OHTA Occupational Hygiene Training Association

STUDENT MANUAL

Measurement of Hazardous Substances

February 2009

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ABBREVIATIONS

µg	Microgram
µg/m^3	Microgram per Cubic Metre
µm	Micrometre
AAS	Atomic Absorption Spectroscopy
ACGIH	American Conference of Governmental Industrial Hygienists
AIDS	Acquired Immune Deficiency Syndrome
AIHA	American Industrial Hygiene Association
AIOH	Australian Institute of Occupational Hygienists
AM	Arithmetic Mean
AS	Australian Standard
AS/NZS	Australian Standard/New Zealand Standard
BEI®	Biological Exposure Indices
BCIRA	British Cast Iron Research Association
BIOELV	Binding Occupational Exposure Limit Values
BMGV	Biological Monitoring Guidance Values
BOHS	British Occupational Hygiene Society
CIS	Conical Inhalable Sampler
cm	Centimetre
CNS	Central Nervous System
COSHH	Control of Substances Hazardous to Health
CS_2	Carbon Disulphide
CV	Coefficient of Variation
ES	Exposure Standard
FID	Flame Ionisation Detector
g/cm^2	Grams per Square Centimetre

ABBREVIATIONS (Cont'd)

g/L	Grams per Litre
GC	Gas Chromatography
GHS	Globally Harmonised System of Classification and Labelling of Chemicals
GM	Geometric Mean
GSD	Geometric Standard Deviation
HEG	Homogeneous Exposure Group
HF	Hydrofluoric Acid
HPLC	High-Performance Liquid Chromatography
HSE	Health & Safety Executive (UK)
IARC	International Agency for Research on Cancer
ICP	Inductively Coupled Plasma Spectrometry
ILO	International Labor Organisation
IOELV	Indicative Occupational Exposure Limit Values
IOM	Institute of Occupational Medicine (UK)
IR	Infra-red
ISO	International Standards Organisation
L	Litre
LD_{50}	Lethal Dose $_{50\%}$
LEL	Lower Explosive Limit
L/M	Litre per Minute
LOD	Limit of Detection
LOQ	Limit of Quantitation
m^3	Cubic Metre
MCE	Mixed Cellulose Ester

ABBREVIATIONS (Cont'd)

MDA	Methylene dianiline
MDHS	Methods for the Determination of Hazardous Substances
MEL	Maximum Exposure Limits
mg/m^3	Milligrams per Cubic Metre
MHSWR	Management of Health and Safety at Work Regulations
ml	millilitre
MMMF	Man Made Mineral Fibre
Mins	Minutes
MOCA	Methylene bis-orthochloroanaline
MS	Mass Spectrometer
MSDS	Material Safety Data Sheet
MSHA	Mine Safety & Health Administration (USA)
MVUE	Minimum Variance Unbiased Estimate
NATA	National Association of Testing Authorities (Australia)
NIOSH	National Institute of Occupational Safety & Health (USA)
N/A	Not Applicable
nm	Nanometre
NMAM	NIOSH Manual of Analytical Methods
NOAEL	No Observed Adverse Effect Level
NOHSC	National Occupational Health & Safety Commission (Australia)
OD	Outside Diameter
OEL	Occupational Exposure Limits
OES	Occupational Exposure Standards
OSHA	Occupational Health & Safety Administration (USA)

ABBREVIATIONS (Cont'd)

PAT	Proficiency Analytical Testing Programme
PCB	Polychlorinated Biphenyls
PCM	Phase Contrast Microscopy
PDM	Personal Dust Monitor
PEL	Permissible Exposure Limits
PM10	Particulate Matter less than 10 micrometres
PNA	Polynuclear Aromatics
PNS	Peripheral Nervous System
PPE	Personal Protective Equipment
ppb	Parts Per Billion
ppm	Parts Per Million
ppt	Parts Per Trillion
PTFE	Polytetrafluoroethylene (Teflon)
PVC	Poly-Vinyl Chloride
REL	Recommended Exposure Limit
RPE	Respiratory Protective Equipment
S (or SD)	Standard Deviation
SCBA	Self Contained Breathing Apparatus
SEG	Similar Exposure Groups
SEN	Sensitisation
SIMPEDS	Safety In Mines Personal Environmental Dust Sampler
SiO_2	Silicon Dioxide
SMF	Synthetic Mineral Fibre
STEL	Short Term Exposure Limit
$T_{½}$	Half Life

ABBREVIATIONS (Cont'd)

TD	Thermal Desorption
TDI	Toluene Diisocyanate
TEOM	Tapered Element Oscillating Microbalance
TEL	Tetra Ethyl Lead
TEM	Transmission Electron Microscopy
TLV®	Threshold Limit Value
TNT	Tri-nitrotoluene
TWA	Time Weighted Average
UK	United Kingdom
UKAEA	United Kingdom Atomic Energy Authority
UKAS	United Kingdom Accreditation Service
USA	United States of America
UV	Ultra Violet
WA	Western Australia
WASP	Workplace Analysis Scheme for Proficiency
WEEL	Workplace Environmental Exposure Levels
WEL	Workplace Exposure Limits
WHO	World Health Organisation
XRD	X-ray Diffraction Spectrometry
XRF	X-ray Fluorescence Spectrometry
Zn	Zinc

1. COURSE OVERVIEW

1.1 INTRODUCTION

This Course has been developed in accordance with the international module syllabus W501 – Measurement of Hazardous Substances (including risk assessment) published by the British Occupational Hygiene Society (BOHS), Faculty of Occupational Hygiene. The BOHS administers a number of such modules; further information on which can be obtained by visiting the BOHS website at www.bohs.org.

At the time of publication every care has been taken to ensure all topics covered in the BOHS syllabus for the subject (W501) has been included in this Student Manual. Providers of training courses should check the BOHS website for any changes in the course content.

The developers of this Student Manual take no responsibility for any material which appears in the current BOHS syllabus for Module W501 which is not covered in this manual.

1.2 AIM OF COURSE

To provide students with a sound understanding of the techniques for assessing exposure to hazardous substances in the workplace and with an understanding of how exposure information can be used to assess risk.

1.3 LEARNING OUTCOMES

On successful completion of this module the student will be able to:

- describe the general approach to occupational chemical health risk assessment, including the role of atmospheric monitoring;
- select appropriate equipment to measure specific airborne contaminants and devise a suitable sampling strategy;
- present the results in a form useful for health risk assessment purposes to enable management to comply with relevant legislation.

1.4 FORMAT OF MANUAL

This manual has been specifically designed to follow the syllabus for this course as published by the BOHS. Similarly, the material provided in this manual has been aligned with the presentations for each topic so students can follow the discussion on each topic.

It should be recognised that the format presented in this manual represents the views of the authors and does not imply any mandatory process or format that must be rigidly observed. Presenters using this manual may well choose to alter the teaching sequence or course material to suit their requirements. In this regard the case studies are provided as illustrative examples and alternate case studies relevant to a particular industry may be used if desired.

In the final outcome, the aim of this manual is to transmit the principles of hazardous substances measurement to attendees and provide guidance as to how those principles should be applied.

2. INTRODUCTION TO PHYSIOLOGY & TOXICOLOGY

2.1 THE HUMAN BODY

The human body has many different interacting sub-systems. It is important to have some understanding of the function and features of these systems to appreciate the effects that exposure to occupational hygiene hazards and in particular exposure to hazardous substances may have.

2.1.1 Cardiovascular System

The main components of the cardiovascular or circulatory system are the heart, the blood and the blood vessels. The blood vessels consist of arteries, capillaries and veins.

Arteries bring the oxygenated blood, pumped from the heart, to the tissues and the veins bring the deoxygenated blood back to the heart. Blood passes from arteries to veins through capillaries, which are the thinnest and most numerous of the blood vessels.

2.1.2 Digestive System

The digestive system takes in food, digests it to extract energy and nutrients for the body and expels the remaining waste. It consists of:

Upper gastrointestinal tract – mouth, oesophagus and stomach
Lower gastrointestinal tract – small and large intestine
Related organs including liver, gall bladder and pancreas

2.1.3 Endocrine System

The endocrine system is a control system of ductless glands that secrete “instant messengers” or hormones that circulate within the body via the bloodstream to affect distant cells within specific organs. Endocrine glands secrete their products immediately into the blood or interstitial fluid, without storage of the chemical.

Hormones act as messengers and are carried by the bloodstream to different cells in the body which then interpret the message and act on them. Examples include the pituitary gland, the thyroid gland, adrenal gland and the pancreas and gonads.

2.1.4 Immune System

The immune system protects the body from infection by creating and maintaining barriers that protect bacteria and viruses from entering the body. If a pathogen breaches the barriers and gets into the body the innate immune system is equipped with specialised cells that detect, and often eliminate, the invader before it is able to reproduce, potentially causing serious injury to the host. A pathogen that successfully invades the innate immune cells faces a second, adaptive immune system. It is through the adaptive response that the immune system gains the ability to recognise a pathogen and to mount stronger attacks each time that pathogen is encountered. Examples of disease that arise from damage or impairment of the immune system are Hepatitis, Ebola, AIDS, Influenza, Cholera, Typhoid and Malaria.

2.1.5 Integumentary System

The integumentary system comprises of the skin (cutaneous membrane) and its accessory structures of hair, nails and exocrine glands. There are three layers of skin – epidermis, dermis and subcutaneous tissue. The cutaneous glands include the sweat glands, oil glands, glands of the ear and the mammary glands.

The skin is often known as the largest organ of the body and as the interface with the surroundings it provides protection against the physical hazards such as heat, radiation and abrasion, chemicals and bacteria. Its other important functions are insulation and temperature regulation, sensation and Vitamin D and B synthesis.

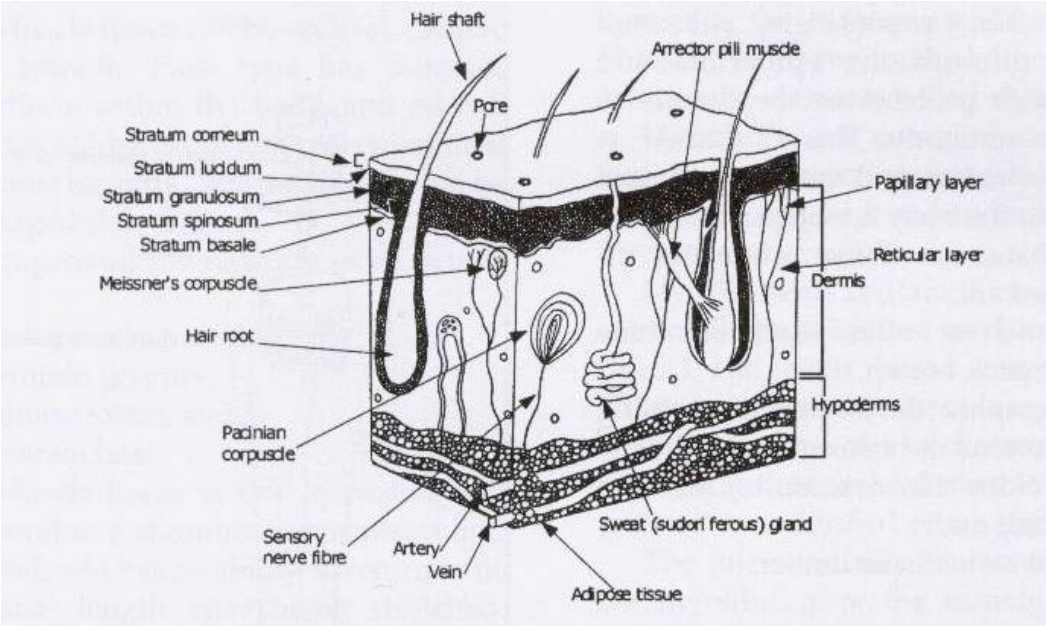

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Figure 2.1 – Diagram of the Layers of the Human Skin

2.1.6 Lymphatic System

The lymphatic system is a complex network of lymphoid organs, lymph nodes, lymph ducts and lymph vessels that produce and transport lymph fluid from tissues to the circulatory system. It is a major component of the immune system.

The lymphatic systems has three interrelated functions

- removal of excess fluids from body tissues
- absorption of fatty acids and subsequent transport of fat to the circulatory system
- production of immune cells (such as lymphocytes, monocytes and antibody producing cells called plasma cells.

2.1.7 Muscular System

The muscular system is the biological system that allows us to move. It is controlled by the nervous system, although some muscles (such as the cardiac muscle within the heart) can be completely autonomous.

In general the function of muscle is to produce movement, maintain posture, stabilise joints and to generate heat.

Muscles are attached to bone by tendons and other tissues. They exert force by converting chemical energy into force. Nerves link the muscles to the central nervous system.

2.1.8 Nervous System

The nervous system is often divided into the central nervous system (CNS) and the peripheral nervous system (PNS). The CNS consists of the brain and the spinal cord and functions as the body's control centre. The PNS consists of all of the other nerves and neurons in the body that do not lie within the CNS and carry electrical impulses to and from the spinal cord and cranial nerves that carry electrical impulses to and from the brain.

The peripheral nervous system is divided into the somatic nervous system and the autonomic nervous system.

The somatic nervous system is responsible for co-ordinating the body's movements, and also for receiving external stimuli. It is the system that regulates activities that are under conscious control.

The autonomic nervous system is then split into the sympathetic division, parasympathetic division, and enteric division. The sympathetic nervous system responds to impending danger or stress, and is responsible for the increase of one's heartbeat and blood pressure, among other physiological changes, along with the sense of excitement one feels due to the increase of adrenaline in the system. The parasympathetic nervous system, on the other hand, is evident when a person is resting and feels relaxed, and is responsible for such things as the constriction of the pupil, the slowing of the heart, the dilation of the blood vessels, and the stimulation of the digestive and genitourinary systems.

