	Metal oxide sensor is chemically reduced	1 to 50
ppm			
sensors	alcohol, and halogenated	by the gas, increasing its electrical resistance	
	hydrocarbons (specific)		
Thermal	Carbon monoxide, carbon dioxide,		Uses
specific heat of combustion of a gas or		Percentage gas	
conductivity	nitrogen, oxygen, methane, ethane,		vapor
sensors	propane, and butane		
Portable gas	Organic and inorganic gases and		Uses a
packed column to separate complex		0.1 to 10,000 ppm	
chromatographs		vapors (specific)	mixtures
of gases. Detectors available include			
		flame ionization, electron capture, thermal	
		conductivity, flame photometric, and photoionization	

Commonly Used Direct-Reading Instruments for Gases and Vapors (continued)

Instrument	Common Analytes	Principle of Operation	Range
Detectors for Gas Chromatographs			
Electron capture detector	Halogenated hydrocarbons, nitrous oxide, and compounds containing cyano or nitro groups	Uses a radioactive source such as 63Ni to supply energy to the detector that monitors the intensity of the electron beam arriving at a collection electrode. When an electron-capturing species passes through the cell the intensity of the electron beam decreases.	0.1 ppb to low ppm
Flame ionization detectors	Organic compounds including aliphatic and aromatic hydrocarbons, ketones, alcohols, and halogenated hydrocarbons	Creates organic ions by passing a hydrogen gas through flame. Measures conductivity of the flame.	0.1 to 100,000 ppm
Photoionization detectors	Most organic compounds, particularly aromatic compounds	Creates ions by exposing test gas to ultraviolet light. Measures conductivity of the gases in the light field.	0.2 to 2000 ppm

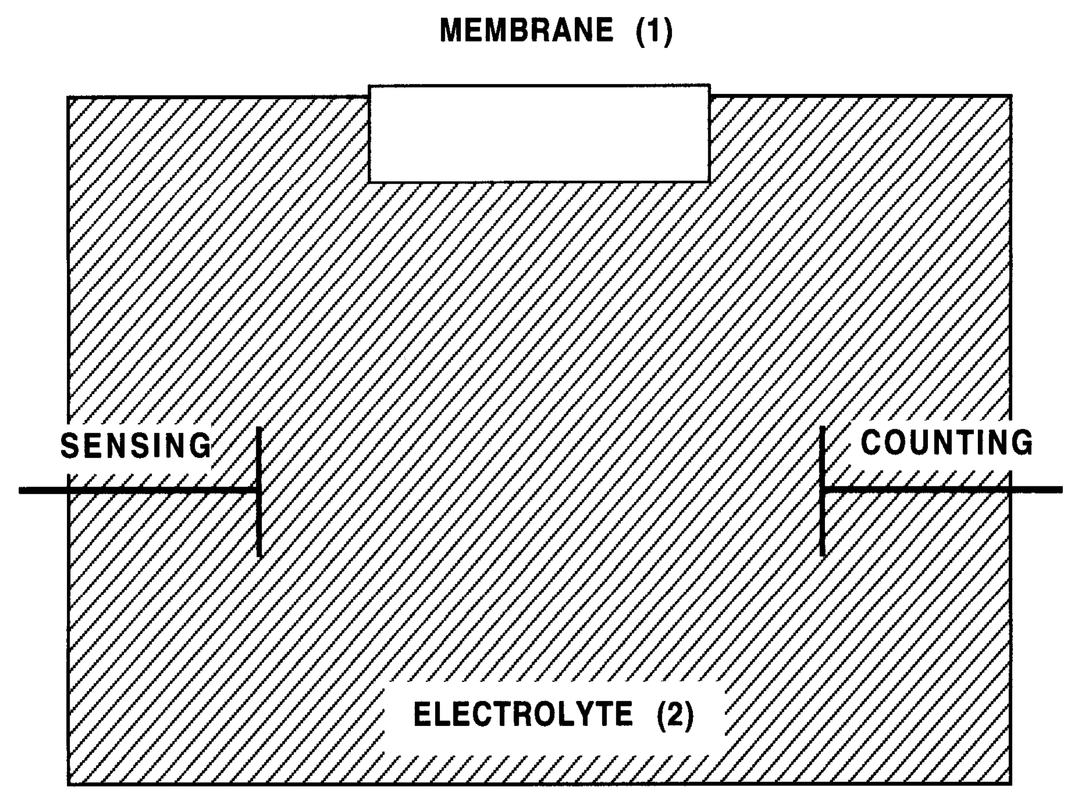
Commonly Used Aerosol Monitors

Instrument	*Sample Flow*	*Size Range*	*Concentration Range*
Light-scattering photometers	passive to 100 L/min	0.1 to 20 μm	0.0001 μm/m^3 to 200 g/m^3
Light-scattering particle counters	0.12 L/min to 28 L/min	0.1 to 8000 m (up to 32,000 μm for drop size analyzers)	1 particle/L to 10^5 particles/cm^3
Condensation nucleus counters	0.003 L/min to 4.2 L/min	1.6 nm to 20 nm	0.1 to 10^6 particles/cm^3
Single Particle Aerosal Relaxation Time (SPART)	0.5 to 5 L/min	< 0.3 to 10 μm	NA
Beta attenuation aerosol mass monitors	15 L/min	< 10 μm	10 mg/m^3 max
Piezoelectric crystal microbalance	0.24 to 1 L/min	0.05 to 35 μm	100 g/m^3 to 100 mg/m^3
Tapered Element Oscillating Microbalance (TEOM)	NA	0.5 to 35 μm	5 μg/m^3 to 2000 mg/m^3

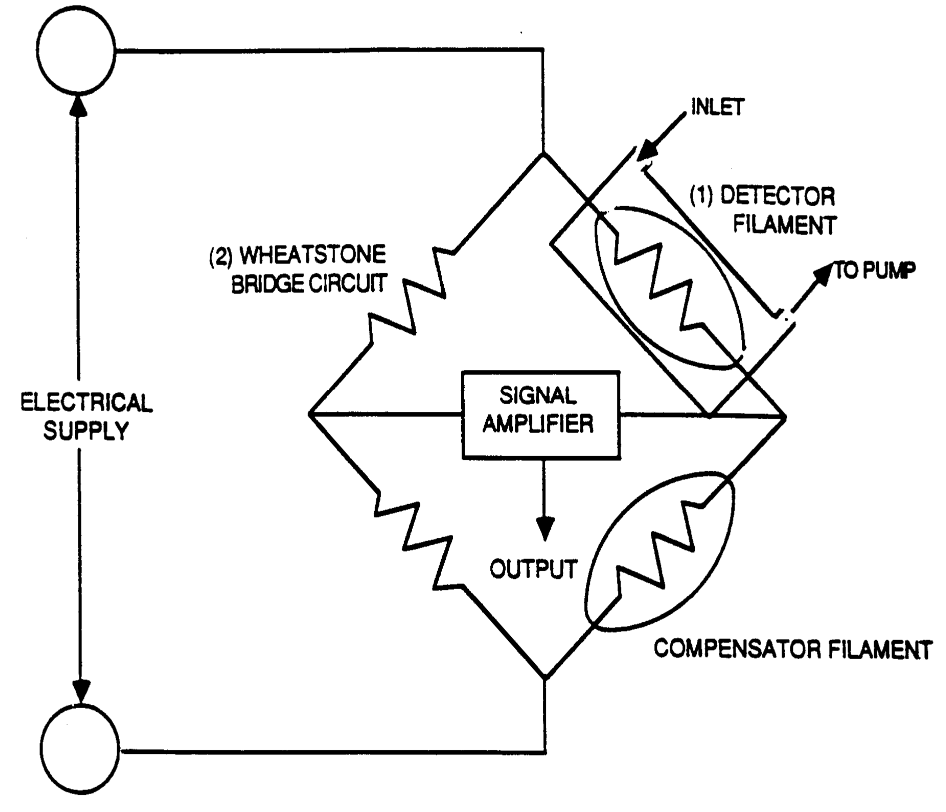
Gases Detectible by Electrochemical Sensors

- Ammonia
- Arsine
- Bromine
- Carbon dioxide
- Carbon monoxide
- Chlorine
- Ethylene oxide
- Fluorine
- Formaldehyde
- Formic acid
- Freon
- Germane
- Hydrazine
- Hydrochloric acid
- Hydrogen
- Hydrogen chloride
- Hydrogen cyanide
- Hydrogen fluoride
- Hydrogen sulfide
- Nitric acid
- Nitric oxide
- Nitrogen dioxide
- Nitrogen oxides
- Nitrous oxide
- Oxygen
- Ozone
- Phosgene
- Phosphine
- Silane
- Silicon tetrafluoride
- Sulfur dioxide
- Tetrachloroethylene
- Trichloroethylene
- Tungsten hexafluoride