The role of the enteric nervous system is to manage every aspect of digestion, from the oesophagus to the stomach, small intestine and colon.

2.1.9 Reproductive System

The role of male and female reproductive systems is to produce offspring. The male reproductive organs include the sperm producing region – the testes located inside the scrotum and the duct system comprising the epididymis, the vas deferens and the urethra.

The female reproductive system consists of the internal organs including the ovaries, fallopian tubes, uterus, cervix and vagina.

2.1.10 Respiratory System

The respiratory system consists of the airways, the lungs and the respiratory muscles that mediate the movement of air into and out of the body. Inhaled air passes from the nose and mouth through the trachea and into the branched structures of the lungs called bronchi.

Air then travels along the bronchioles to its ending (the terminal bronchiole) which is covered in tiny multi lobed sacs called alveoli where most of the gas exchange occurs.

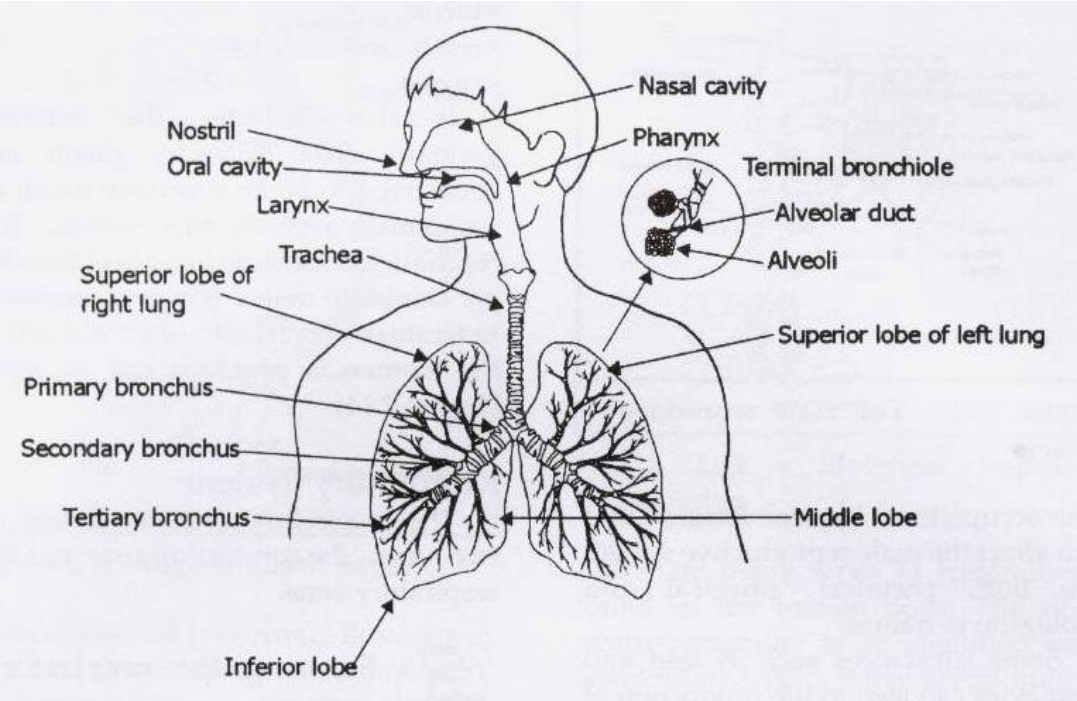

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Figure 2.2 – Respiratory System

2.1.11 Skeletal System

The human skeleton is made of 206 individual or joined bones, such as the skull, supported and supplemented by a structure of ligaments, tendons, muscles, cartilage and other organs.

The most obvious function of bone is to support the body. It is also the site of haematopoiesis, the manufacture of blood cells that takes place in bone marrow and why bone marrow cancer is very often a terminal disease. The skeleton is also necessary for the protection of vital organs. Human movement is dependent on the skeletal muscles which are attached to the skeleton by tendons. Without the skeleton to give leverage movement would be greatly restricted. Bone also serves as a storage deposit in which fat and minerals such as calcium and phosphorous can be stored and retrieved.

2.1.12 Urinary System

The urinary system is the organ system that produces, stores and eliminates urine. In humans it includes two kidneys, two ureters, the urinary bladder, two sphincter muscles and the urethra.

The kidneys' are one of the various organs (together with the lungs, intestine and skin) that participates in the elimination of the wastes of the organism. The kidneys are bean-shaped organs about the size of a bar of soap. They are near the middle of the spine, just below the ribcage. They are situated behind the organs of digestion within the abdominal cavity. Situated on the superior surface of each kidney is an adrenal gland.

A kidney consists of about 1 million filtering units termed nephrons, each consisting of a glomerulus, ball-shaped network of capillaries, and a network of tubules. Blood plasma is filtered by the glomerulus, and the resultant "prourine" passes through the tubular system where water, and nutrients are reabsorbed under the supervision of hormone activity and the autonomic nervous system.

Humans produce about 1.5 litres of urine over 24 hours, although this amount may vary according to circumstances. Increased fluid intake generally increases urine production, while increased perspiration and respiration may decrease the amount of fluid excreted through the kidneys. A reduced intake of water will normally result in less urine production as well. Some medications interfere directly or indirectly with urine production, such as diuretics.

The kidney plays a crucial role in regulating electrolytes in the human blood (e.g. sodium, potassium, calcium). pH balance is regulated by the removal of excess hydrogen ions (H^+) from blood. In addition, they remove urea, a nitrogenous waste product from the metabolism of proteins from amino acids. The metabolism process forms ammonia which is transported by blood to the liver and detoxified to a less harmful byproduct called urea.

2.2 ROUTES OF ENTRY

There are four primary routes of entry for contaminants into the human body;

1. Inhalation

The requirements of a man in a normal day are approximately 3.4 kg food and water (water is obtained in the food we eat and as direct ingestion).

For light physical work an average person breathes in between 1-1.2 m^3 of air per hour. This rate would be much higher for heavy physical exertion.

Therefore it is easy to understand why inhalation is by far the most common route of entry due to both the volume of air coming into contact with the large surface area of the lungs and the thin cell layer in the lungs separating the air from the blood, with skin absorption next (especially pesticides) and ingestion last. Inhalation is the major route of entry of dusts, fumes, mists, gases and vapours into the body.

2. Skin Absorption (includes injection)

Skin absorption via direct contact with chemicals especially organic solvents and organophosphate pesticides is the second most important route of entry to the body.

3. Eye

The eye is a relative minor route of entry into the body. It should also be noted that the eye is also at risk from direct contact with chemicals.

4. Ingestion

Ingestion is a relatively minor route of absorption of chemicals in the workplace. It is usually as a result of an accidental ingestion or as from poor personal hygiene eg eating with dirty/contaminated hands.

It should be noted that insoluble aerosols can end up in the digestive tract from where they can be absorbed into the body. Additionally, involuntary ingestion as a result of clearance mechanisms in the upper respiratory tract can also be another route of entry, especially in the case of large particles of toxic substances.

2.3 TARGET ORGANS AND SYSTEMS

There are numerous target organs for contaminants in the human body such as;

- Heart
- Lungs
- Kidneys
- Liver
- Brain
- Central Nervous System
- Bones
- Thyroid
- Blood

Target organs are defined as organs in which critical effects are observed as the result of exposure to a harmful input. There are many identifiable instances of inputs which affect a number of critical organs. Which they affect depends upon the circumstances of exposure, the interplay of defence processes and the susceptibility of the individual, as well as the tissues of the target organ. Thus, in discussing effects it is required that all possible target organs are considered.

The definition of 'target organs' must, necessarily, be wide, and must include, where appropriate, systems and tissues as well as organs.

For example, the target organ of hydrogen sulphide, which attacks the nerve tissue and causes respiratory paralysis, might be categorised as the central nervous system.

Crocidolite induces serious disease of the pleura and peritoneum (the tissue lining in the inner surface of the chest wall, and the lungs or the inner surface of the abdominal cavity and the abdominal organs). In this instance the pleura and peritoneum are the target organs.

A series of target organs and an outline of their principal functions are given in Table 2.1.

Table 2.1 – Target Organs, With an Outline of Their Principal Functions

TARGET ORGAN	PRINCIPAL FUNCTIONS	
Skin	Protects against friction, water/fluid loss, entry of harmful inputs; thermal insulation; self-greasing by means of sebaceous glands; thermoregulatory by means of sweat glands; receives afferent information.	
Respiratory tract	Oxygen and carbon dioxide exchange; defence against aerosols; warming and moistening of incoming air; excretion of gases, vapours.	
Blood, plasma, blood-forming organs: circulatory system	Metabolism: transformation and conjugation. Chief transport system for oxygen, carbon dioxide nutrients, heat and fluids.	
Kidney, urinary tract	Excretion:	Water, salts and nitrogenous wastes (includes homeostasis as well as bio-dumping).
	Secretion:	Hormones for controlling blood pressure and production of red blood cells
	Metabolism:	Transportation and conjugation
Liver	Secretory:	a) Bile - contains waste non-nutrients, aids digestion b) Heparin - anti-coagulant for blood
	Storage:	a) Vitamins b) Iron (for haemoglobin) c) Glycogen-energy store substance
	Metabolism:	Transformation and conjugation
Brain and nervous system	Information processing and control of bodily activities.	
Bone	Support framework for movement and protection (certain bones house blood-forming organs; but those are functionally separate from bone).	

TARGET ORGAN	PRINCIPAL FUNCTIONS
Gut	Input of nutrients; digestion; excretion of non nutrients; defensive processes of gastric-acid barrier.
Lymphoid system and lymphatics	Tissue drainage; filtration; site of defensive processes such as immune response and phagocytosis.
Ductless glands	Such as thyroid, parathyroids, adrenals (suprarenals); produce hormones - substances exercising key control over function and morphology.

2.4 CONCEPT OF DOSE RESPONSE

"No substance is a poison by itself, it is the dose that makes a substance a poison."

Paracelsus 1540

Ideally dose should be defined as the concentration of a substance at the site of effect, regard being made for the time for which the substance concentration is maintained. For practical purposes dose refers to the amount of a substance to which a person is exposed and is a combination of the amount or concentration of exposure and the duration of exposure. Exposure can arise from inhalation (most common route) or skin absorption (common with some substances) or via eye absorption (rare).

In simplistic terms dose can be expressed as:

Dose = Concentration of exposure x duration of exposure

This simplistic equation does not account for the following factors:

- Dose may be less than the amount inhaled if most is exhaled without any absorption (eg many gases)
- Heavy physical workload results in higher breathing rates than light workloads and thus have higher doses.
- Dose may depend on an individual being a mouth or nose breather.

- Additional exposure may come from non occupational sources (carbon monoxide from smoking).

Effect can be any observable, biological change associated with the input concerned, and ideally it should be quantifiable. It is implicit in dose-effect relations that effect is related to and caused by the dose.

Effect does not necessarily denote an adverse biological change, but embraces any biological change. Certain effects can be beneficial and only become adverse if the dose is excessive or remains for a critical period of time.

Types of toxic effects include acute, chronic, local and systemic.

Acute or immediate effects occur during or immediately after exposure and last for a short period of time. Examples of acute effects include the immediate eye and respiratory tract response to exposure to, and inhalation of, chlorine or burns to the skin caused by direct contact with strong acids or alkalis.

Chronic effects are long lasting and may be, but not necessarily, permanent. Some examples of chronic exposures are pneumoconiosis from long term exposure to coal dust, silicosis after exposures to quartz dusts.

Local effects occur at the point of entry to the body of the toxin and systemic effects are associated with distant target organs (eg with lead the main route of entry is by inhalation but the toxic effect is upon the blood forming process, nervous system, kidneys and reproductive functions).

Critical organ concentration seems, given the present state of knowledge, to be the parameter of greatest utility in estimating dose. Whole body concentration provides a less useful criterion, because the organs in which greatest accumulation occurs may not be critical organs.

Bone, for example, accumulates lead, but the critical organ is bone marrow, which is functionally separate from the bone which surrounds it.

At some time in the future it will, no doubt, be possible to estimate dose in terms of critical cell concentrations - or subcellular concentration - but at present this is impracticable.

There are complexities in the specification of effect, since certain effects, such as death, are of an all-or-none character, while others are of a graded nature, such as occupational deafness.

Specification is further complicated by the fact that certain all-or-none effects (cancer, for example) require only a trigger. Once triggered they continue by self-propagation or by the other processes independent of the dose of the triggering input. On the other hand, many observable and gradable effects are both trivial and reversible.

However, the complexities do not end here. The specification of dose needs to take account of all possible modes of input, and the non-occupational as well as the occupational possibilities. For example, in the case of metals like lead, in most if not in all countries, input by ingestion from the normal diet is inevitable. Any occupational exposure, probably by inhalation, will be supplemented by the non-occupational dose. Combination of the two may cause a critical organ concentration to be reached in the bone marrow or in other organs.

2.4.1 Dose Response

Dose response is that proportion of a human population which experiences a specific effect following exposure of the total population to specified harmful contaminant. The correlation of the response with estimates of the dose provides a dose-response relation, which is normally expressed as a graph, with percentage of population affected on the y axis and estimated dose on the x axis (Figure 2.3).

2.4.2 No Observed Adverse Effect Level

The “no observed adverse effect level” (NOAEL) is the term used to define that point below which adverse effects cannot be observed. Effects, particularly adverse effects, are generally manifestations of the change in an organ and particularly the cells of the organ.

In toxicology, the NOAEL is specifically the highest tested dose or concentration of a substance at which no adverse effect is found in the exposed test species (usually animals or cells)

This level is commonly used in the process of establishing a dose response relationship, a fundamental component in most risk assessment strategies.

Another important toxicological concept is “lowest observed adverse effect level” (LOAEL) or the lowest dose or concentration that causes any observed adverse effect. Thus by definition the NOAEL is less than the LOAEL.

As these determinations of exposure and effect have generally been established in species other than humans, various safety factors or uncertainties are applied before this data is used in the establishment of workplace exposure standards.

2.4.3 Threshold

The term "threshold" is used in toxicology to describe the dividing line between no-effect and effect levels of exposure. It may be considered as the maximum quantity of a chemical that produces no effect or the minimum quantity that does produce an effect. Every change produced by a chemical, whether it is beneficial, indifferent, or harmful, has a threshold. (Perhaps the word "change" should be qualified with an adjective such as "biological" or "clinical" to anticipate the reader with a literal bent who will say that the mere exposure of an organism to a chemical represents a change and that such a change obviously does not have a threshold).

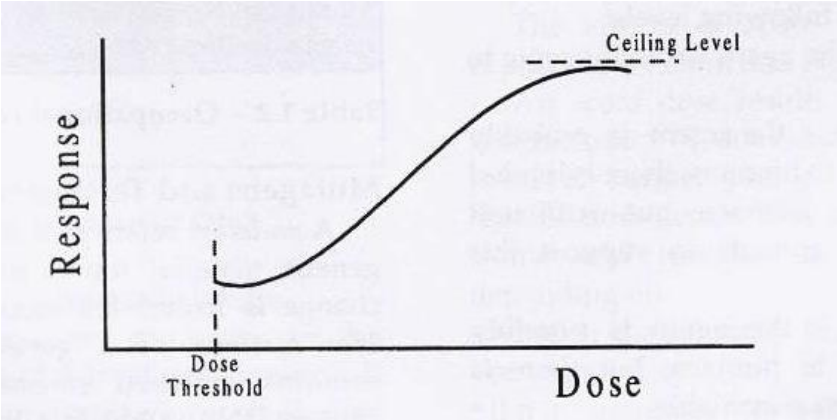
The precise threshold for a given effect can, and usually does, vary within certain limits with species, with individuals within a species, and perhaps even with time in the same individual.

For a given population, as illustrated by the dose response relationship (Figure 2.3), it is clear that thresholds exist because it can be determined experimentally that certain low levels of exposure will produce no detectable effect, and that as the dosage is increased the effect appears.

Since the dose-response relationship is a continuum, somewhere between the experimental no-effect and effect levels is the turning point known as the threshold.

Dose-response curves typical of those plotted from data obtained in chronic toxicity experiments exist for a number of contaminants. It is very important to recognise that such a curve is drawn from only several points, one for each exposure group in the experiment. The greater the number of exposure groups, the greater the number of points, and hence, the greater the accuracy of the curve that is drawn. But without an infinite number of points, the precise shape of the dose-response curve cannot be known.

The curve is interpreted as follows: with chronic exposure of increasing doses up to the threshold, no effect is detectable because some biochemical or physiologic mechanism, handles the chemical in a manner that prevents an effect from occurring. At the threshold, the defence mechanism is saturated, or in some manner overwhelmed, for the more susceptible individuals and the effect begins to appear. With increasing doses, increasing numbers of individuals show the effect until finally a dose is reached where all of the members of the population show the effect (ceiling level).



(Source: Tranter 1999 – *Reproduced with permission*)

Figure 2.3 – Dose Response Curve

The threshold concept is of great importance to toxicologists because it permits them to make judgements about the potential hazard, or lack thereof, to humans from exposure to chemicals.

Another toxicologic question relates to the shape of dose-response curves for carcinogens as they approach zero dose. The inability of toxicology to answer this question by experiment has given rise to a scientific controversy concerning whether or not there is a threshold (no-effect level) for carcinogenic effects. If there is no threshold, extension of the experimentally derived dose-response curve to zero effect would yield a line that would go through the origin (zero dose). If there is a threshold, the extended line would meet the abscissa at some point greater than zero dose.

In regard to carcinogens, it is important to note that it is rare to have any data except for high doses, so the estimate of the shape of the dose response curve below the lowest actual data point must typically cover many orders of magnitude. Where a threshold cannot be identified, limits are generally risk based and dependent upon the dynamics of the particular substance.

It is extremely important, as background to all considerations of the threshold, to recognise that detectable biological effects are not universally adverse.

What should be recognised is that in any group of test subjects there are some susceptible individuals (hypersensitive) who are affected at low concentrations of the test contaminant and there are also some highly resistant individuals (hyposensitive) who are not affected at high concentrations but there are the vast majority of “average” individuals in the middle (Figure 2.4).

Consequently exposure standards tend to be based on dose response relationships applicable to “average” individuals and thus it is important to recognise that some hypersensitive individuals may be in a work group and that they may suffer adverse health effects at exposures below the recognised exposure standard.

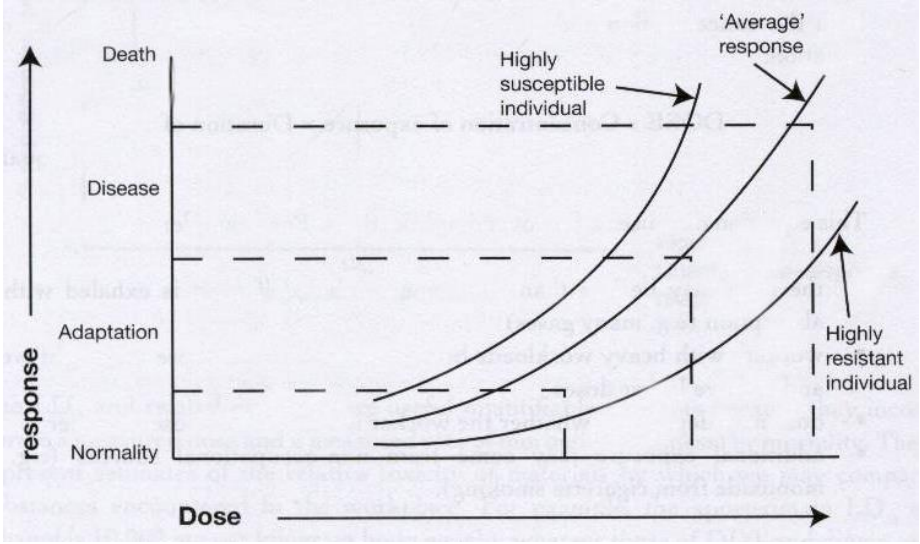


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Figure 2.4 – Variability of Human Exposure to Dose

2.4.4 Threshold of Intoxication

The threshold of intoxication can be defined as:

For each substance, no matter how toxic, there exists a dose level called the threshold of intoxication, which the human body is capable of accepting and detoxifying without injury to itself.
It is this principle that the major exposure standards used within the western world are based upon.

3. RISK ASSESSMENT

3.1 DEFINITIONS

3.1.1 Introduction

Many formal definitions of “risk” and “hazard” have been put forward covering all situations (eg health, safety, finance, and engineering), however they all strive to communicate similar messages.

In this publication the terms “risk” and “hazard” will be treated solely in relation to chemical risk and not in any broader concept. In the context of this course, “hazard” and “risk” is not the same thing.

3.1.2 Hazard

The “hazard” of a chemical substance is the potential for that substance to cause harm, injury, etc. Concentrated acids, for example, pose a clear hazard because incorrect handling of these chemicals could result in serious burns.

3.1.3 Exposure

In terms of chemical substances “exposure” can be defined as the ability (or potential) for someone to come into contact with a substance by breathing it in (inhalation), getting it onto the skin or into the eyes (absorption), or swallowing it (ingestion).

Thus, if a chemical is completely enclosed within a process (eg pipework) the potential for worker exposure to the chemical is low (except during maintenance or failures when the process integrity is breached), however if the chemical can readily escape from the process the potential for exposure is high.

In many cases it will be necessary to undertake workplace monitoring to have an understanding of the true exposure of a worker to a chemical.

In the vast majority of cases the focus will be on airborne exposure as this is the major route of entry to the body but with some chemicals other pathways (eg skin) must be considered.

3.1.4 Risk

The “risk” presented by a chemical substance is the likelihood that the substance will cause injury or illness in the conditions of its use. Thus, if we consider life savers (life guards) on beaches who are surrounded by tonnes of silica sand yet the incidence of silicosis in such persons is incredibly low. This is because the particle size of the sand is such that it is not inhaled and also that each particle has an “aged” surface rendering it less biologically active. In this case the risk is low.

If however the same sand is crushed or abraded and used in the construction industry for example, where workers breathe in the material during their work duties, then the risk is much higher as the material is inhaled and more biologically active due to “fresh” surfaces being exposed.

In general, the risk to health usually increases with the severity of the hazard, the amount used and the duration and frequency of exposure.

3.2 THE RISK ASSESSMENT PROCESS

3.2.1 Introduction

The risk management process can be applied across all sectors of the political, business and community environment. In many instances we do this as part of our everyday activities (eg driving to work), however the concept of risk assessment lies central to the occupational health and safety legislative framework of many countries. The process extends in many countries to occupational hygiene hazards with some statutory authorities requiring the mandatory conduct of risk assessments for specific hazards (eg hazardous substances).

In general all risk assessments for hazardous substances follow a similar pattern, however regulatory authorities or businesses may require a specific process to be followed to ensure consistency.

Notwithstanding these requirements the key steps to a successful risk assessment are indicated in Figure 3.1.

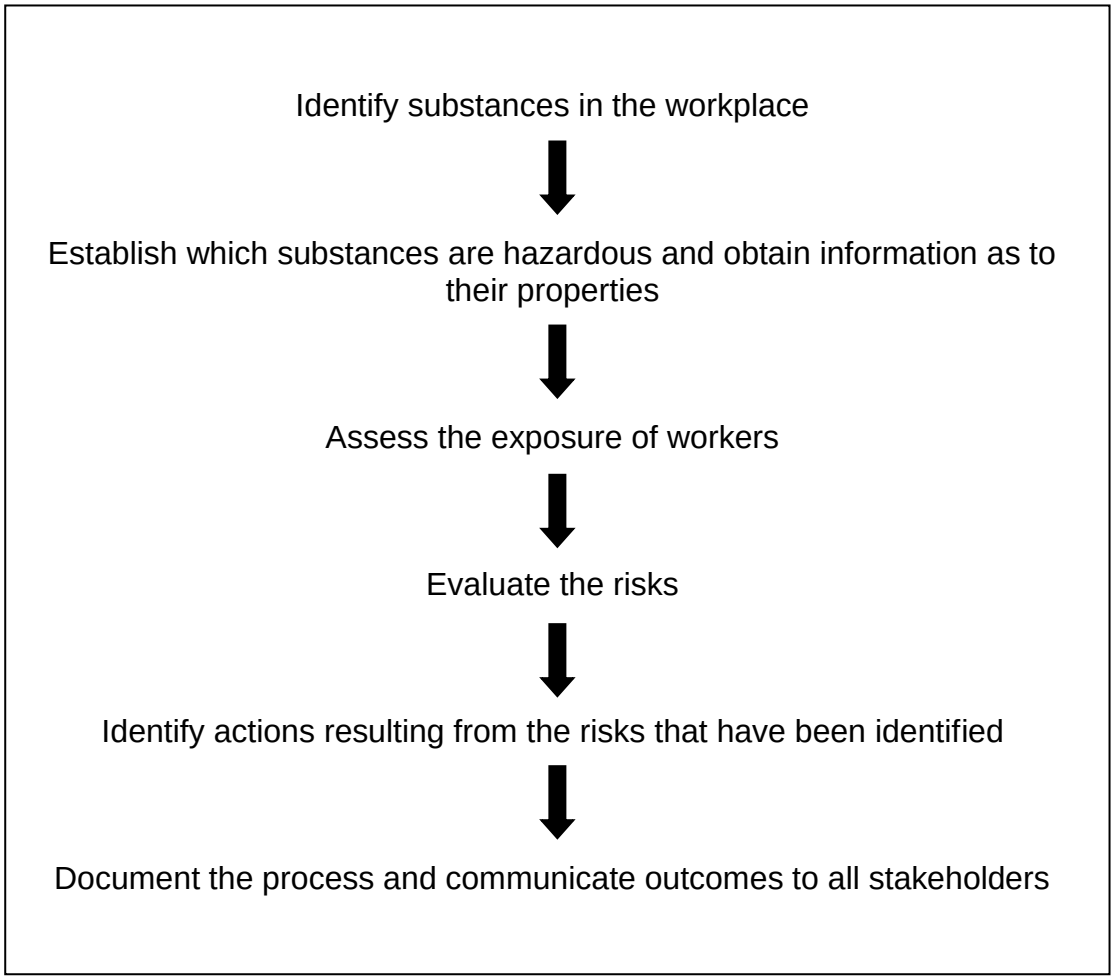


Figure 3.1 – Generic Risk Assessment Process for Hazardous Substances

3.2.2 Information

The outcome of any risk assessment will largely depend on the quality and amount of information available as an input to the risk assessment process (eg good quality detailed information will ensure a realistic assessment of the risks involved is obtained).

Where can information be obtained on hazardous substances? In general the primary source of information about any substance will be the supplier's Material Safety Data Sheet (MSDS) and the label fixed to the product. Care must however be exercised when using suppliers MSDS as an information source as the hazard information in the data sheet is sometimes incomplete or inaccurate.

Most countries require suppliers to provide users with a MSDS and under a United Nations sponsored scheme such documentation is moving towards a uniform format.

As previously indicated, a significant number of countries are participating in the development of a Globally Harmonised System of Classification and Labelling of Chemicals (GHS) through the United Nations. The GHS provides a uniform way of classifying chemicals, as well as informing chemical users about chemical hazards they may be exposed to.