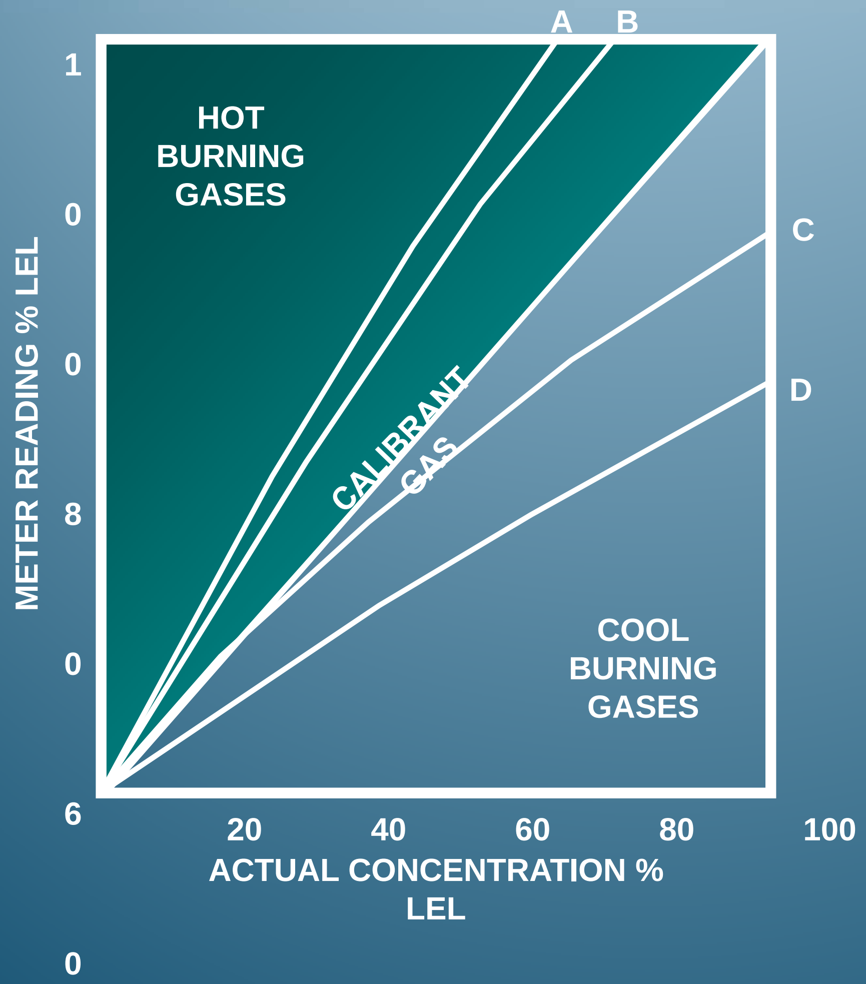
A Typical Electrochemical Sensor



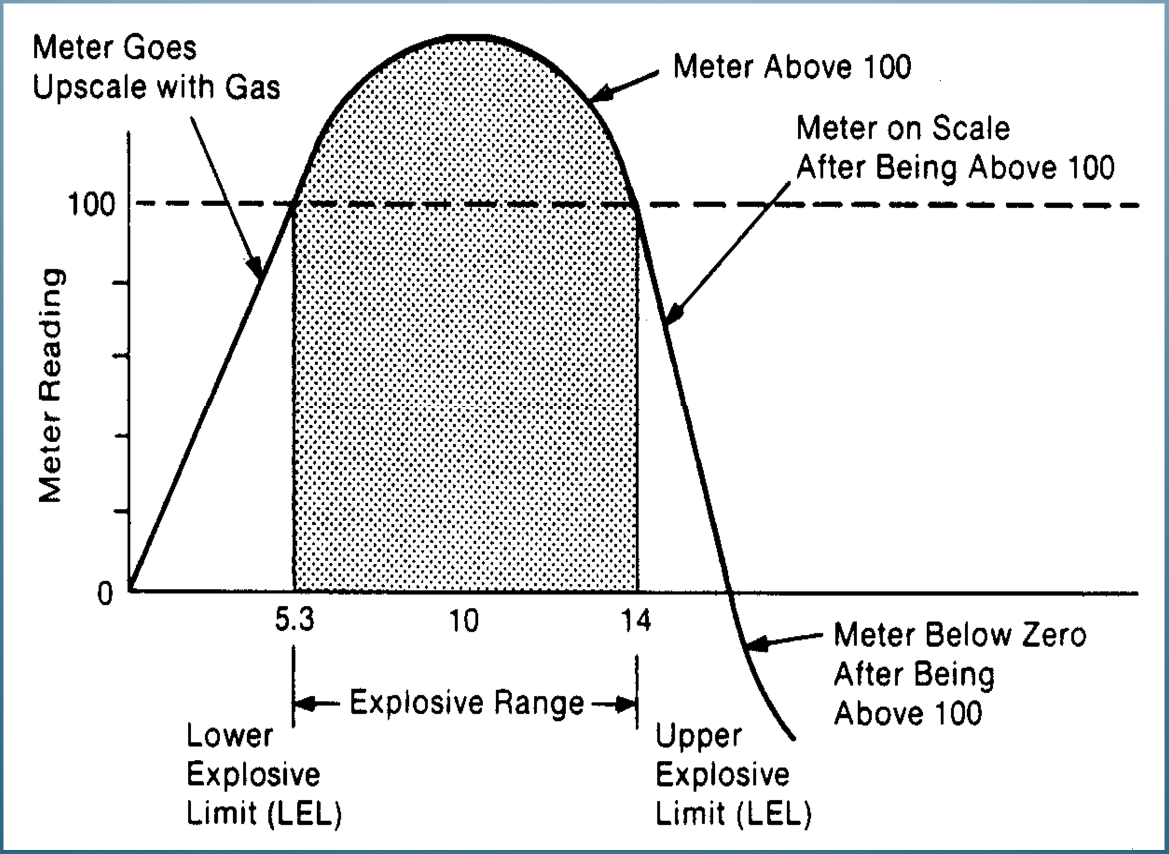
A Wheatstone Bridge



Combustible gas instrument response curve for conversion of a meter reading to concentration.



Sensor response range from lower explosive limit to upper explosive limit.



Ionization Potentials of Selected Chemicals

Compound	*IP (eV)*
Acetaldehyde	10.21
Acetic acid	10.37
Acetone	9.69
Acrolein	10.10
Allyl alcohol	9.67
Allyl chloride	10.20
Ammonia	10.15
Aniline	7.70
Benzene	9.25
Benzyl chloride	10.16
1,3-Butadiene	9.07
n-Butyl amine	8.71
Carbon disulfide	10.13
Chlorobenzene	9.07
Crotonaldehyde	9.73
Cyclohexane	9.98
Cyclohexanone	9.14
Cyclohexene	8.95
Diborane	11.4
1,1-Dichloroethane	11.06

Compound	*IP (eV)*
Dimethyl amine	8.24
Ethyl acetate	10.11
Ethyl amine	8.86
Ethyl benzene	8.76
Ethyl bromide	10.29
Ethyl butyl ketone	9.02
Ethyl chloride	10.98
Ethylene chlorohydrin	10.90
Heptane	10.07
Hydrogen cyanide	13.91
Hydrogen sulfide	10.46
Isoamyl acetate	9.90
Isoamyl alcohol	10.16
Isopropyl acetate	9.99
Isopropyl alcohol	10.16
Isopropyl amine	8.72
Isopropyl ether	9.20
Methanol	10.85
Methyl acetate	10.27
Methyl acrylate	10.72

Compound	*IP (eV)*
Methyl ethyl ketone	9.53
Methyl mercaptan	9.44
Morpholine	8.88
Nitrobenzene	9.92
Octane	9.9
Pentane	10.35
2-Pentanone	9.39
Phosphine	9.96
Propane	11.07
n-Propyl acetate	10.04
n-Propyl alcohol	10.20
Propylene dichloride	10.87
Propylene oxide	10.22
Styrene	8.47
Toluene	8.82
Triethylamine	7.50
Vinyl chloride	10.00
Water	12.61
m-Xylene	8.56

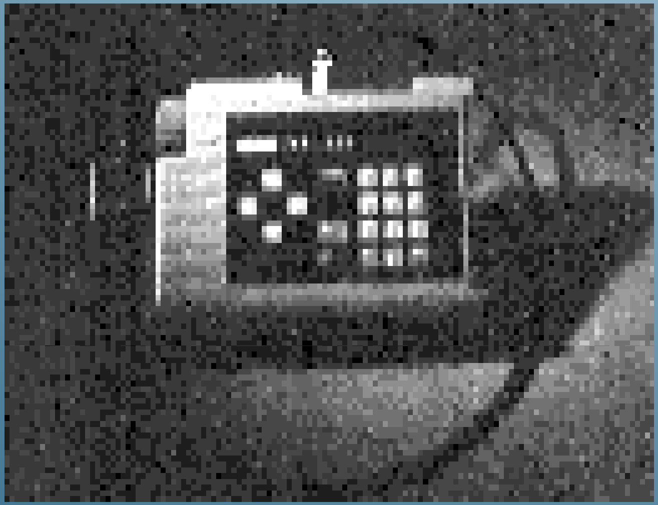
PID: The HNU 101 Models

PID: The Photovac 2020

Relative Response of the OVA (FID Instrument) to Different Chemicals (if Calibrated to Methane)

Compound	*Relative Response (%)*	*Compound*	*Relative Response (%)*
Acetaldehyde	25	Ethylene	85
Acetic acid	80	Ethylene oxide	70
Acetone	60	Hexane	75
Acetylene	225	Isopropyl alcohol	65
Acrylonitrile	70	Methane (calibrant)	100
Benzene	150	Methanol	12
n-Butane	63	Methyl ethyl ketone	80
1,3-Butadiene	28	Methylene chloride	90
Carbon tetrachloride	10	Octane	80
Chloroform	65	Phenol	54
Cyclohexane	85	Tetrachloroethylene	70
Diethylamine	75	Toluene	110
Diethyl ether	18	Trichloroethylene	70
Ethane	110	Vinyl chloride	35
Ethanol	25	o-Xylene	116
Ethyl acetate	65		

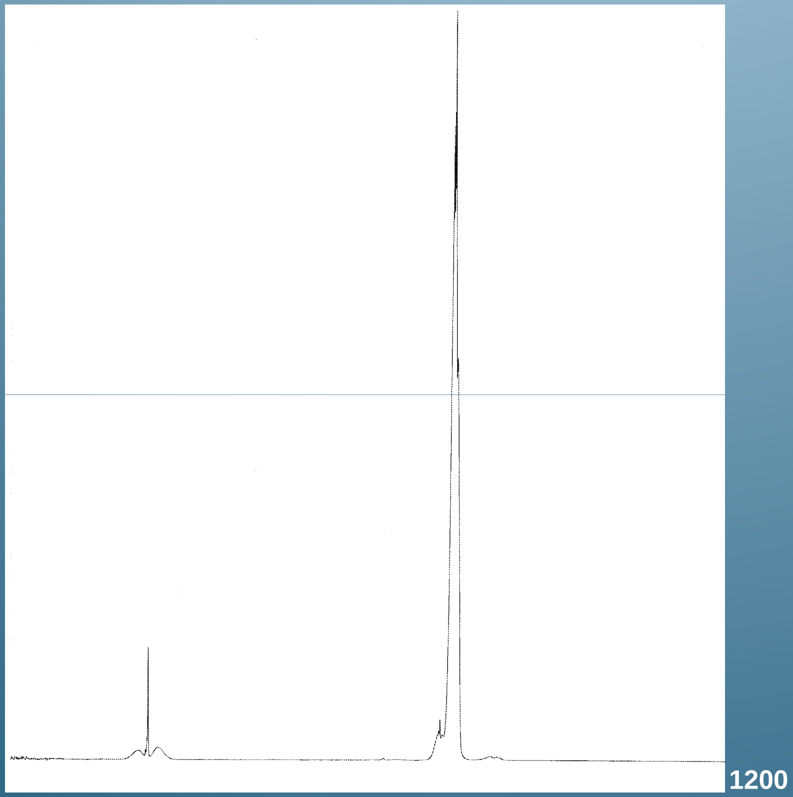
Organic Vapor Analyzers (OVA): The Century TVA 1000



Specific Infrared Absorption Bands for Hydrocarbons

Chemical Groups	*Absorption Band (µm)*
Alkanes (C-C)	3.35–3.65
Alkenes (C=C)	3.25–3.45
Alkynes (C_C)	3.05–3.25
Aromatic	3.25–3.35
Substituted aromatic	6.15–6.35
Alcohols (-OH)	2.80–3.10
Acids (C-OOH)	5.60–6.00
Aldehydes (COH)	5.60–5.90
Ketones (C=O)	5.60–5.90
Esters (COOR)	5.75–6.00
Chlorinated (C-Cl)	12.80–15.50

An Infared Spectrum for the Chemical Sulfur Hexafluoride.