The GHS builds on the attributes of existing national regulatory systems to form a single international system that has application across a wide range of chemicals and hazard types. The GHS when implemented will:

- enhance the protection of human health and the environment by providing an internationally comprehensible system for hazard communication
- provide a recognised framework for those countries without an existing system
- reduce the need for testing and evaluation of chemicals, and
- facilitate international trade in chemicals whose hazards have been properly assessed and identified on an international basis.

Pictograms are a key hazard communication tool within the GHS. They are designed to appear on chemical labels. The pictograms give an immediate indication of the type of hazard that the chemical may pose.

They are intended to be used in combination with other harmonised GHS elements which together convey information about the type, severity and management of chemical hazards. An example of the pictograms to use is provided in Figure 3.2.

Under the GHS these pictograms will be supported by hazard statements which will replace the risk and safety phrases (eg R26 – very toxic by inhalation or S3 – keep in a cool place), which are currently used in many countries.

A significant number of countries have indicated they will implement the GHS as a key part of their national chemical regulation systems.

(Source: ASCC Information Sheet)

Figure 3.2 – GHS Pictograms

In some cases the hazardous substance present in a process may be generated as a result of the process. Moreover it may be the process itself which results in a change in the form of a material (eg generation of fine dusts from solid materials, fumes from heating of a chemical) which may be a cause for concern. In such cases it is generally possible to obtain useful information by conducting interviews of workers, managers, engineers, medical and safety personnel. An indication of the types of information that it is possible to obtain from this process is provided in Table 3.1. Additional information may also be obtained from records, government and industry standards, as well as the scientific literature.

Table 3.1 – Sources of Additional Information

Collection Method	**Type of Information**
Interviews of workers, managers and engineers	Tasks Work practices Health issues Processes Exposure controls Maintenance Environmental agents
Interviews of medical and safety staff	Health problems Patterns of problems Work practices Exposure history Environmental agents
Records: Process standards Standard operating procedures Production Personnel Medical Engineering Environmental reports Process flow diagrams	Historic conditions Chemical inventories Usage amounts Tasks Work histories Performance of engineering controls Past environmental monitoring results Past biological monitoring results
Governmental and non-governmental standards	Current exposure limits Proposed exposure limits
Literature	Epidemiological studies Toxicological studies Emerging issues

Experience has long demonstrated that the simple process of conducting a “walkthrough survey” can provide information that may otherwise not be evident. The walkthrough survey involves commencing at the starting point of a process and physically following the various components of a process until the end product is reached. To obtain value from the exercise it must be conducted in the company of someone familiar with each step of the process.

The basic observations arising from a walkthrough survey include:

a) An understanding of the process

b) The number of workers involved

c) The materials (including quantities) used or handled

d) Evidence of reactions and any material transformations

e) Engineering controls in place and their effectiveness

f) Housekeeping standards

g) Visible conditions at the site (any dusts, mists, etc)

h) Possible routes of entry to the body

i) Personal protective equipment and its use

j) An understanding of ancillary activities, eg waste management, maintenance procedures, laboratory facilities, etc

Using information from the above sources, it is then possible to assess the risks presented by using the hazardous substance(s) in question.

3.2.3 Assessing the Risk

When assessing the risk of a hazardous substance it is important to understand that a number of factors influence the level of risk. These include

a) How much a worker is exposed to a hazardous substance (exposure)

b) How the worker is exposed to the substance (inhalation, skin contact, ie route of entry to the body)

c) How severe are the adverse health effects under the conditions of exposure (hazard)

d) Duration and frequency of exposure (a single short exposure or continuous long term exposure)

Thus the level of risk posed by using a hazardous substance (without controls) depends on the combination of the hazard of that substance and the duration and frequency of exposure.

ie Risk (uncontrolled) α hazard x exposure

Thus, if the exposure is zero (exposure controlled) then the risk will be zero (controlled). Conversely, reducing the hazard (by, for example, substitution of a hazardous product with a non hazardous one) will also reduce the risk.

In order to estimate the level of risk of a hazardous substance it is necessary to draw together all available information about the substance (health effects), its use (the quantity involved and control technologies), and the degree of exposure.

Before undertaking such a step it is of value to understand the types of risk analysis possible. In general, analysis may be qualitative or quantitative or a combination of these depending upon circumstances. In practice, qualitative analysis is often used first in order to obtain a general indication of the level of risk and to highlight the major risk issues. Subsequent to this process it may be necessary (and often is) to undertake a more detailed quantitative analysis of the major risk issues. These two types of analysis can be described as follows:

a) *Qualitative Analysis*

Qualitative analysis uses words to describe the magnitude of potential consequences and the likelihood that those consequences will occur. These scales can be adapted or adjusted to suit the circumstances, and different descriptions may be used for different risks.

Qualitative analysis may be used:

- as an initial screening activity to identify risks which require more detailed analysis;
- where this kind of analysis is appropriate for decisions;

  or

- where the numerical data or resources are inadequate for a quantitative analysis.

Qualitative analysis should be informed by factual information and data where available.

b) *Quantitative Analysis*

Quantitative analysis uses numerical values (rather than the descriptive scales used in qualitative and semi-quantitative analysis) for both consequences and likelihood using data from a variety of sources.
The quality of the analysis depends on the accuracy and completeness of the numerical values and the validity of the models used.

Consequences may be determined by modelling the outcomes of an event or set of events, or by extrapolation from experimental studies or past data. In some cases, more than one numerical value is required to specify consequences for different times, places, groups or situations.

The Health & Safety Executive (HSE) in the United Kingdom has regulated the Control of Substances Hazardous to Health (COSHH Regulations 2002) and in its guidance material highlights the importance of considering the risks hazardous substances present to people's health.

When assessing the risk that any hazardous substance may present to people's health, there are some basic steps that can be followed. For example, ask yourself the following questions and seek to find the appropriate answers before making any judgement.

- How much of the substance is being used and how could people be potentially exposed?

- Who could be exposed to the substance and importantly, how often?

- What is the route of entry to the body (eg absorbed through the skin, ingestion or inhalation)?

For a number of substances the HSE has developed a generic risk assessment tool called “COSHH Essentials: Easy steps to control chemicals”. The guide uses information on the hazardous nature of the substance, amount used, estimates of exposure (based on simple definitions of dustiness for solids or volatility for liquids) to establish a level of risk. The process also provides suggested actions that can be used to control the risks and therefore control exposure.

A free version of COSHH Essentials can be found on the internet at www.coshh-essentials.org.uk.

The International Labor Organisation (ILO) Tool Kit (see section 5.2.1), offers a similar approach to that of the UK COSHH Essentials system. It should be noted that neither of these approaches are validated methodologies but were developed as an approach to assist small to medium enterprises who do not usually have access to risk assessment expertise.

From the preceding information, it is evident that the process of assessing the risk of using a hazardous substance depends on obtaining adequate information on the hazards of a substance and the degree of exposure. Subsequent chapters of this manual will discuss how the degree of exposure to a hazardous substance can be evaluated and assessed against recognised exposure standards.

Once information on exposure has been obtained (for a quantitative risk assessment this will need to be evaluated to cover all situations), some estimate of risk can be obtained by considering this and the hazards involved.

The risk may generally be described as ‘significant’ or ‘not significant’. The risk can be regarded as ‘not significant’ if it is unlikely that the work will adversely affect the health of people in the workplace. A ‘significant risk’ means that the work is *likely* to adversely affect the health of people in the workplace. For example, there would be a ‘significant risk’ if:

- exposure is high or the substance used is highly toxic;
- a dangerous reaction with other substances might occur; or
- it is reasonably foreseeable that leaks or spills of a hazardous substance might occur.

In the event of a significant risk being established it is important that actions are taken to ensure that the risks are adequately controlled. In these circumstances, further work may be required to ensure that control measures are maintained and implemented. This could include the need for regular workplace monitoring or health surveillance, or a repeat of the assessment.

3.2.4 Actions

The process of risk evaluation provides a list of risks requiring control, often with priorities. The next step in the process involves identifying a range of control options for minimising these risks, evaluating those options, developing appropriate control technologies and implementing them in the workplace.

Development of options to control individual risks will seldom occur in isolation and should be part of an overall strategy. Having a clear understanding of a complete strategy is important to ensure that critical links are maintained.

It is wise in the development of any control strategy to be flexible and be prepared to consult with stakeholders as well as specialists. It is important that workers have some participation in this process if the controls are to be effective and sustainable.

Thus, if the risk assessment indicates a significant risk then further actions are necessary to control the risk. Such actions may include:

- **Selection of appropriate measures to achieve control**

  These measures may include, *in priority order:*

  - elimination of the hazardous substance from the workplace;
  - substitution with a less hazardous substance;
  - isolation (separating the employees from where the substance is used);
  - engineering methods (for example, local exhaust ventilation systems);
  - administrative control (for example, work procedures designed to prevent or minimise exposure to chemicals);
  - personal protective clothing and equipment (gloves, safety glasses, respirators, etc).

  The above approach is referred to as the “hierarchy of control”.

  It might be necessary to use a combination of these control measures to eliminate or minimise exposure.

  To ensure that adequate control is maintained, all control measures should be reviewed at regular intervals. Routine checks, regular maintenance and appropriate supervising procedures are also necessary.

- **Arrange induction and training**

  The extent of training will depend on the level of risk, with more extensive training being required for workers who are exposed to significant risks. The information collected during the assessment about the nature of the hazards and the control measures required should be used in preparing induction and training.

- **Determine if workplace monitoring is required**

  Ongoing monitoring may be required where the assessment indicates that it is necessary to check the effectiveness of control measures or where serious health effects might result if control measures fail because the substance is highly toxic, or the potential exposure is high.

- **Determine if health surveillance is required**

  Health surveillance is required for those substances nominated under the relevant regulations, and where the information gathered during the assessment shows that:

  - there is an identifiable work-related disease or adverse health effect for a hazardous substance used in the work;
  - the risk assessment indicates that it is likely the disease or condition might occur during the conditions of the work; and
  - valid techniques are available to detect early signs of the disease or condition.

- **Establish emergency procedures and first aid when necessary**

  Appropriate procedures should be established if an assessment suggests a risk of leaks, spills or other uncontrolled releases of hazardous substances. These include procedures for prevention, provision of first aid, safety showers and eye wash facilities, evacuation procedures, emergency procedures, etc.

The UK HSE COSHH regulations require employers to prevent exposure to hazardous substances if it is reasonably practicable to do so. This may be done by:

- change the process or activity so that the hazardous substance is not needed or generated;
- replace it with a safety alternative;
- use it in a safer form, eg pellets instead of powder.

If prevention is not reasonably practicable, employers must adequately control exposure. Employers are required to consider and put in place measures appropriate to the activity and consistent with the risk assessment, including, in order of priority, one or more of the following:

- use appropriate work processes, systems and engineering controls, and provide suitable work equipment and materials, eg use processes which minimise the amount of material used or produced, or equipment which totally encloses the process;

- control exposure at source (eg local exhaust ventilation), and reduce the number of employees exposed to a minimum, the level and duration of their exposure, and the quantity of hazardous substances used or produced in the workplace;

- provide personal protective equipment (PPE) (eg face masks, respirators, protective clothing), but only as a last resort and never as a replacement for other control measures which are required.

The above is provided as an example of what one regulatory authority requires in terms of actions to control the risks identified in using hazardous substances. Many other countries have similar approaches, however the degree of prescription depends totally on the local regulatory authority.

What should be clearly understood is that emergency response planning is a critical function. This must be done well in advance of an incident; personnel must be trained and be adequately equipped to handle any potential significant incident the risk assessment process identifies.

3.2.5 Records

Documentation of risk assessments is a fundamental step in the process and should be given adequate attention. Some reasons for documenting each step of the risk assessment process are:

a) to demonstrate to stakeholders that the process has been conducted properly;

b) to provide evidence of a systematic approach to risk identification and analysis;

c) to enable decisions or processes to be reviewed;

d) to provide a record of risks and to develop the organisation's knowledge database;

e) to provide decision makers with a risk management plan for approval and subsequent implementation;

f) to provide an accountability mechanism and tool;

g) to facilitate continuing monitoring and review;

h) to provide an audit trail; and

i) to share and communicate information.

Most organisations choose to document their risk assessments in a form that is familiar to site personnel no matter what risk is involved (ie finance, health, production). This brings benefits in familiarity with the process and ensures that the level of detail provided in the documentation is sufficient so that the whole process can be reviewed at regular intervals in an effective manner.

In some jurisdictions, specific requirements are set down in law as to the risk assessment process including the level of documentation required.

3.2.6 Management

In many countries throughout the world the degree of prescription in occupational health and safety legislation has diminished. Over the past 15-20 years most statutory authorities have moved to a risk based approach whereby employers must establish the level of risk for all operations within their organisation. This can range from tasks such as electrical connections to our area of interest, hazardous substances.

Most statutory authorities produce guidance material which essentially defines minimum standards, however the onus is solely on the employer to establish the level of risk associated with any activity.

In large mature organisations this has become standard practice, however small to medium enterprises still struggle with the concept. Occupational hygienists fill an important role in establishing the level of risk in workplace through the evaluation of hazards, etc.

4. HYGIENE STANDARDS

4.1 PRINCIPLES OF CALCULATION/SETTING OF STANDARDS

A standard is any rule, principle or measure established by an authority. Occupational hygiene is about minimising risks of ill health caused by the working environment.

By “hygiene standard” we are referring to the level of exposure, via inhalation, that should not cause ill health to a healthy adult when exposed to a contaminant. The results from air sampling can thus be compared against these standards and can be used as a guide to assist in the control of health hazards. Other names for hygiene standards commonly used throughout the world are Threshold Limit Values (TLVs®), Exposure Standards (ES), Occupational Exposure Limits (OEL), Workplace Exposure Limits (WEL). In general all such terminology is interchangeable.