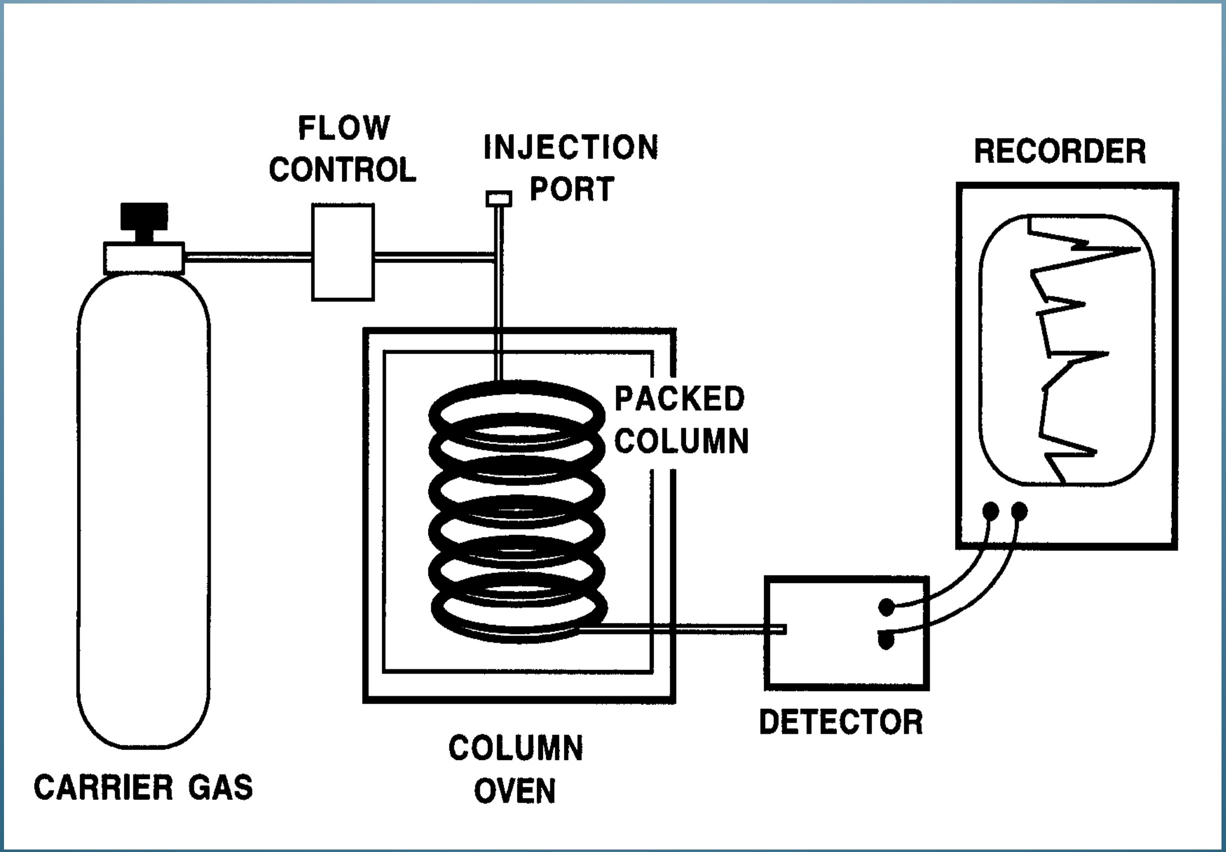


Absorbance/Wavenumber (cm-1)

Y axis is absorbance unit.

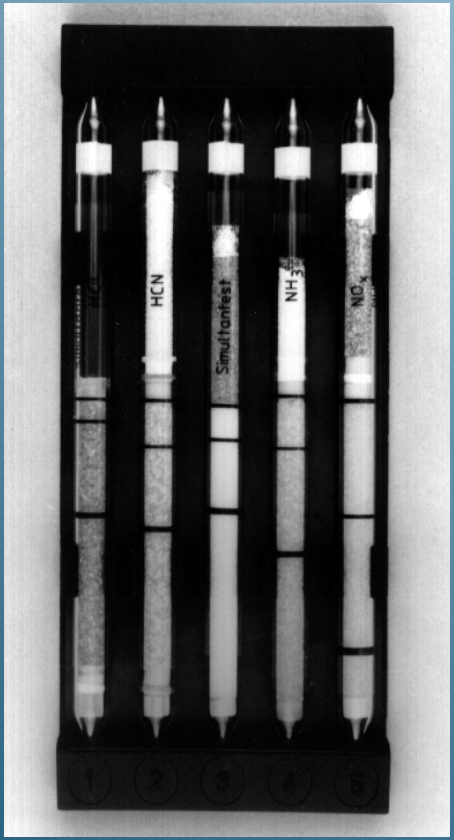
Portable Infared Analyzer:
The MIRAN Sapphire Analyzer

Schematic for a Typical Gas Chromatograph

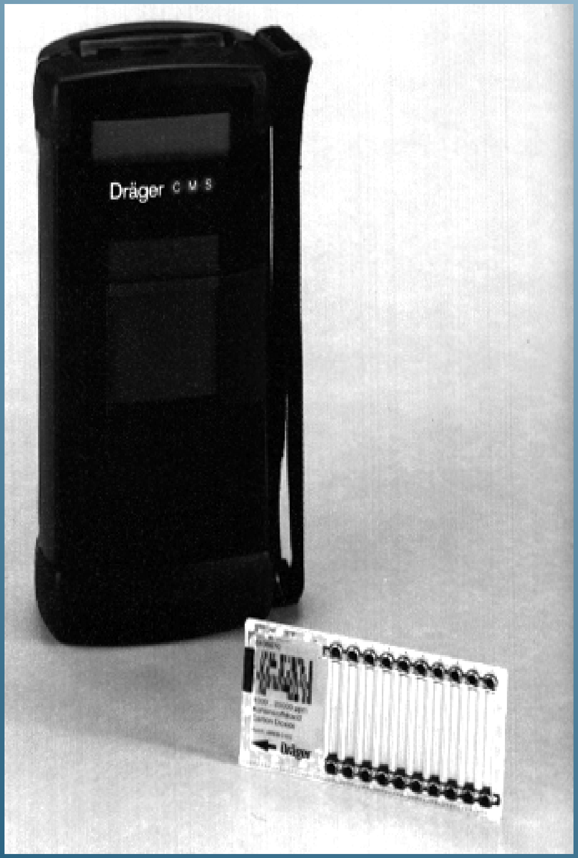


Portable Field Gas Chromatograph: The Photovac Voyager

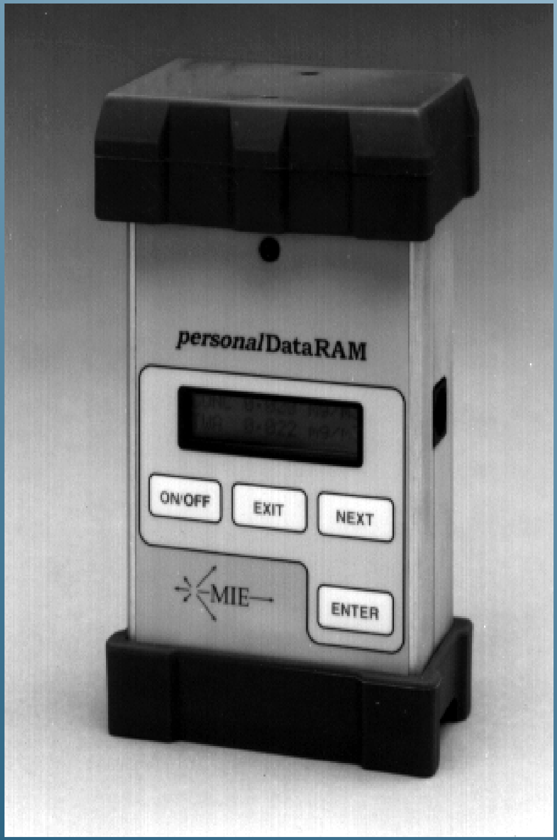
Detector Tubes, or Colormetric Indicator Tubes, and Pumps From National Draeger



A New Generation of Tubes and Pumps From National Draeger



Multiple Particle Optical Monitor: The MINIRAM



Selecting Sampling Method / Equipment

- Is it comprehensive?
- Is it convenient?
- Is it cost effective?
- Is it sensitive enough?
- Is it selective enough?
- Does it provide rapid response/results?

AIRBORNE PARTICULATE HAZARDS

Airborne particulate hazards may include:

- Dusts
- Fumes
- Mists
- Smokes

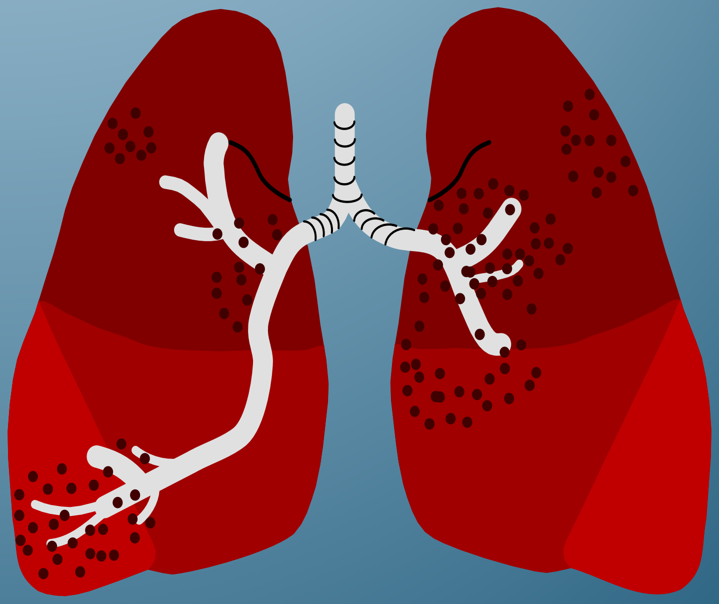
THE HAZARD POTENTIAL OF AIRBORNE PARTICULATES

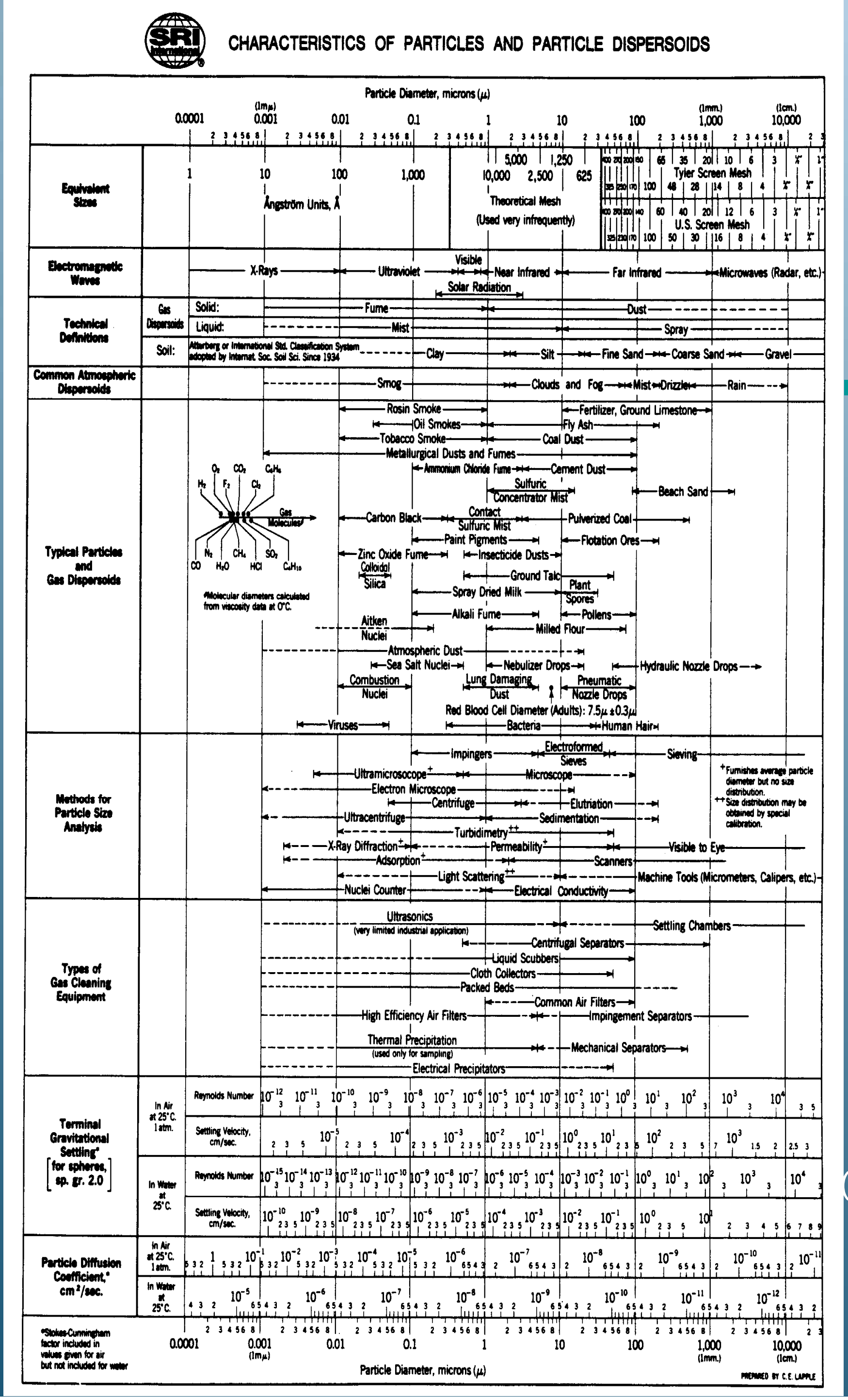
Is determined by several parameters including:

- Chemical composition
- Mass concentration
- Size characteristics

Instruments to Classify Particle Size

Determine the deposition site in the respiratory tract. Smaller particles will tend to deposit deep into the gas exchange region of the lung.





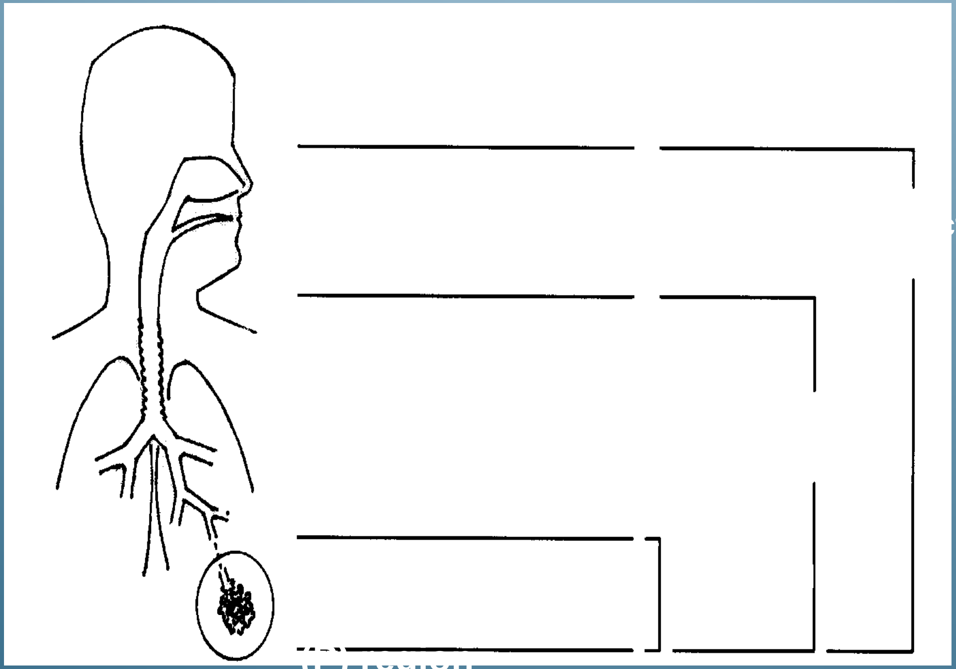
Characteristics of Particles and Particle Dispersoids

(Source: C.E. Lappler, SRI Journal 5:94 [1961].)

SIZE-SELECTIVE EXPOSURE GUIDELINES

To more appropriately assess the possible health effects of airborne particulate matter, exposure guidelines have typically been issued for different aerodynamic sizes of particles. [example USBM]

Regions of the Respiratory Tract



(a) the NP region conditions inhaled air to body temperature and essentially 100% relative humidity and efficiently removes larger particles; (b) the TB region conducts inhaled air quickly and evenly from the mouth and nose to the pulmonary spaces; (c) the P region performs the gas exchange function of respiration.

WORKPLACE EXPOSURE GUIDELINES

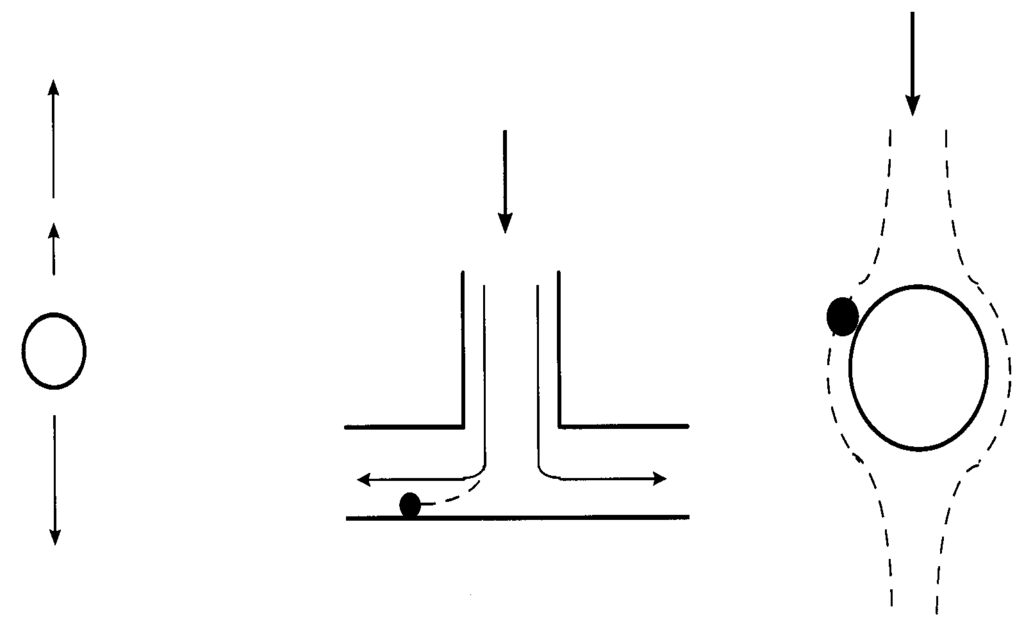
- Have traditionally been expressed as
  - *TOTAL DUST
  - *RESPIRABLE DUST

TOTAL DUST

- Is collected by using a filter of a type and pore size appropriate to the particulate being sampled.
- The filter is loaded into a cassette and connected to a sampling pump that has been calibrated to a flowrate of at least

  1 L/min.
- Samples are collected in an area or in the breathing zone of workers.

Aerosol Particle Collection Mechanisms

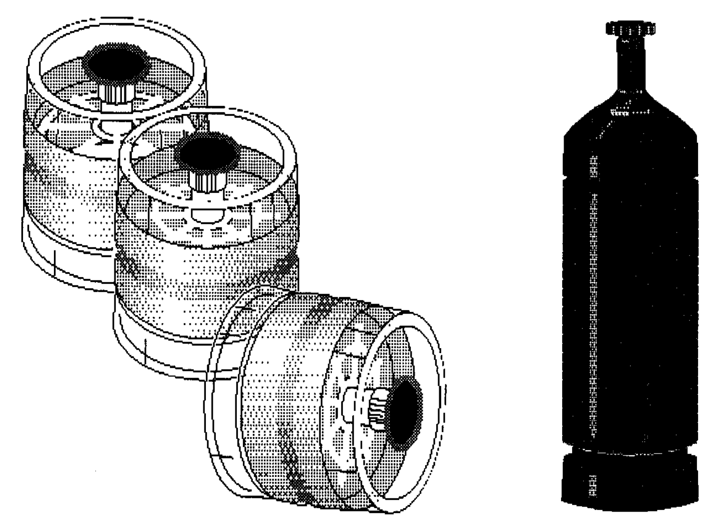


(a) sedimentation — at terminal (maximum) settling velocity, the fluid drag and buoyant forces will exactly offset the particle’s weight; (b) inertial impaction — the particle’s inertia carries it across airflow streamlines as the air changes direction; and (c) interception — the flow streamline passes the collecting body (such as a filter fiber) within a distance of one-half the particle’s diameter.

ACTIVE SAMPLING FOR PARTICULATES

- To sample for particulates, a filter loaded into a filter cassette will be used.
- The filter diameter, type and pore size will vary depending on the chemical being sampled and will be specified in the sampling method.

Filter Cassettes



Commonly used filter holders include (a) the 37-mm three-piece styrene acrylonitrile cassette used as shown or in open-face mode with one end removed, and (b) the polypropylene 25-mm cassette with cowl, specifically for use in asbestos sampling (end cap shown is removed during sampling) (graphics courtesy SKC, Inc., Eighty Four, Pa.).

FILTER SAMPLING TRAIN

AFTER SAMPLE COLLECTION

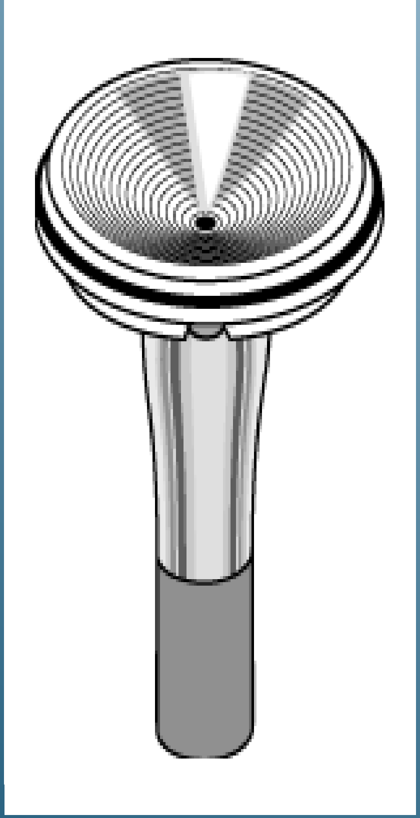
Filters can be analyzed by a variety of methods depending upon the chemical:

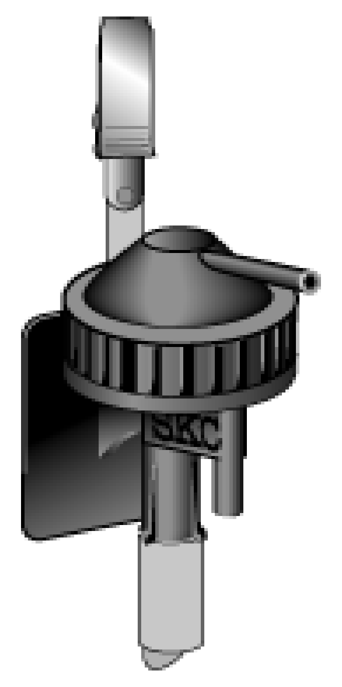
- Gravimetric-Weighing the sample before and after collection
- Atomic Absorption/ICP-Performing chemical analysis to determine specific compounds
- Microscopic-Counting individual fibers

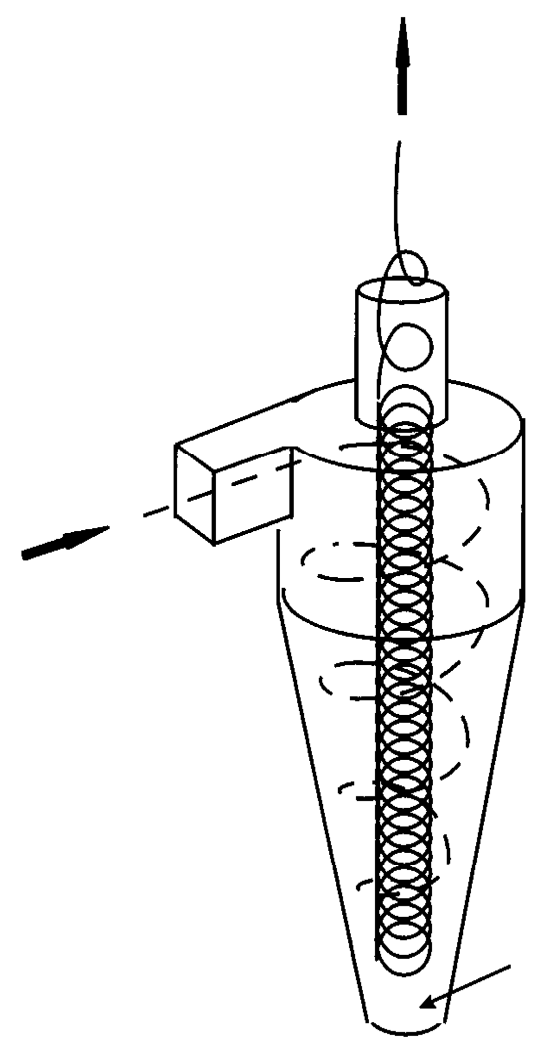
RESPIRABLE DUST

- Is collected onto a filter of a type and pore size that is appropriate for the particulate being sampled.
- Preceding the filter, however, is a particle size-selective device, typically a cyclone, that will separate the respirable fraction from the non-respirable fraction when connected to a pump sampling at the designated flow rate.

RESPIRABLE DUST CYCLONES







Cyclone Separator

Suspended particles are captured by increasing centrifugal forces as the air spirals down the cone of the cyclone; the airflow and uncaptured particles spiral back up the central axis and exit through the top. In a personal respirable aerosol sampler the exiting air, carrying the respirable particle fraction, passes through a cassette filter, where the particles are captured for gravimetric or other analysis.

Some regulations require the measurement of respirable dust.

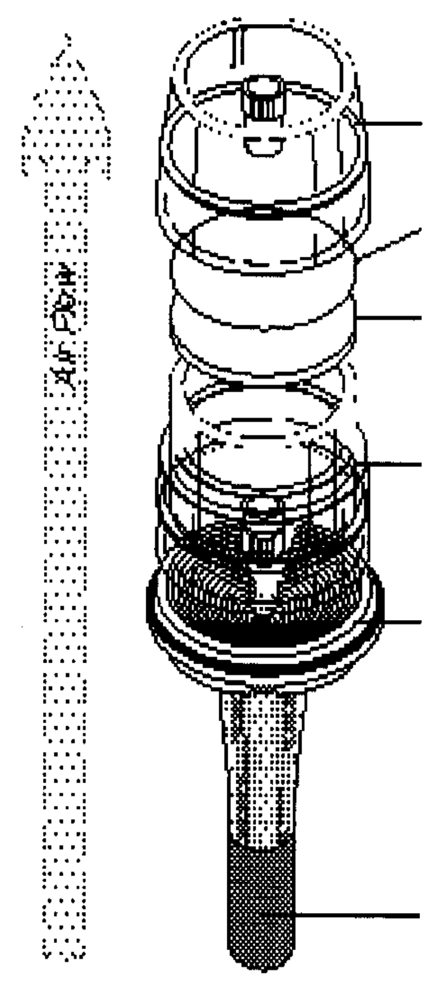
Respirable dust is dust so small in size that it can get through the protective mechanisms of the human body and get down deep into the gas exchange region of the lung. To sample respirable dust, you will need to use a cyclone.

When sampling with cyclones

The smaller respirable particles will be collected onto the filter for subsequent analysis.

Larger particles will fall into the grit pot and will be discarded.

Personal Cyclone



Exploded view of a personal respirable dust sampling assembly incorporating an SKC aluminum cyclone and 37-mm three-piece filter cassette. Nonrespirable particles are collected in the grit pot at the base of the cyclone, and the respirable fraction is collected on the filter for subsequent weighing or chemical analysis (graphic courtesy SKC, Inc.).

Note About Cyclone Sampling

- Be sure to calibrate your pump to the flow rate specified to achieve the desired 50% cut-point.

- Cut-point is the size of dust that the cyclone will collect with 50% efficiency.

NOTE ABOUT CYCLONE SAMPLING

- NIOSH and ACGIH recommend a 4 micron cut-point.

- To achieve this cut-point, a flow rate of 2.5 l/min is recommended using the SKC aluminum cyclone.

NEW WORKPLACE EXPOSURE GUIDELINES

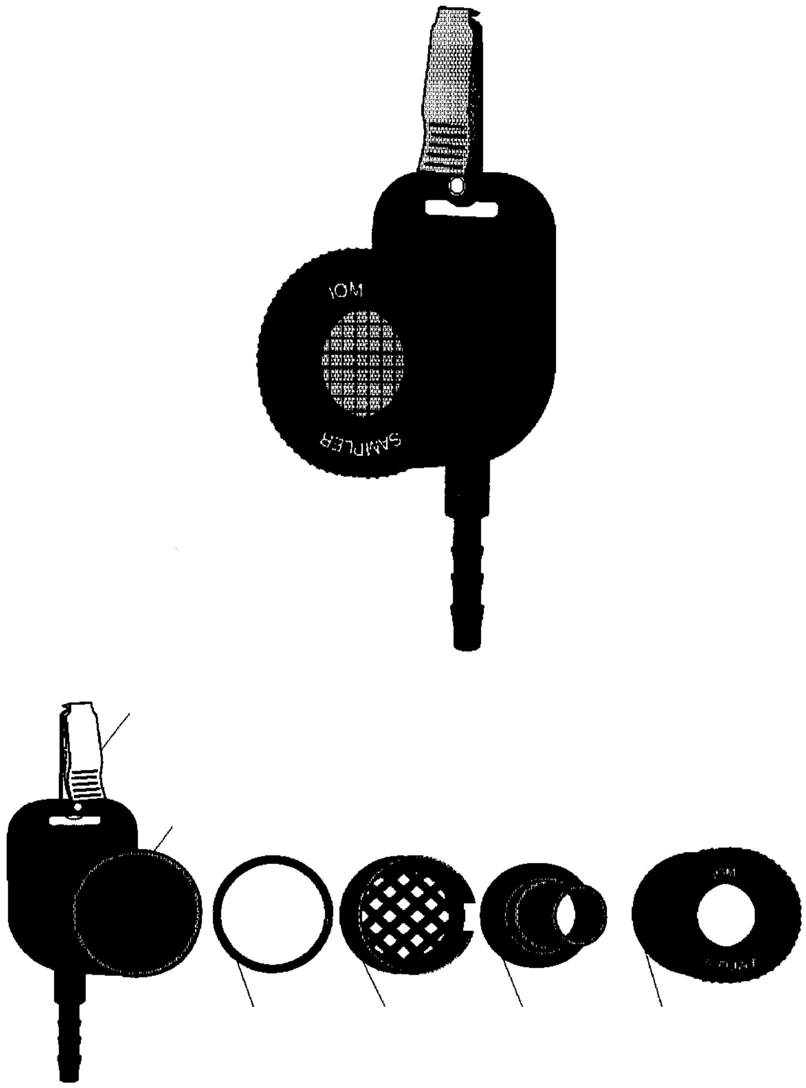
- Inhalable Particulate Mass
- Thoracic Particulate Mass
- Respirable Particulate Mass

Adopted by several
International agencies:

INHALABLE DUST

- Is a new term used to describe dust that is hazardous when deposited anywhere in the respiratory tree including the nose and mouth
- Includes the larger and the smaller particles

IOM Inhalable Dust Sampler



Developed by J.H. Vincent and D. Mark at the Institute of Occupational Medicine, Edinburgh, Scotland. For gravimetric analysis the interior cassette, containing the filter, is weighed before and after sampling. The sampler meets international sampling criteria for inhalable particulate matter (graphic courtesy SKC, Inc.).

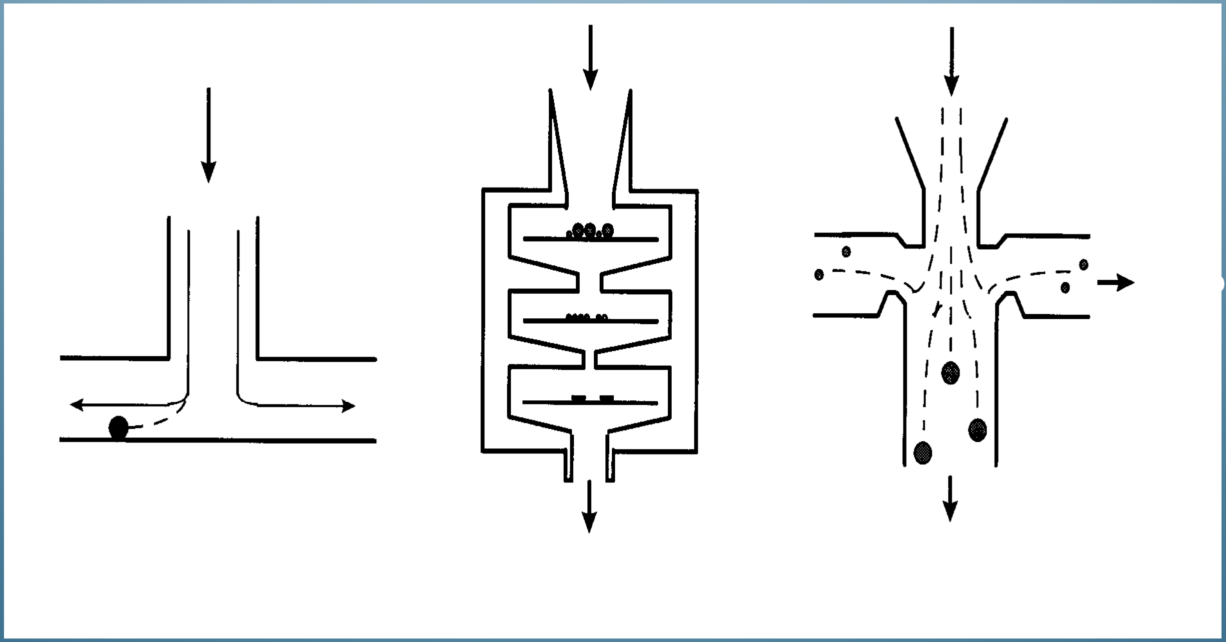
TO COLLECT A SAMPLE FOR INHALABLE DUST

- A 25-mm filter is loaded into the cassette using forceps and wearing gloves.
- The filter and cassette are equilibrated to standard laboratory conditions then weighed as a unit.
- The sample is collected at 2 L/min.
- The sample is weighed again following the procedures described above.