Hygiene standards in many cases are based on the concept of the “no observed adverse effect level”, while in other cases many are based on the lowest observed adverse effect level and some are by analogy to similar substances with better data sets. This is possible because for many chemicals there seems to be a “threshold dose” below which no significant adverse effect will occur in most people. Epidemiological and toxicological studies coupled with occupational hygiene measurements help to identify this threshold.

Occupational hygiene standards include allowances variously referred to as uncertainty or safety factors. The magnitude of the cumulative factor is based on many considerations (data quality, length of exposure in studies, routes of exposure in the studies, severity of effect, species with available data, etc). The cumulative uncertainty factor could range from 1, such as irritants where there is human data, to several thousand for extremely serious effects with great uncertainty.

A “hygiene standard” represents an airborne concentration of a particular substance in the workers breathing zone, exposure to which, according to current knowledge, should not cause adverse health effects nor cause undue discomfort to nearly all workers. The “hygiene standard” can be of three forms; Time-Weighted Average (TWA), Short Term Exposure Limit (STEL) or Ceiling or Peak.

It is important to realise that “hygiene standards” are based on the concept of the threshold of intoxication - for each substance, no matter how toxic, there exists a dose level, called the threshold of intoxication, which the human body is capable of accepting and detoxifying without injury to itself.

It should also be appreciated that the “hygiene standards” which have been established for chemical and physical agents are based on a number of factors including toxicity, physiological response (biologic action) and unbearable odours. Examples of such factors include:

Irritants - Ability to cause inflammation of mucous membrane with which they come in contact eg. hydrochloric acid fumes, ammonia, ozone, acrolein.

Asphyxiants - Ability to deprive the tissue of oxygen. Simple asphyxiants eg. nitrogen, carbon dioxide, helium. Chemical asphyxiants eg. carbon monoxide, cyanides.

Anaesthetics - Depressant action upon the central nervous system, particularly the brain eg. ether, chloroform.

Carcinogens - Cancer causing substances eg. asbestos, vinyl chloride monomer.

Unbearable Odour - eg Mercaptans

Toxic Effect - eg silica, lead

4.2 THRESHOLD LIMIT VALUES

The best known list of “hygiene standards” is the Threshold Limit Values (TLVs®) produced by the American Conference of Governmental Industrial Hygienists (ACGIH 2007), and this list will be used as an example (see section 4.9 for exposure standards used in some other countries) in the following discussion as the principles discussed are used by many standard setting bodies throughout the world.

“Threshold Limit Values (TLVs®) refer to airborne concentrations of chemical substances and represent conditions under which it is believed that *nearly all* workers may be repeatedly exposed, day after day, over a working lifetime, without adverse health effects. TLVs® are developed to protect workers who are normal, healthy adults.”

People who use TLVs® must refer to the latest “Documentation of Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices” by the ACGIH to ensure they understand the basis for the setting of the TLV®.

Included in the TLV® List is a column outlining the Basis and or Critical Effect(s) and are intended to provide a field of reference for symptoms of overexposure and as a guide for determining whether components of a mixed exposure should be considered as acting independently or additively. However the use of the TLV® Basis/Critical Effects column is not a substitute for the reading of the Documentation.

The ACGIH TLV booklet is updated annually and contained in it is an overview of the TLV® and BEI® development process and should be referred to for further information.

4.3 TLV® DEFINITIONS, TERMINOLOGY, UNITS

There are three types of TLVs®

1. TLV-Time Weighted Average (TLV-TWA)
2. TLV-Short Term Exposure Limit (TLV-STEL)
3. TLV-Ceiling (TLV-C)

4.3.1 TLV-TWA

"The TWA concentration for a conventional 8-hour workday and a 40-hour work week, to which it is believed that nearly all workers may be repeatedly exposed, day after day, for a working lifetime without adverse effect."

However, during this eight hour averaging period, excursions above the TLV-TWA are permitted providing these excursions are compensated for by equivalent excursions below the standard during the working day. Because some substances can give rise to acute health effects even after brief exposures to high concentrations, it is prudent that excursions above the TWA concentration should be restricted, moreover, the magnitude of excursions is an indication of the true degree of effective control over the release of contaminants from a process.

The 8-hour reference period may be represented mathematically by:

$$\frac{C_1T_1 + C_2T_2 + ... + C_nT_n}{8}$$

Where C_1 is the Concentration for Time period 1, C_2 is the Concentration for Time period T2 and so on.

Example: Calculate the 8-hour TWA for the following sampling periods

Working period	Exposure (mg/m^3)	Duration of sampling (h)
0800 - 1030	0.32	2.5
1045 – 1245	0.07	2
1330 – 1530	0.2	2
1545 – 1715	0.1	1.5

Answer: Assumed exposure is zero during the periods 1030 to 1045, 1245 to 1330 & 1530 to 1545 as the worker was away from the work area having a rest break and was considered to be non exposed.

$$\text{The 8 hour TWA} = \frac{C_1T_1 + C_2T_2 + \ldots\ldots + C_nT_n}{8}$$

$$= \frac{(0.32 \times 2.5) + (0.07 \times 2) + (0.2 \times 2) + (0.1 \times 1.5) + (0 \times 1.25)}{8}$$

$$= \frac{0.8 + 0.14 + 0.4 + 0.15 + 0}{8}$$

$$= 0.19 \text{ mg/m}^3$$

4.3.2 TLV-STEL

"A 15 minute TWA exposure that should not be exceeded at any time during a workday, even if the TWA is within TLV-TWA. The TLV-STEL is the concentration to which it is believed that workers can be exposed continuously for a short period without suffering from:

1. irritation
2. chronic or irreversible tissue damage
3. dose-rate dependent toxic effects, or
4. narcosis of sufficient degree to increase the likelihood of accidental injury, impaired self rescue, or materially reduced work efficiency."

The TLV-STEL is not a separate, independent exposure guideline, but it supplements the TLV-TWA where the recognised acute effects from a substance whose toxic effects are primarily of a chronic nature.

Exposures above the TLV-TWA up to the TWA-STEL should be less than 15 minutes, should occur less than four times a day, and there should be at least 60 minutes between successive exposures.

4.3.3 TLV-C

"The concentration that should not be exceeded during any part of the working exposure.

If instantaneous measurements are not available, sampling should be conducted for the minimum period of time sufficient to detect exposures at or above the ceiling value."

The ACGIH believes that the TLVs® based on physical irritation should be considered no less binding than those based on physical impairment. There is increasing evidence that physical irritation may initiate, promote, or accelerate adverse health effects through interaction with other chemical or biological agents or through other mechanisms.

4.3.4 Excursion Limits

In practice the actual concentration of airborne substances can and does vary significantly. For many substances with a TLV-TWA there is no TLV-STEL. However the excursions above the TLV-TWA should be controlled even if the recommended 8-hour TLV-TWA is not exceeded. Excursion limits are applied to TLV-TWAs that DO NOT have TLV-STELs.

Excursions in worker exposure levels may exceed 3 times the TLV-TWA for no more than a total of 30 minutes during the workday, and under no circumstances should they exceed 5 times the TLV-TWA (3 times the workplace exposure limit (WEL) in the UK), provided the TLV-TWA is not exceeded. A process is not considered to be under reasonable control if these levels occur.

Where the toxicological data exists to establish a TLV-STEL or TLV-C these values take precedence over the excursion limits.

4.3.5 Mixtures

When two or more hazardous substances have a similar toxicological effect on the same target organ or system, their combined effect rather than that of either individually, should be given primary consideration.

In the absence of information to the contrary, different substances should be considered as additive where the health effect and target organ or systems is the same ie:

$C_1/TLV_1 + C_2/TLV_2 + \ldots\ldots + C_n/TLV_n \leq 1$

the threshold limit of the mixture should be considered as being exceeded (where C_1 is the airborne concentration and TLV_1 is the corresponding threshold limit value etc).

The additive formula applies to simultaneous exposures for hazardous agents with TWA, STEL and Ceiling values.

Example: A worker's exposure to solvents was measured for a full shift and for one short term exposure with the following results:

Agent	Full Shift Results ppm	TLV-TWA ppm	Short Term Results ppm	TLV-STEL ppm
acetone	160	500	490	750
Sec-butyl acetate	20	200	150	N/A
methyl ethyl ketone	90	200	220	300

From the TLV® basics column, the Documentation of the TLVs® and BEIs®, all three substances indicate irritation effects on the respiratory system and would considered as additive.

Full shift calculation:

$C_1/TLV_1 + C_2/TLV_2 + C_3/TLV_3 \leq 1$

therefore 160/500 + 20/200 + 90/200

= 0.32 + 0.10 + 0.45

= 0.87

This is less than 1 – hence full shift additive limit is not exceeded

Short term calculation:

$C_1/TLV\text{-}STEL_1 + C_2/TLV\text{-}STEL_2 + C_3/TLV\text{-}STEL_3 \leq 1$

therefore 490/750 + 150/(200 x 5)* + 220/300

= 0.65 + +0.15 + 0.73 = 1.53

* Where no STEL exposure standard exists the general approach is to multiply the TWA exposure standard by 5 in many countries or 3 in the UK.

This is greater than 1 – hence short term additive limit is exceeded.

4.3.6 Units of Measure - Conversion of ppm to mg/m^3.

The unit of measure of TLVs depends on the nature and physical composition of the contaminant.

For aerosols, (dusts, mists and metallic welding type fumes) the contaminant is typically measured and expressed as a weight in a given volume of air
Example: mg/m^3.

For gases and vapours the concentrations may also be expressed volumetrically as a number of volumes of the substance in a number of volumes of air.
Example: % or ppm

1 litre of contaminant per 100 litres of air = 1%.

1 litre of contaminant per 1,000,000 litres of air = 1 part per million (1 ppm).

NB 1 ppm = 0.0001%

Gases and vapours while typically expressed in ppm can also be expressed gravimetrically by using the following equation:

$$\text{Concentration in mg/m}^3 = \frac{\text{Concentration in ppm x Molecular Weight}}{24.45}$$

where 24.45 = molar volume of air in litres at NTP conditions (25°C and 1 atm)

Note: International Union of Pure & Applied Chemistry (IUPAC) use 0° and 100 kPa but the ACGIH and other bodies use 25°C and 1 atmosphere

where STP conditions are used ie 20° C not 25°C then the equation is

$$\text{Concentration in mg/m}^3 = \frac{\text{Concentration in ppm x Molecular Weight}}{24.06}$$

Example: What would be the concentration of 5,000 ppm carbon dioxide in mg/m^3 (at 25°C and 1 atm)? Molecular weight of carbon dioxide = 44

$$\text{Conc (mg/m}^3) = \frac{5{,}000 \times 44}{24.45}$$

$$= 9{,}000 \text{ (rounded to nearest 10 mg/m}^3)$$

4.4 NOTATIONS

A notation is a designation that appears as a component of the adopted TLV® value to provide additional information with respect to the particular chemical:

4.4.1 Biological Exposure Indices (BEIs®)

The notation BEI® is listed when a BEI® (or BEIs®) is (are) recommended for the substance. Biological monitoring is recommended for such substances to determine the exposure from all sources, including dermal (skin) ingestion or non-occupational.

Most BEIs® are based on a direct correlation with the TLV® (ie the concentration of the determinant that can be expected when the airborne concentration is at the TLV) with an assumption that there is no exposure by skin absorption or ingestion. Further information can be found in section 6.8 of this manual or in the TLV book or in the documentation for the TLVs® and BEI® for these substances.

Correct application of BEIs® requires significant knowledge of the accompanying documentation and may be valuable in evaluating what exposure has actually occurred in an incident. Employee resistance may be encountered with this type of monitoring as many BEIs® require the use of invasive collection techniques.

4.4.2 Carcinogenicity

“A carcinogen is an agent capable of inducing benign or malignant neoplasms. Evidence of carcinogenicity comes from epidemiology, toxicology, and mechanistic studies.

There are a number of different schemes for the classification of carcinogenicity and it is important to note that the classification is complicated and is not universally agreed upon. Two schemes in common use are the International Agency for Research on Cancer (IARC) and the ACGIH.

The IARC Monographs on the Evaluation of Carcinogenic Risks to Humans have been evaluated for more than 900 environmental agents and exposures. Each exposure is classified into one of five groups according to the strength of the published evidence for carcinogenicity.

Group 1	Carcinogenic to humans
Group 2A	Probably carcinogenic to humans
Group 2B	Possibly carcinogenic to humans
Group 3	Not classifiable as to carcinogenicity to humans
Group 4	Probably not carcinogenic to humans

The complete list of the evaluations can be found at http://monographs.iarc.fr (accessed March 2007)

The ACGIH system uses the following notations:

A1 Confirmed Human Carcinogen: The agent is carcinogenic to humans based on the weight of evidence from epidemiologic studies.

A2 Suspected Human Carcinogen: Human data are accepted as adequate in quality but are conflicting or insufficient to classify the agent as a confirmed human carcinogen; OR, the agent is carcinogenic in experimental animals at dose(s), by route(s) of exposure, at site(s), of histologic type(s) or by mechanism(s) considered relevant to worker exposure.

The A2 is used primarily when there is limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals with relevance to humans.

A3 Confirmed Animal Carcinogen with Unknown Relevance to Humans: The agent is carcinogenic in experimental animals at relatively high dose, by route(s) of administration, at site(s), of histologic type(s) or by mechanism(s) that may not be relevant to worker exposure. Available epidemiologic studies do not confirm an increased risk of cancer in exposed humans. Available evidence does not suggest that the agent is likely to cause cancer in humans except under uncommon or unlikely routes or levels of exposure.

A4 Not Classifiable as a Human Carcinogen: Agents which cause concern that they could be carcinogenic for humans but which cannot be assessed conclusively because of a lack of data. In vitro or animal studies do not produce indications of carcinogenicity which are sufficient to classify the agent into one of the other categories.

A5 Not Suspected as a Human Carcinogen: The agent is not suspected to be a human carcinogen on the basis of properly conducted epidemiologic studies in humans. These studies have sufficiently long follow-up, reliable exposure histories, sufficiently high dose, and adequate statistical power to conclude that exposure to the agent does not convey a significant risk of cancer to humans, OR, the evidence suggesting a lack of carcinogenicity in experimental animals is supported by mechanistic data.

Other systems are used throughout the world and reference should be made to the system used by local regulatory or standard setting bodies.

4.4.3 Sensitisation

The notation SEN refers to the potential for the chemical to produce sensitisation. Sensitisation may relate to respiratory, dermal or conjunctival exposures. Once a person has become sensitised, subsequent exposure to the agent, even at very low levels, usually results in an adverse allergic reaction.

Example: Toluene diisocyanate (TDI) often found in 2-pack paints is a respiratory sensitiser and subsequent exposure can result in severe asthmatic reactions to those sensitised.
When considering substances with a SEN notation it is important to understand:

1. Occupational exposure limits are not meant to be protective of those who are sensitised.

2. When there is a SEN notation, reference must be made to the documentation to understand the nature of the sensitisation and the potency of the sensitiser.

3. Some bodies (eg AIHA) use different notation to indicate specific sensitisation, eg DSEN for dermal sensitisers, RSEN for respiratory sensitisers.

4.4.4 Skin

The Skin notation ‘refers to the potential significant contributions to the overall exposure by cutaneous route, including mucous membranes and the eyes, either by contact with vapours or, of probable greater significance, by direct skin contact with the substance. Typically skin exposure is from splashes or wearing of contaminated clothing.

Example: Organophosphate pesticides such as Malathion.

It is important to note that skin notations are not assigned on the basis of any harmful effects on the skin such as irritation or allergic contact dermatitis. Substances with a skin notation are not necessarily harmful to the skin.

The use of a skin notation is to alert the reader that air sampling alone is not sufficient to quantify worker exposure, biological monitoring may also be required in addition to changes to work practices including the use personal protective equipment to prevent cutaneous absorption from occurring.

4.5 APPLICATION OF STANDARDS

When measuring the airborne concentration of a particular contaminant it is imperative that the measurement is representative of the workers exposure to that contaminant. Therefore the contaminant is measured in the breathing zone of the worker. The breathing zone is defined as a hemisphere of 300mm radius extending in front of the face and measured from the midpoint of a line joining the ears.

If the sample is collected in this fashion it is referred to as occupational or personal sampling and the occupational hygiene standards for the contaminant can then be applied.

If para-occupational or static or area sampling is carried out the results should not be compared directly with exposure standards as they are not indicative of the worker’s actual exposure and hence risk.

4.6 EXTENDED WORK SHIFTS

Almost all occupational exposure limits are derived on the assumption that exposures would follow a traditional work week of a conventional 8-hour workday followed by a 16-hour break from the exposure over a 40-hour work week. Many models have been used to adjust TWA for unusual and extended work schedules. It is not necessary to adjust TWA-STEL and TWA-Ceiling values as these are associated with acute rather than chronic exposures.

It should be noted that before any adjustment of an exposure standard is attempted, the basis of that occupational exposure limit must be understood so as to determine whether it is appropriate to adjust for non-traditional work shifts, and if so, which model to apply.

4.6.1 Brief and Scala Model

This model, originally derived within the petroleum industry, reduces the 8-hour OEL proportionally for both increased exposure and reduced recovery time. The suggested approach is set out below.

Daily Adjustments of Occupational Exposure Limits:

$$\text{Daily Reduction Factor} = \left\{ \frac{8}{h} \times \left[\frac{24 - h}{16} \right] \right\}$$

Where h = hours worked per day

Adjusted Exposure Limit = 8 hr OEL x Daily Reduction Factor

Weekly Adjustments of Occupational Exposure Limits:

$$\text{Weekly Reduction Factor} = \left\{ \frac{40}{h} \times \left[\frac{168 - h}{128} \right] \right\}$$

Where h = hours worked per week

Adjusted Exposure Limit = 8 hr OEL x Weekly Reduction Factor

Note: The adjusted exposure limit should be calculated using each equation and the most restrictive value adopted.

Example: A worker is exposed to toluene for a 12-hour shift. The 8-hr OEL for Toluene is 50 ppm. Using the Brief and Scala model the adjusted OEL is calculated

$$\text{Adjusted Exposure Limit} = \frac{8 \times (24 - h) \times \text{OEL}}{16 \times h}$$

$$= \frac{8 \times (24 - 12) \times 50 \text{ ppm}}{16 \times 12}$$

$$= 25 \text{ ppm}$$

4.6.2 OSHA (Direct Proportion) Model

Another approach, which was formerly used by the OSHA in the US, was to adjust the occupational exposure limit in direct proportion to the hours worked.

This type of adjustment may be particularly appropriate for substances where the exposure limit is based upon estimated life-time excess risk (parts per million – years) rather than a specific toxic threshold.

For example if a 10-hour shift is being worked:

$$\text{Adjusted OEL} = \text{OEL (8/hours worked)}$$

$$= \text{OEL} \times \frac{8}{10}$$

If we use the example in Section 4.6.1 and apply the OSHA model we would have the following:

$$\text{Adjusted OEL} = 50 \times \frac{8}{12}$$

$$= 33 \text{ ppm}$$

As can be observed, the Brief & Scala model is significantly more conservative than the OSHA model.

4.6.3 Pharmacokinetic Model

Other more complex models, such as the Pharmacokinetic Model of Hickey and Reist (1977) have been based on pharmacokinetic actions that consider metabolism, biotransformation and excretion. This model is described by the formula

$$\text{Modified TLV} = \text{TLV} \times \frac{[1-e^{-8k}]\quad[1-e^{-120k}]}{[1-e^{-t_1 k}]\quad[1-e^{-t_2 k}]}$$

Where t_1 = hours worked per day on usual schedule

t_2 = 24 times days worked/week on unusual schedule

$$k = \frac{\ln 2}{t_{½}}$$

(Note: If half life ($t_{½}$) not known, use 16 hours)

A detailed understanding of this model is beyond the scope of this course.

4.6.4 Western Australian Department of Minerals & Energy

A much more practical approach (albeit based on the Brief and Scala Model) has been adopted by the Western Australian (WA) Department of Minerals & Energy (1997) as demonstrated in Table 4.1.

Table 4.1 – WA Department of Minerals & Energy Altered Workshift Model

EXPOSURE STANDARD	TIMEFRAME FOR ACTION	HEALTH EFFECT	TYPICAL SUBSTANCES	SHIFT ROSTER	EXPOSURE REDUCTION FACTOR
Peak	Fast - immediate	Acute poisoning	Cyanide, Caustic, Acid mists	n/a	**1**
STEL	Fast - immediate	Acute irritation	Nitrogen dioxide Sulphur dioxide Hydrogen sulphide Ammonia	n/a	**1**
TWA	Medium – within shift or over a few shifts	Respiratory irritation, narcosis	Solvents, Nitrogen dioxide, Sulphur dioxide, Hydrogen sulphide, Carbon monoxide	10 h/day	**0.7**
				12 h/day	**0.5**
TWA	Long – over many shifts or years	Cumulative poisoning, respiratory disease (silicosis, asbestosis) , cancer	Silica, Asbestos, Nickel, Lead, Welding fumes, Talc, Inspirable dust, Respirable dust, Diesel fume	<170 h/mth	**1**
				> 170 h/mth	**170/*x****
TWA	Unknown or unsure			10 h/day	**0.7**
				12h/day	**0.5**

LEGEND

* x	Average number of hours worked in the month; 170 is the typical hours worked in a month for a normal 8 h/day, 5 day/week work cycle
STEL	Short Term Exposure Limit
TWA	Time Weighted Average Exposure Standard
n/a	Not Applicable
h	hours
mth	Calendar month

(Source: *Reproduced with permission from* - "Table 1 Recommended Exposure Reduction Factors for the Western Australian Mining Industry" that is located in the Appendix of the Guideline for Adjustment of Exposure Standards for Extended Workshifts available from: http://www.docep.wa.gov.au/resourcessafety/Sections/Mining_Safety/Guidance_material_and_publications/Guidelines.html)

4.7 PROBLEMS

Many people in the Occupational Environment fail to understand that Exposure Standards are not fine lines between safe and unsafe but are merely guides for the use of occupational hygienists in the control of potential health problems.

In countries or jurisdictions where occupational exposure standards are used as regulatory limits they are of course legally binding and not guidelines. Their application to situations outside the norm (eg. 12 hour shifts) for which they were designed can be disastrous. Effects such as synergism and potentiation, addition etc need to be understood and allowances made.

With many new products coming onto the market, it is impossible for any group to develop appropriate Exposure Standards for each before they are in Commercial use. With this in mind, analogy to other compounds of similar type, common-sense and good Occupational Hygiene practice may reduce any unnecessary exposure.

It should be noted that regulatory standards usually include consideration of many policy concerns, such as engineering feasibility, economic impact, analytical limits etc. Non government guides such as the ACGIH TLVs® and the Workplace Environment Exposure Limits from the AIHA are usually health based and do not take any other factors into consideration.

A simple guide to follow is if you are not familiar with the application of exposure standards in workplace situations seek out the services of someone with good professional experience in this area, **before** making any decisions.

4.8 LIMITATIONS

Occupational exposure limits, such as the Threshold Limit Values, apply only to the workforce. In deriving Occupational Exposure Limits, it is presumed that workers are in reasonably good health. Industrial environments usually exclude the very young, the very old and those unable to work due to illness and physical impairment or disability.

Occupational exposure limits are not meant to apply to the general public. They are set to protect worker health and while zero exposure is a goal to strive towards, exposures are likely to be higher and sometimes significantly higher than those encountered by the general public. They must not be divided by an arbitrary number such as 100 and turned into environmental or boundary emission standards.

Occupational exposure limits are generally described in supporting information as not being fine lines between safe and dangerous conditions and should not be used by anyone who is not trained in the discipline of industrial/occupational hygiene. They were never intended to be regulatory standards, however this has occurred in some countries and is thus legally binding.

Regulatory standards usually include consideration of various policy concerns such as engineering feasibility, economic impact etc, while non governmental guides are usually based entirely on health effects. Consequently, indiscriminate mixing of the two approaches can lead to difficulties.

4.9 HYGIENE STANDARDS USED IN OTHER COUNTRIES

Many other countries have established their own lists of exposure standards, a brief overview of which is provided below. It is important that reference always be made to local exposure standards if they are published but if none are available reference to one of the more established lists is appropriate.

4.9.1 Australia

The first edition of an Australian list of exposure standards was published in 1990 by WorkSafe Australia under the title of:

Exposure Standards for Atmospheric Contaminants in the Occupational Environment - Guidance Note and National Exposure Standard.

These were based on ACGIH TLV® list but also cross referenced exposure standards from Germany, Sweden and the UK. Specific differences included reference to Workplace Exposure Standards and the use of Peaks rather than Ceilings.

The second edition was published in October 1991, and a third edition (the latest) in May 1995 by the National Occupational Health and Safety Commission.

Updates are now published on the Australian Safety & Compensation Council ASCC website: www.ascc.gov.au (accessed January 2008) where a database exists of the 696 current national exposure standards (Hazardous Substances Information System or HSIS).

While these standards do not automatically have the force of law behind them the various States and the Commonwealth are actively moving towards these standards becoming uniform in law across Australia.

4.9.2 United Kingdom

The UK Health & Safety Commission has established Workplace Exposure Limits (WELs) for a number of substances hazardous to health as part of The Control of Substances Hazardous to Health Regulations. WELs replaced the previously adopted Occupational Exposure Standards (OESs) and the Maximum Exposure Limits (MELs).

HSE's publication EH40 (Workplace Exposure Limits) includes the list of substances assigned WELs and provides more detailed guidance on their use. They are maximum acceptable levels of exposure and should not be exceeded. Moreover, exposure should be reduced below the limit as far as is reasonably practicable by applying the principles of good occupational hygiene practice. The listing includes: 8-hour TWA, STEL, the Comments Column containing Safety & Risk Phrases plus the Carcinogen, Skin, Respiratory Sensitiser and Biological Monitoring Guidance Value notations.

4.9.3 European Limits

There are two kinds of Occupational Exposure Limit Values in European Legislation: Indicative (directive 98/24/EC on chemicals) and Binding (directive 2004/37/EC on carcinogens and mutagens) and there are also biological limit values.

Indicative Occupational Exposure Limit Values (IOELVs) can be established when an assessment of the available scientific data leads to the conclusion that a threshold can clearly be identified below which exposure to the substance should not have an adverse impact on human health.

When establishing IOELVs feasibility factors (including socio-economic and technical) are not taken into account.

Binding Occupational Exposure Limit Values (BIOELVs) reflect socio-economic and technical feasibility factors, plus criteria taken into account when establishing IOELVs.

The Occupational Exposure Limits Values can be 8-hour TWA, short term, and/or biological limit values and can be supplemented by further information such as notations and routes of absorption.

The original list has been expanded and up-to-date information can be found at
http://ec.europa.eu/employment social/health safety/occupational en.htm
http://osha.europa.eu/good practice/risks/ds/oel/notes.stm (accessed December 2006)

If substances not assigned then the individual states are responsible for setting their own.

4.9.4 USA – OSHA

In the USA, the Occupational Safety and Health Administration has established Permissible Exposure Limits (PEL), most of which are based upon the 1968 Threshold Limit Values. They have subsequently promulgated a limited number of detailed regulatory requirements applicable to specific substances such as benzene, asbestos and vinyl chloride. These are contained in Title 29 of the US Code of Federal Regulations. Most of the applicable regulations can be found at: http://www.access.gpo.gov/nara/cfr/waisidx_06/29cfrv6_06.html (accessed March 2007)

4.9.5 USA - NIOSH

National Institute of Occupational Safety and Health (NIOSH) in the USA has established Recommended Exposure Limits (RELs).