AFTER SAMPLE COLLECTION

- Remove the cassette containing the filter from the sampling head and equilibrate the cassette and filter again for 24 hours to get a post-sample weight.
- Alternatively, chemical analysis can be done on the filter sample.

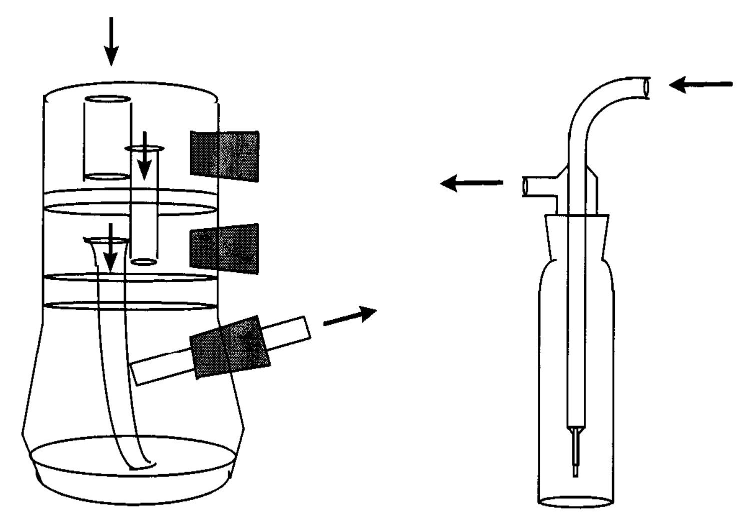
Inertial Impactors



r flow

(a) conventional jet-to-pate impactor collecting a single size fraction (say all particles over 10 µm); (b) multistage or cascade impactor in which each stage collects a different size fraction; and (c) virtual impactor or dichotomous sampler in which size fractions are separated but not removed from the airstream.

Liquid Impingers

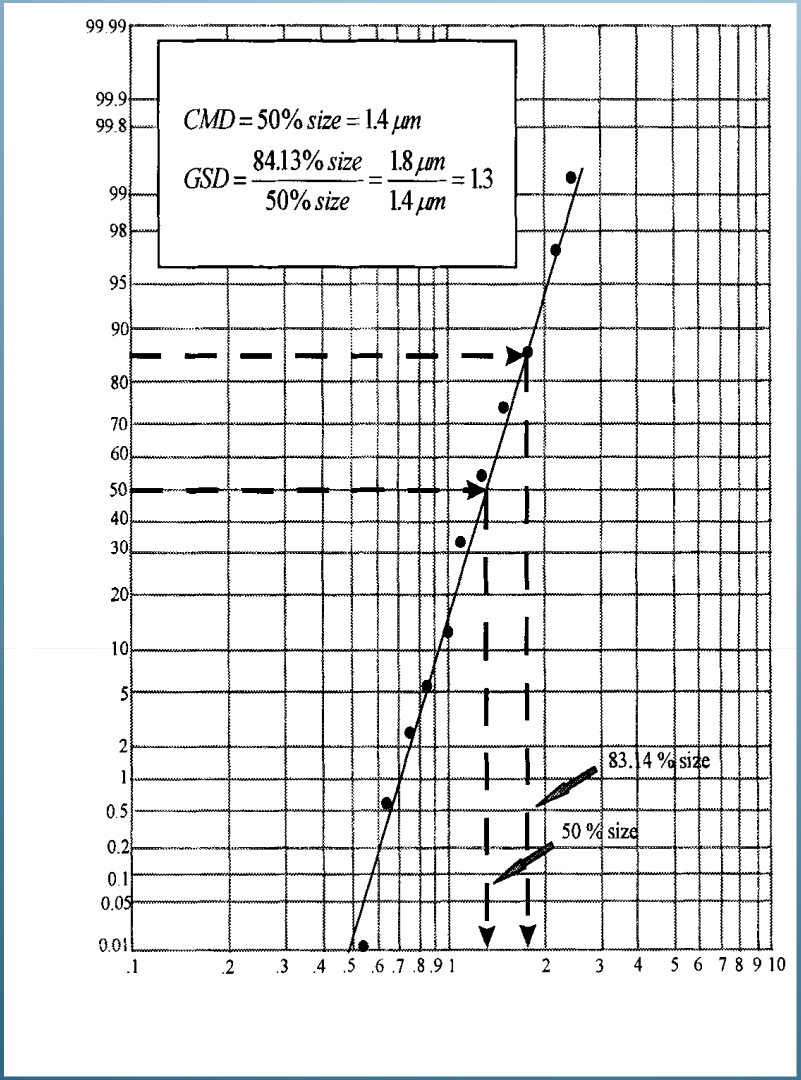


(a) multistage impinger in which a jet impinges on a wet surface, and (b) all glass impinger in which a jet impinges on a liquid surface or a submerged jet impinges on the bottom of the impinger.

Analysis of Particle Count Data

Lower Interval Size (µm)	*Upper Interval Size (µm)*	*Midpoint Interval Size d_i (µm)*	*Number in n_i*	*Fraction Interval (%)*	*Cumulative Interval Fraction less Than d_i (%)*
0.46	0.54	0.50	3770	0.74	0.74
0.54	0.63	0.585	13,000	2.56	3.30
0.66	0.74	0.685	55,100	10.84	14.14
0.74	0.86	0.80	62,900	12.38	26.52
0.86	1.0	0.93	98,800	19.44	45.96
1.0	1.2	1.1	109,000	21.45	67.41
1.2	1.4	1.3	98,800	19.44	86.85
1.4	1.6	1.5	37,200	7.32	94.17
1.6	1.8	1.7	17,000	3.35	97.52
1.8	2.2	2.0	9710	1.91	99.43
2.2	2.5	2.35	2850	0.56	99.99
2.5	2.9	2.7	52	0.01	100
			508,182		

Aerosol Size Distribution Cumulative Probability Plot



The aerosol particle sizes are approximately lognormally distributed if a straight line provides a good fit to the measurement data. CMD and GSD are determined from the plotted line. Count-based distributions result from optical measurement instruments that estimate particle size by examining particle light scattering behavior.

Sampling Gases and Vapors

For most industrial hygiene applications- GASES AND VAPORS are sampled at low flow rates to allow effective adsorption to occur onto the sorbent material. PARTICULATES are sampled at high flow rates so that airborne particles can be effectively trapped onto the filter material.

LOW FLOW PUMP

HIGH FLOW PUMP
also with low flow capabilities

Calibration Standards

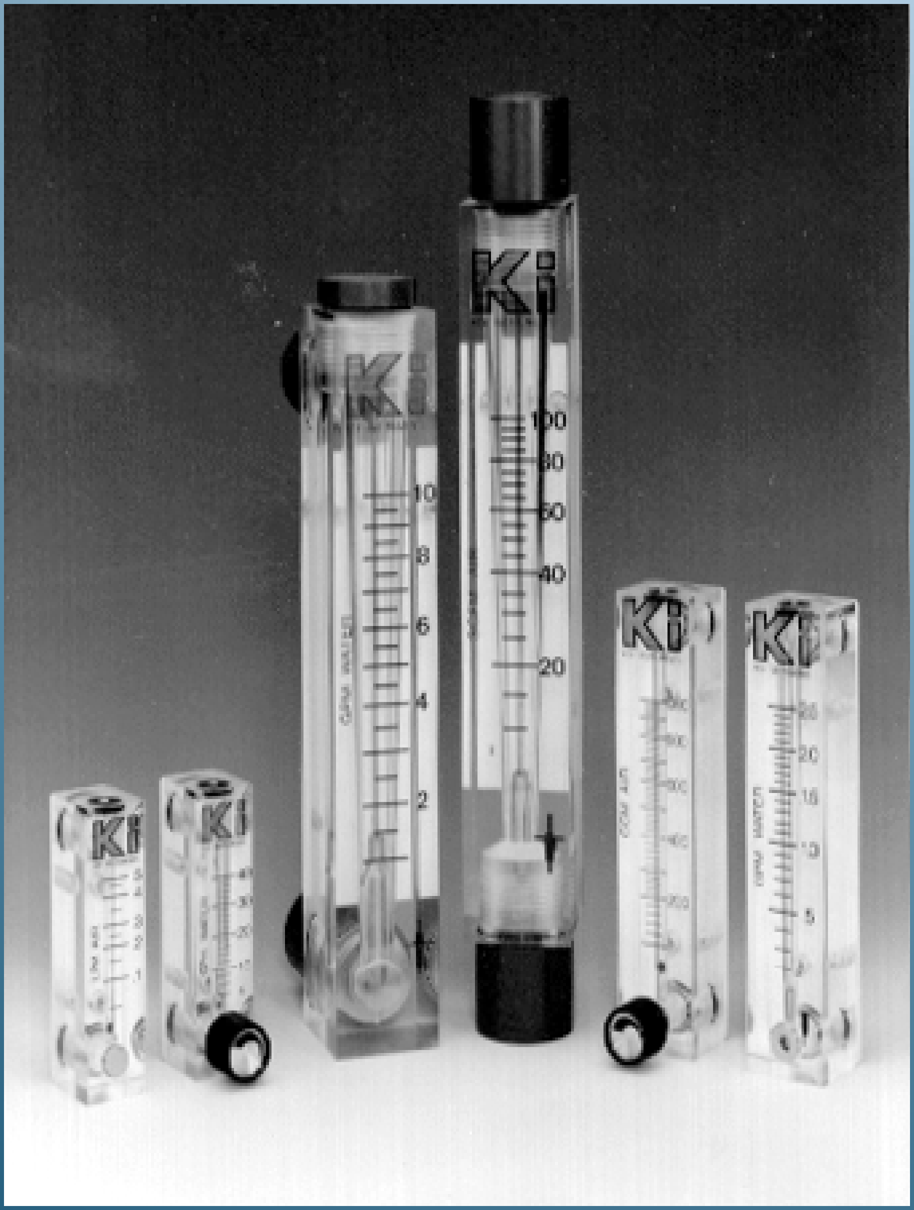
- Exposure Chambers
- Primary Standards
- Secondary Standards
- Calibration Gases
- Calibration Curves
- Ambient Measurements
- Standard Blanks

Manual Flowmeter Kit Model 302 With a Range of 100 to
4000 ml/min

An Electronic Soap Bubble Flowmeter

The Gilibrator-2, shown being used to calibrate a personal air sampling pump using one of three possible interchangeable cells (courtesy Sensidyne Inc., Clearwater, Fla.).