NIOSH recommends standards to OSHA/MSHA (Mine Safety & Health Administration) and some of the recommended exposure limits are lower than PELs, TLVs etc.

It should also be noted that NIOSH has language in its enabling legislation that directs it to recommend limits that will ensure protection of “all” workers rather than “nearly all” workers. This has driven many of their recommendations to be lower than those established by others.

The NIOSH list of Recommended Exposure Limits is available on CD-ROM or http://www.cdc.gov/niosh (accessed December 2006).

4.9.6 USA - AIHA

Since 1980 the American Industrial Hygiene Association has produced Workplace Environmental Exposure Levels (WEELs) which, together with their documentation, are updated annually. The current list of over 100 substances is available at:

http://www.aiha.org/Content/InsideAIHA?Volunteer+Groups/WEELcomm.htm (accessed March 2007).

WEELs are intended to provide guidance on exposure levels where no legal or authoritative limits exist eg benzyl alcohol, butylenes oxide. They include recommendations for 8-hour TWA, Ceiling limit and a Short Term TWA limit plus Skin, Dermal sensitiser and Respiratory sensitiser notations.

The AIHA also publishes Emergency Response Planning Guidelines. These should be used for risk assessments when considering exposures of either the workforce or for the public for accidental releases. Information on these guides is available at:
http://www.aiha.org/Content/InsideAIHA/Volunteer+Groups/WEELcomm.htm (accessed March 2007).

4.9.7 Germany – MAK Commission

The Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK Commission) is responsible for determining the current state of research relating to the health risks posed by substances and materials used at the workplace and for advising public authorities accordingly. To this end, the MAK Commission draws up proposals for MAK values (maximum concentration at the workplace) for volatile chemicals and dusts, BAT values (biological tolerance values), and also develops procedures to analyse chemical substances in the air and in biological materials. Substances that are carcinogenic, germ cell mutagenic, sensitising or percutaneously absorbed, as well as those that pose a risk to the embryo or foetus, are classified accordingly.

Each year the proposals for the MAK and BAT values and the classifications are published in the annual List of MAK and BAT values which is presented to the German Federal Minister of Labour and Social Affairs. The Ministry's Committee of Hazardous Substances subsequently reviews the proposals and makes a recommendation for their inclusion in the Hazardous Substances Ordinance.

5. AIR SAMPLING THEORY & PRACTICE

5.1 WORKPLACE SAMPLING STRATEGIES

5.1.1 Strategies

A possible objective of a monitoring strategy is to provide analytical information about the workplace, which workers and management can use to ensure that, as far as is reasonably practicable, no-one in that workplace suffers injury or illness as a result of exposure to hazardous contaminants. Other objectives could include: determining exposures in response to complaints, determining compliance with respect to various recommended occupational health exposure limits, or to evaluate the effectiveness of engineering controls installed to minimise workers' exposure.

A sampling strategy, like any other experimental design, cannot be formulated until the objectives of the exercise are clearly understood and documented. The concept of just collecting a few samples to see how "good" or "bad" a workplace may be, is potentially biased and may not give an accurate picture of workplace exposures.

Thus, when developing any monitoring strategy it is important to ask the fundamental question:

"How will the data generated from this exercise be used?"

Without a reasonable answer to this question the survey merely becomes the collection of data "for the sake of it", which is a wasteful and meaningless exercise.

The British Occupational Hygiene Society (BOHS 1993) also suggests other factors should be considered before developing any monitoring programme. These include:

- The requirement for a qualitative risk assessment and appraisal of the workplace prior to doing any measurements.

- The need to obtain measurements other than those of airborne contaminant concentrations, eg wipe tests to determine surface cleanliness as a way of assessing the potential for skin contact or measurements of ventilation plant performance.

- Any requirements for biological monitoring and the integration of these into the overall survey strategy.

- Any requirements for monitoring overall performance or auditing the process.

- Any other health hazards which may exist within the workplace, eg noise or biological hazards, etc which may also need to be considered.

- Any environmental or personal characteristics of the workers which may affect the measurement.

Once all these factors have been assessed it is appropriate to develop a workplace exposure sampling strategy. In doing so it is appropriate to consider the following:

- What type of sample(s)? (area vs personal)
- Where should the sampling device be located?
- How many samples should be taken?
- How long should the sampling interval be?
- What periods during the work day should the employee's exposure be determined?
- How should the samples be taken?
- What contaminants are likely to be present?
- What is (are) the expected concentration(s)?
- What (if any) compounds are present which may interfere with the sampling (or analytical) procedure?

- What analytical methods are to be used and what (if any) constraints will these place on sampling techniques?

When developing a sampling strategy it is important to understand that the variability of the workplace environment is such that no universal approach is possible to cover all possible situations.

The inconsistency of the workplace, in terms of density and intensity of activity, variability of activity, variability of exposure cloud and the influence of uncontrolled factors such as wind direction, employee practices, etc results in the fact that data can only be related to the situation being studied at the time it was studied.

Any exposure assessment based on a single worker for a single day will have errors of space (location) and time and we will have little to link this outcome to the real situation.

Individual measurements will not necessarily represent the group, but by accounting for as many influencing factors as is practicable, we can ensure that some assessments are substantially better than others.

Other factors affecting the measurement results include:

- The choice of monitoring equipment
- The choice of the sampling method
- The choice of the analytical method
- The skill level of persons conducting the sampling and analysis

All the above factors need to be considered when considering a sampling strategy. It is important to appreciate that monitoring the workplace does not in itself protect anyone, it merely provides information; however in some circumstances the mere act of monitoring does raise awareness of the workforce and management which often results in initiatives to reduce exposure, regardless of the actual results of the measurements.

The sampling system should be appropriate to the situation being studied and part of an overall occupational hygiene monitoring strategy.

Guidance on the assessment of exposure can also be obtained from other sources such as BSEN 689 (1996) “Workplace Atmospheres – Guidance for the Assessment of Exposure by Inhalation to Chemical Agents for Comparison to Limit Values and Measurement Strategy”.

5.1.2 Surveys

Regulatory authorities throughout the world have different approaches to the design of monitoring surveys. Some bodies are very prescriptive whereby individual workers in a workplace are listed in regulation to be monitored at set frequencies using prescribed methods. In recent years this approach has changed, with a move by some authorities to a risk based approach.

In such situations it is not unusual for a common approach to be adopted with following components:

- Initial appraisal
- Basic survey
- Detailed survey
- Routine survey

While the names given to these components may be different in various countries and some components may be combined (eg initial appraisal and basic survey), the concept remains the same.

- ***Initial Appraisal***

  In many situations this is commonly referred to as a “walkthrough survey” (see section 3.2.2) and has the objective of being able to provide sufficient information to answer these questions:

  - What are the potential exposures?
  - Where and when do they occur?

- Can the exposures be prioritised in terms of risk?
- Is further evaluation necessary?
- If further evaluation is necessary what is the preferred approach?

As previously indicated, collection of sufficient information to answer these questions is paramount. While the walkthrough survey provides valuable information on the process, (eg materials being used and current controls), it may be necessary to seek further details. Such information regarding the substances being used could include:

- *Physical properties.* For example boiling point, vapour pressure, relative evaporation rate, dustiness, particle size distribution, ability to sublime, etc.

- *What form is the substance?* Is it a gas, vapour, mist, fume, or if it is an aerosol, is it fibrous?

- *Hazardous nature of the substance*. This could include any known toxic effects in man (both acute and chronic); other indications of toxicity (eg animal studies, *in vitro* tests, structural factors, etc); any special toxic potential (carcinogenicity, respiratory sensitisation, reprotoxicity, etc); and any indication of increased hazard from exposure to mixtures of substances.

- *Potential routes of entry to the body*.

- *Any effects on skin* (eg corrosion, dermatitis) or mucous membranes (eg drying, irritation).

- *Any available exposure limits* and the documentation for these.

During this initial information collection stage the use of direct reading instruments or detector tubes may be helpful in identifying emission sources or employees with potentially significant exposures.

This information will be very limited and should only be used to support observations. At the conclusion of the information collection exercise it may be possible to make a reasonable assessment of potential risk. It should at least provide sufficient information to decide if a more detailed study is required or if a non sampling approach would be effective.

- ***Basic Survey***

A basic survey is generally required when one or more of the following situations arise:

- The initial appraisal suggests that unacceptable exposures may be present in the workplace.
- A new process is being started up.
- Substantial changes have been made to the process, operations or control measures.
- Unusual, infrequent or intermittent processes or operations are to be conducted, eg maintenance.
- An occupational exposure limit has been set where one did not previously exist.

A basic survey will have limited objectives but these should include obtaining sufficient information to answer the following questions:

- Does an exposure problem exist as suggested by the initial appraisal?
- Are available engineering, or other, controls adequate and likely to remain so?
- Is a more detailed survey necessary and what strategy should it follow?

In some cases an initial appraisal may be followed by a detailed survey without the intermediate step of a basic survey.

Such a step would depend on what was found during the initial assessment and the skill and experience of the hygienist performing the evaluation.

At this stage four questions need to be addressed before proceeding. These are:

- *Who should be monitored?*

  The question of whose exposure should be monitored can be answered only by reference to the objectives of the proposed survey and the details of the observed work practices. If the process only involves several workers doing exactly the same thing then the task is relatively easy, however if the process involves large numbers of persons doing different tasks then the choice of who to monitor becomes more difficult.

  In many basic surveys the practice is to target “worse case” situations, however there is merit in including some workers who are expected to have lower exposures. This provides a level of quality control in respect to the initial appraisal and the choice of “worse case” individuals sampled.

- *When should they be monitored?*

  The choice of when to monitor is directly related to what process or tasks give rise to significant exposures. The other major factor that must be considered is the toxicology of the substance under consideration.

  For example if it is an acute acting toxin it is important to undertake short term sampling, whereas with a chronic toxin, longer sampling would be more appropriate.

The other point to consider when considering when to monitor is the type of exposure standard appropriate to the substance of concern (eg TWA, STEL, Ceiling or Peak). These are generally related to the toxicological properties of the substance.

As a general rule it is reasonable to state that if the objective of the survey is to evaluate the exposure of a worker during a specific task then the monitoring duration should equal the whole, or a representative part, of the task.

- *Where should the monitoring take place?*

  Recognition that a contaminant in a workplace is associated with a particular source may be very valuable when designing a monitoring programme. Identification of the source provides a spatial element to the monitoring strategy which may assist in deciding what type of monitoring approach is required (eg direct reading instrumentation).

- *How should sampling be performed?*

  The selection of sampling equipment and analytical methods will in general result from the properties of the contaminant under investigation. Other factors that will come into the equation include:

  * Legislative requirements
  * The accuracy and precision required
  * Intrinsic safety requirements
  * The need for subsequent laboratory analysis
  * Transport of samples to the laboratory
  * Portability of equipment

  In all cases it is prudent to use sampling methods from recognised authorities (eg National Standards, NIOSH, OSHA, HSE).

Both the sampling method and the analytical method are subject to error and thus what may be the most desirable choice from one standpoint may not be from the other.

Ultimately the choice will be a compromise, often dependent on the experience of the occupational hygienist and the working relationship between the hygienist and the laboratory that will perform the analysis.

The BOHS (1993) suggests that the following considerations need to be taken into account when selecting the sampling method.

* Is the sampling device (and collection medium) suitable for collecting the contaminant of interest and is the medium compatible with the subsequent analytical method?

* Is sufficient known about the dynamics of the collection process so that any variables can be accounted for in the design of the sampling programme?

A number of factors can influence the selection of the sampling device and collection medium, but in practice they are generally limited to:

* For aerosols, what is the most appropriate device to collect the size range of particles of interest? Are wall losses (material which sticks to the sampling head and does not lodge on the filter), either within the sampling head or train, of an order such that account needs to be taken of them?

* For mists, especially, does possible vapour loss need to be taken into account?

* For gases and vapours sampled from a mixed atmosphere does preferential sorption of one or more contaminants take place in the collection medium? Does the presence of high water-vapour levels affect sorption characteristics of the sampling medium or the presence of particulate material adversely affect the collection characteristics?

* With all contaminants, is the total capacity of the collecting medium sufficient to cope with the likely loading of the contaminant given the intended sampling rate over the proposed sampling period?

Other issues (such as the number of samples) need to be addressed but these will be discussed in section 5.2.2.

- ***Detailed Survey***

A detailed survey has a clear objective, usually to obtain reliable measurements of personal exposures for comparison to exposure standards, reach conclusions regarding exposure levels and decide (if necessary) what measures need to be taken to control unacceptable exposures.

Thus for a detailed survey, results need to be representative of personal exposures so personal sampling techniques are normally used. Moreover, the appropriate measurement period must be used if the results are to be compared to an exposure standard which has a specific reference period.

In addition, all aspects of the survey need to be reviewed to ensure errors which may affect results are minimised. In many cases statistical based sampling techniques are adopted and detailed statistical analysis of the data undertaken.

No matter what the circumstances, the essential questions of: “Who?, When?, Where and How?” remain central to the development of an effective monitoring strategy.

- ***Routine Survey***

Routine surveys involve periodic sampling of exposed persons (or control measures) to achieve predefined goals.

Such goals may include:

- Checking the performance of control measures
- Ensuring compliance with exposure standards and/or legislation
- Meeting the requirements of large corporations
- Providing data for epidemiological or other studies

No matter what the reason, any routine survey must take account of and be designed on the basis of information gathered in earlier surveys. The various approaches to routine monitoring will be discussed in section 5.1.3.

Irrespective of what type of survey that is used, it is important to recognise that some problems still exist. For example, processes which operate intermittently at irregular intervals or on a campaign basis make it difficult to obtain representative data for even a single substance let alone multiple substances.