Field Rotameters

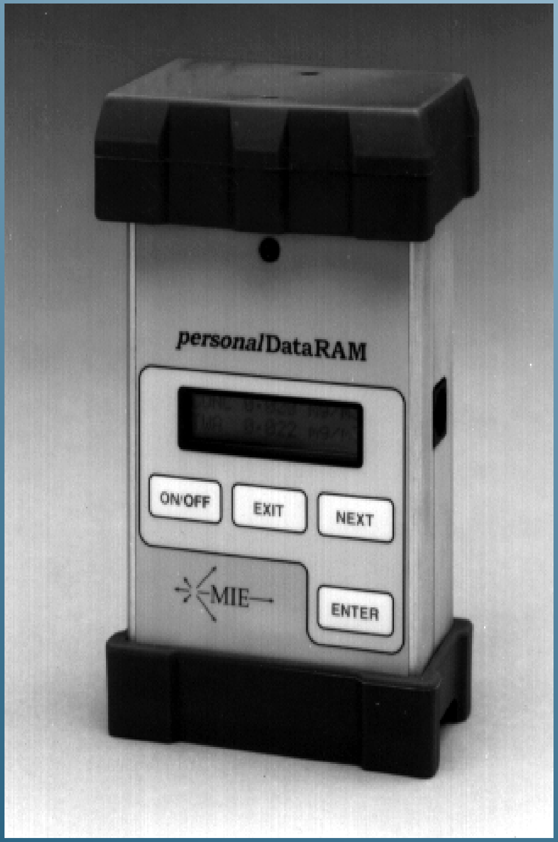


A variety of lightweight (acrylic plastic), single float, field rotameters (courtesy Key Instruments, Trevose, Pa.).

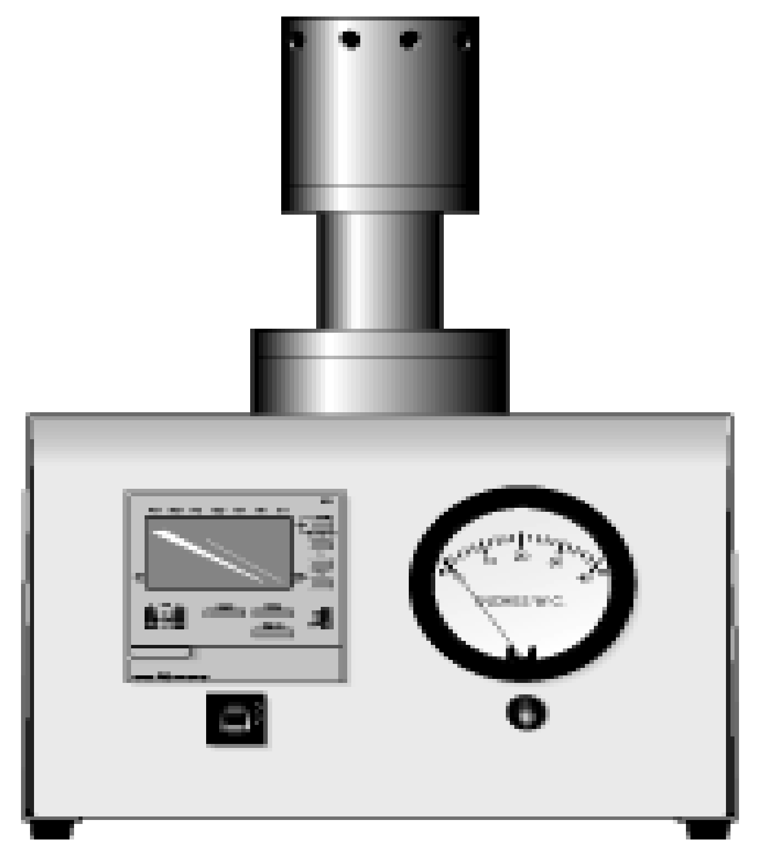
Commonly Used Aerosol Monitors

Instrument	*Sample Flow*	*Size Range*	*Concentration Range*
Light-scattering photometers	passive to 100 L/min	0.1 to 20 μm	0.0001 $\mu m/m^3$ to 200 g/m^3
Light-scattering particle counters	0.12 L/min to 28 L/min	0.1 to 8000 m (up to 32,000 μm for drop size analyzers)	1 particle/L to 10^5 particles/cm^3
Condensation nucleus counters	0.003 L/min to 4.2 L/min	1.6 nm to 20 nm	0.1 to 10^6 particles/cm^3
Single Particle Aerosal Relaxation Time (SPART)	0.5 to 5 L/min	< 0.3 to 10 μm	NA
Beta attenuation aerosol mass monitors	15 L/min	< 10 μm	10 mg/m^3 max
Piezoelectric crystal microbalance	0.24 to 1 L/min	0.05 to 35 μm	100 g/m^3 to 100 mg/m^3
Tapered Element Oscillating Microbalance (TEOM)	NA	0.5 to 35 μm	5 $\mu g/m^3$ to

Multiple Particle Optical Monitor: The MINIRAM



MICROENVIRONMENTAL MONITOR (MEM)

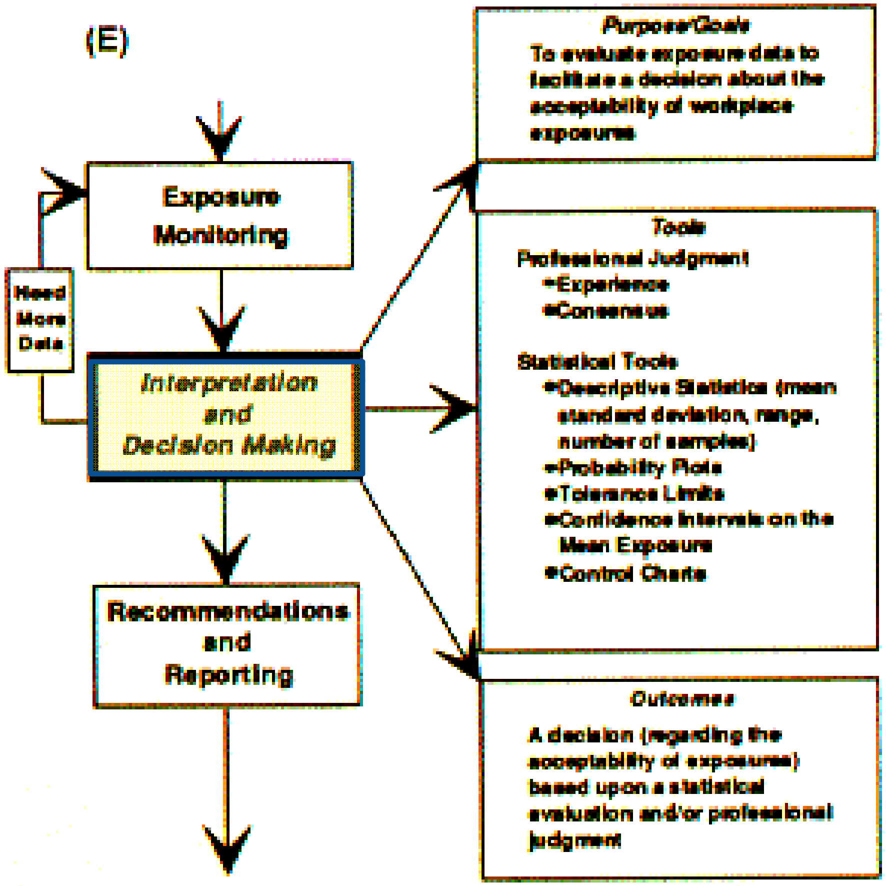


EXPOSURE GUIDELINES
FOR AMBIENT OR INDOOR AIR

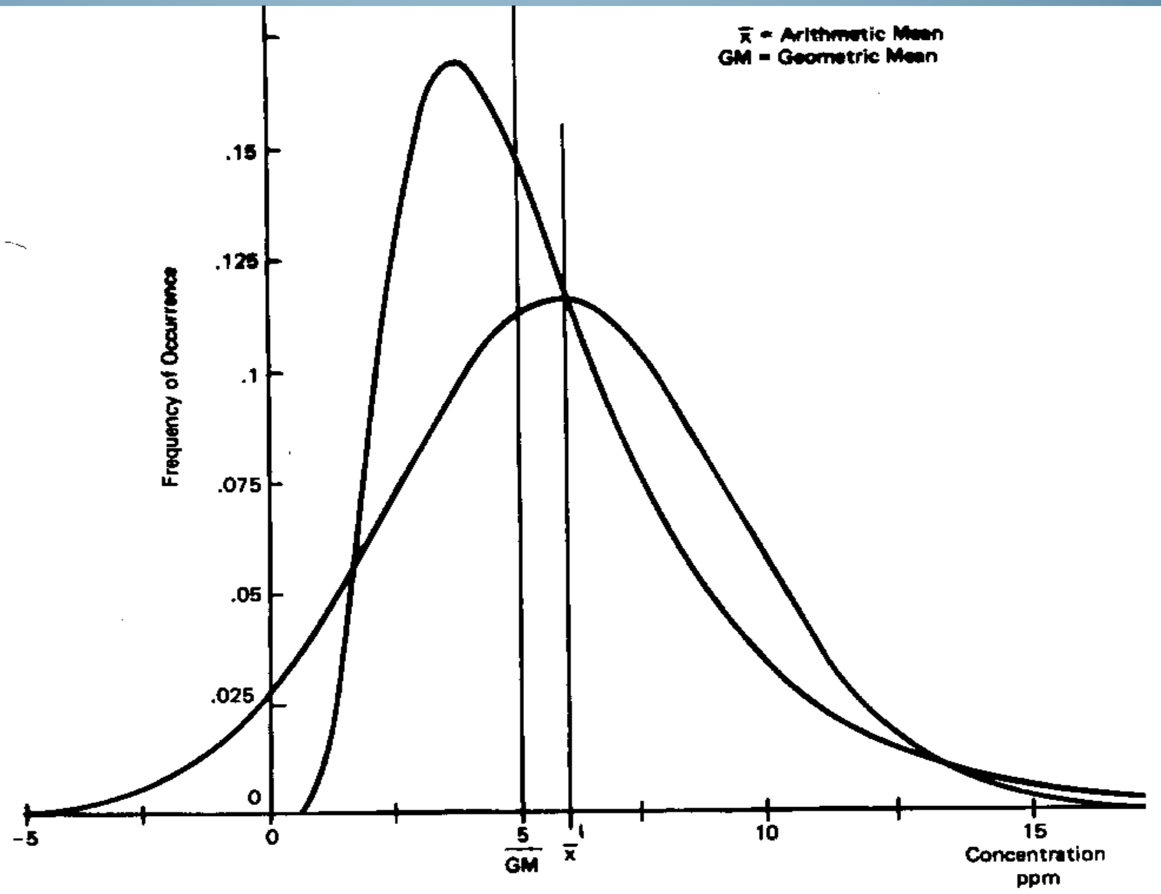
- PM 10-Particulate Matter less than 10 um in aerodynamic diameter

- PM 2.5-Particulate Matter less than 2.5 um in aerodynamic diameter

PERSONAL ENVIRONMENTAL MONITOR (PEM)

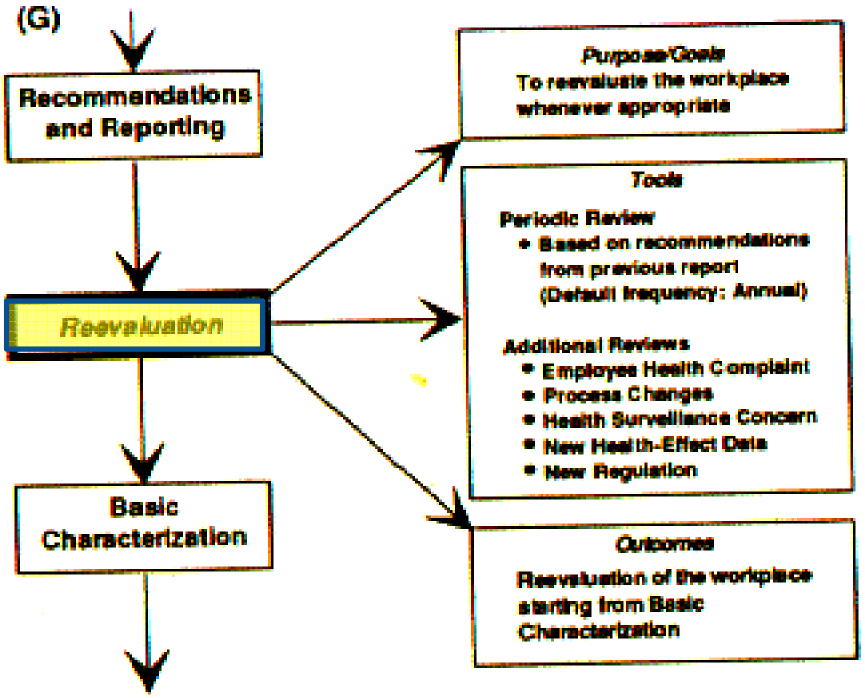


Exposure Assessment Strategy
Log-Normal Distribution

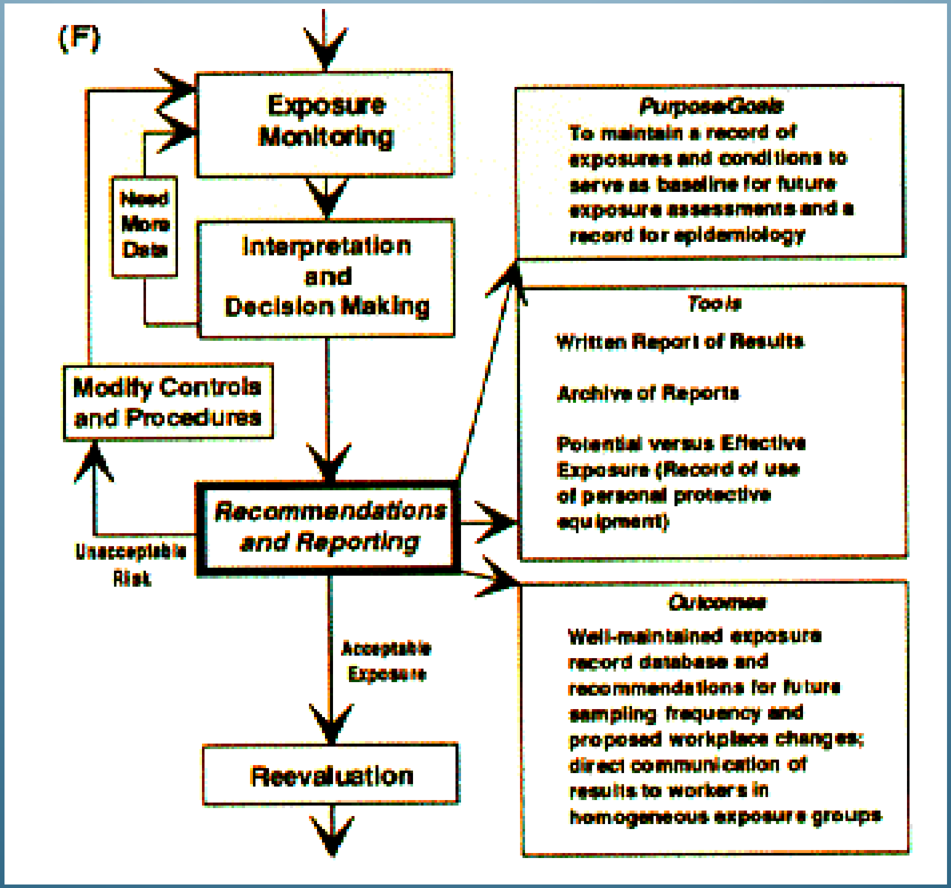


Lognormal and normal distributions with the same arithmetic mean and standard deviation.

Exposure Assessment Strategy



Exposure Assessment Strategy



Purpose/Goals

To maintain a record of exposures and conditions to serve as baseline for future exposure assessments and a record for epidemiology

Tools

Written Report of Results

Archive of Reports

Potential versus Effective Exposure (Record of use of personal protective equipment)

Outcomes

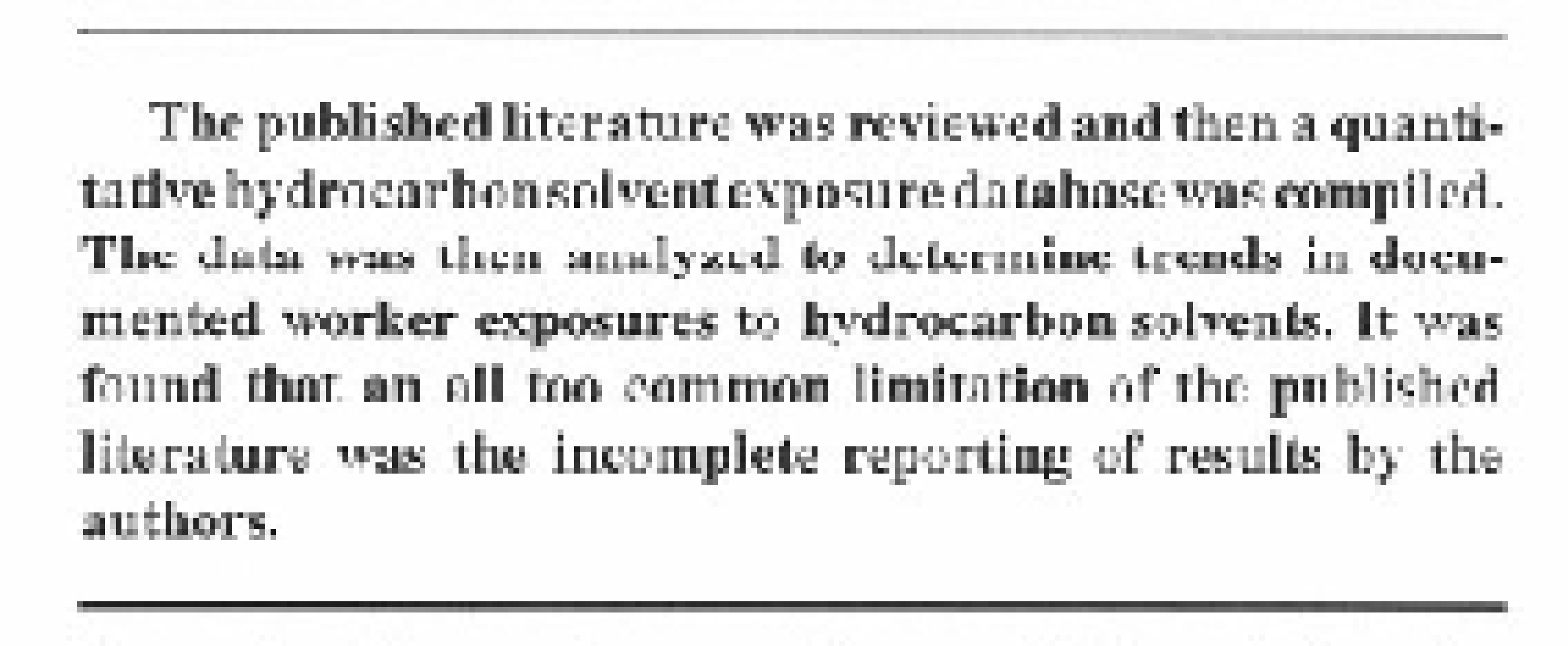
Well-maintained exposure record database and recommendations for future sampling frequency and proposed workplace changes; direct communication of results to workers in homogeneous exposure groups

Mistakes

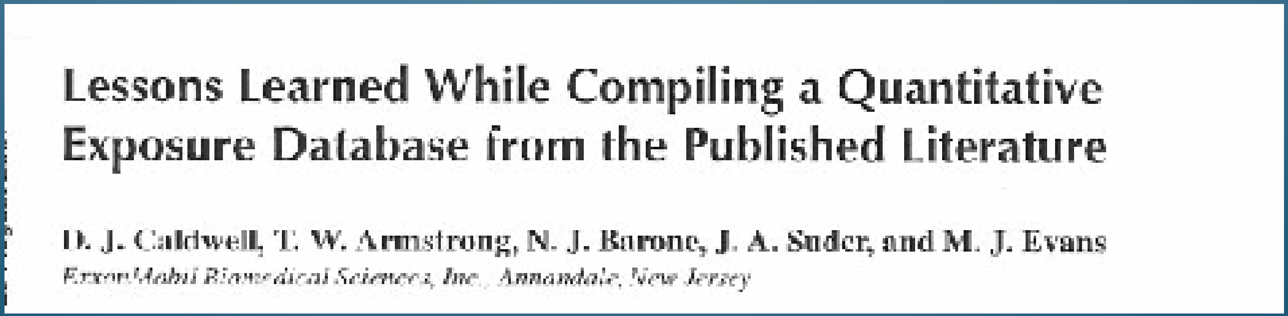
- A compilation of 50 common mistakes is included in reference file. Example:
- Collection of an air sample in the work environment is rarely a simple, straightforward task. Virtually every method has recommended protocols covering the flow rate, the minimum and maximum sample volumes, and the preparation, handling, and storage of collection media. Competent project preparation must include research into these details. It is often desirable to call a trusted technical consultant at the laboratory you are using to update information found in standard references.

Sampling, Calibration and Errors.ppt

USE DATA WITH CAUTION



The published literature was reviewed and then a quantitative hydrocarbon solvent exposure database was compiled. The data was then analyzed to determine trends in documented worker exposures to hydrocarbon solvents. It was found that an all too common limitation of the published literature was the incomplete reporting of results by the authors.



Lessons Learned While Compiling a Quantitative Exposure Database from the Published Literature

D. J. Caldwell, T. W. Armstrong, N. J. Barone, J. A. Suder, and M. J. Evans
ExxonMobil Biomedical Sciences, Inc., Annandale, New Jersey

DATA REPORTING PROBLEMS

- Incomplete record of current or historical exposures
- Incomplete / inaccurate exposure assessment for risk assessment
- Poor regulatory decisions
- Failure to protect individuals

AIHCE 07 posterV3-1a.ppt

Assignment

- Read
  - “Lessons Learned While Compiling a Quantitative Exposure Database fro Published Literature”
  - “Characterizing Historical Industrial Hygiene Data: A Case Study Involving Benzene Exposures at a Chemical Manufacturing Facility (1957 – 1987)
  - Convert 100 ppm xylene to mg / M3