Another limitation would be in the circumstance where excursions above the exposure standard could cause serious, possibly irreversible, acute effects. In such cases a routine survey using a method whereby the substance is collected for subsequent laboratory analysis is obviously not appropriate. Continuous monitoring using alarmed direct reading instrumentation would be more appropriate.

Thus, issues such as the toxicology of the substance concerned and the process itself play an important role in survey design and such factors must be considered when developing the monitoring strategy.

5.1.3 Routine Monitoring

When developing a routine monitoring strategy, four issues need to be considered. These are:

- The frequency at which the monitoring survey is conducted
- The sampling methodology
- The number of samples required to meet the goals of the exercise
- The type of analysis of data that will be undertaken

There are no set rules for the frequency of monitoring except where it is defined in local legislation. Some mathematical models have been developed, however such models are very reliant on the quantity and quality of available data.

Irrespective of the above, there are a few simple guidelines which can be used to help in the decision process regarding the frequency of routine surveys.

- *How close are exposures to the relevant exposure standard* – as exposures approach the exposure standard more frequent monitoring will be required (as distinct from being either well below or excessively above the exposure standard).

- *The effectiveness of controls* – in a well controlled environment where the likelihood of control failure is low, monitoring frequency can be reduced.

- *The process cycle* – monitoring frequency will need to match the process cycle. This is especially important in situations where periodic events occur (eg maintenance shutdowns) or irregular process cycles.

- *The temporal variability of exposures* - consideration needs to be given so as to take account of seasonal and shift variations (eg increased production on night shift).

- *The variability of exposure* - in a process where a high level of variability of exposure is present, increased monitoring would be required to establish the reason for such variability.

Other factors that need to be considered are:

- Changes in sampling methods
- Changes in analytical methods
- Changes in behaviour patterns of workers

Such changes can affect the survey results from year to year and some understanding of these issues is necessary if data from varying years is to be compared.

In recent years many major corporate organisations have adopted a statistical approach to exposure assessment.

The problem of how to correctly (or more accurately) measure workplace exposures has been the subject of debate within the occupational hygiene profession for many years.

In the last 25 years there has been a gradual move to statistically based monitoring programmes where the workforce is divided into groups of similar exposures called “Homogeneous or Similar Exposure Groups” (HEGs or SEGs) and a statistically based subset of each group is monitored on a random basis for an extended period of time. In essence, employees are placed into groups (SEGs) based on past monitoring data or via using the knowledge of persons working in a plant as to possible exposures.

A number of persons in each group are then monitored and it is assumed that the exposures measured represent that of the whole group (SEG).

Once sufficient data has been collected a statistical analysis of the exposures can be undertaken to establish the level of compliance to the relevant exposure standard and to provide an indication in the variability of the data.

While statistically based sampling and evaluation of workplace exposures is very useful in giving a more accurate picture of employee exposures, it should not be considered as being the absolute test. There are many assumptions (and thus potential errors) in such programmes but by controlling as many influencing factors as is practicable a better estimate of exposure will be guaranteed.

Where considered appropriate, evaluation of workplace exposures should be conducted using non-biased (random) sampling programmes using the concept of SEGs. The number of samples (NIOSH 1977) in each SEG will be determined using information like that provided in Table 5.1 and the exact sampling days should be determined using random number tables.

Table 5.1 – NIOSH Sample Size Guide

Sample size n for top 10% (τ = 0.1) and 95% confidence (α = 0.05)

Size of Group (N)	12	13-14	15-16	17-18	19-21	22-24	25-27	28-31	32-35	36-41	42-50	∞
Required No. of Measured Employees (n)	11	12	13	14	15	16	17	18	19	20	21	29

If N <= 11 then n = N

(Source: NIOSH 1977)

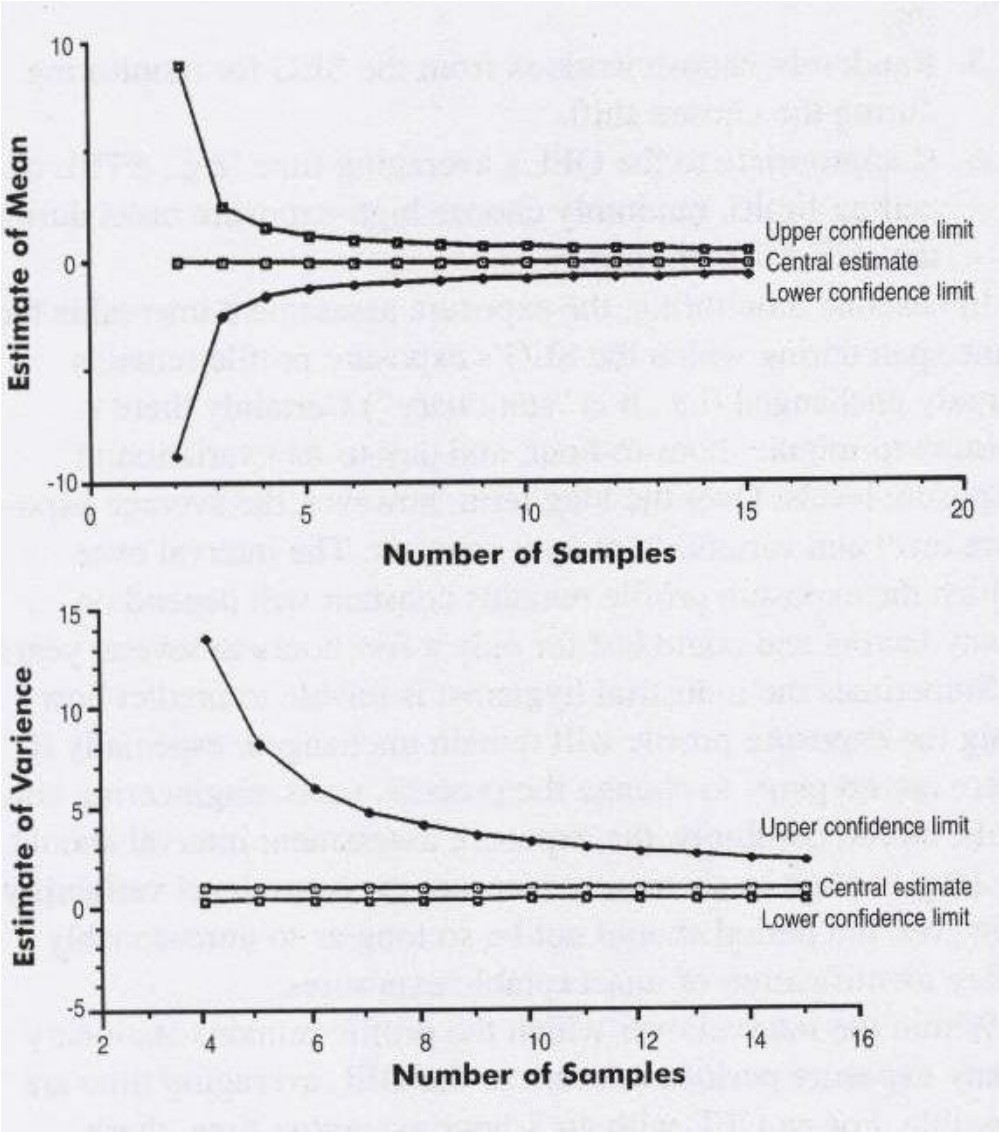
Such an approach should ensure that at least one result should be within the top 10% of exposures with 95% confidence and would satisfy the requirements of a compliance based survey.

It is important to understand that the information provided in Table 5.1 is designed to meet the requirements of compliance based monitoring programmes as suggested by NIOSH and thus may result in the collection of more samples than are necessary to obtain a reasonable estimate of the exposure profile.

A more general approach is taken by the American Industrial Hygiene Association (AIHA 1998 and 2006) who suggest that 6-10 samples should be sufficient to give a picture of an exposure profile.

In respect to the minimum number of samples to be collected, fewer than six (6) samples in any one SEG leaves a great deal of uncertainty about the exposure profile (AIHA 2006).

Figure 5.1 demonstrates this point. Many statisticians will suggest only three samples are required, however a minimum of six gives greater confidence and meets the minimum sample requirements for many computer based statistical packages.



(Source: AIHA 1998 – *Used with permission of the American Industrial Hygiene Association 2007*)

Figure 5.1 – AIHA Sample Guide

Statistical analysis of data using software packages make evaluation of data relatively simple however decisions need to be made by the Occupational Hygienist as to which metric (Mean, Geometric Mean, MVUE, 95%ile, Upper Tolerance Limit etc) should be used to judge compliance (see section 5.1.5). This will depend on statutory or corporate requirements.

Normally monitoring programmes should be conducted so as to ensure weather patterns are considered.

Once a SEG has been evaluated it should be managed as per the flow chart in Figure 5.2.

When considering monitoring strategies for any contaminant, reference should be made to appropriate documentation to ensure that participants have a full understanding of the principles supporting a statistical monitoring programme.

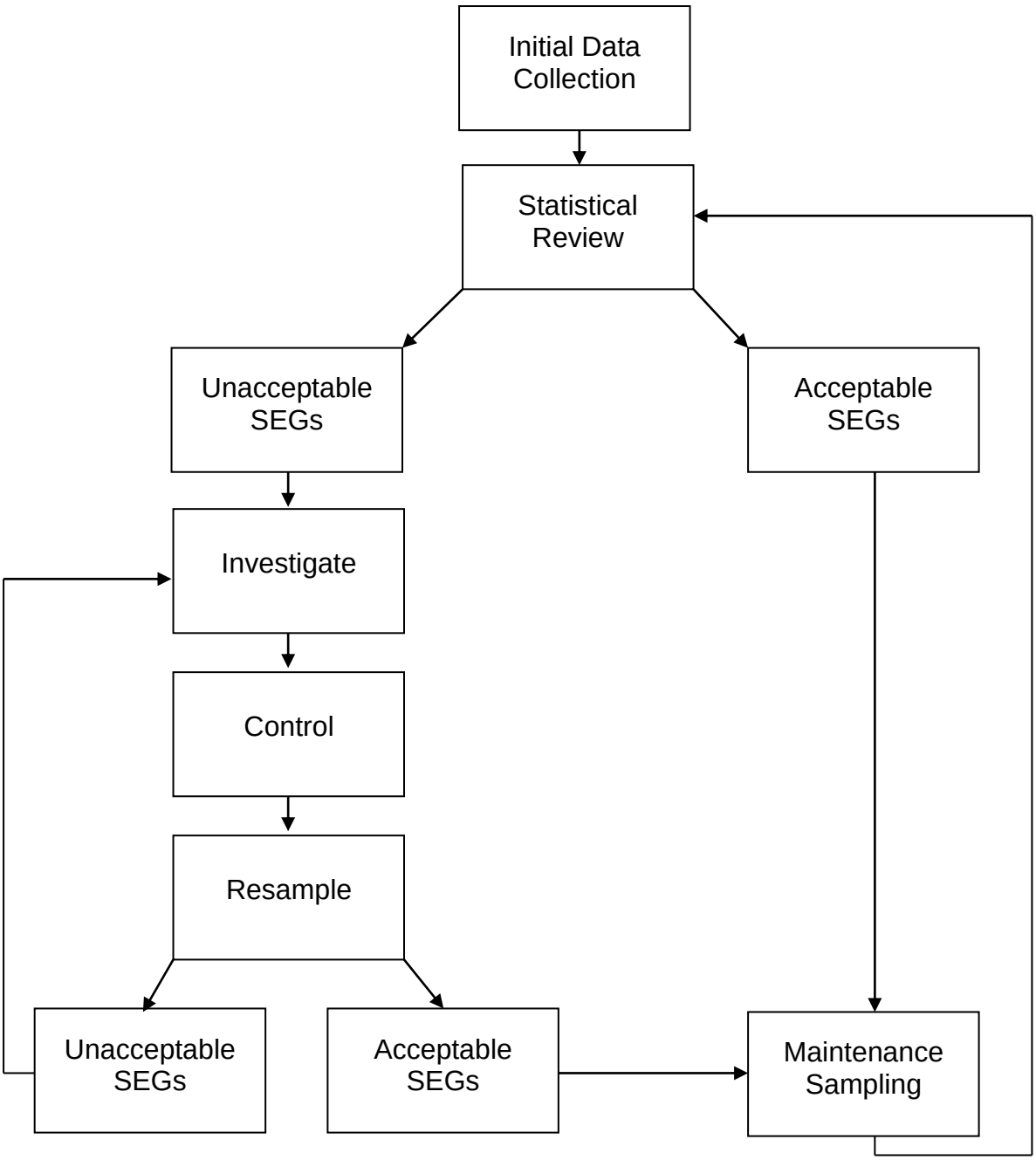


Figure 5.2 – Process for Evaluating Unacceptable SEGs (HEGs)

5.1.4 Interpretation of Results

In its most simplistic form, the interpretation of a set of workplace exposure measurements depends on the original purpose of the sampling exercise.

If the original exercise was for compliance purposes then that legislation will direct how the data is to be evaluated (eg compliance with a prescribed exposure standard). If however, the original purpose of the exercise was to meet either corporate or epidemiological requirements, a different approach will be necessary. An overview of the different approaches is provided below.

- ***Compliance Analysis***

  One of the significant issues that must be understood with all workplace monitoring is the high degree of variability in workplace exposures within a group of workers carrying out similar tasks from day to day. Invariably this variation is much greater than that attributable to sampling and analytical errors.

  In many countries the means of dealing with this variability has been the use of appropriate sampling strategies linked with the professional judgement of the occupational hygienist performing the analysis of the data.

  For example if all the exposures are well below the exposure standard (half of the exposure standard is used by many hygienists), the process is under reasonable control and judged to be acceptable. This does not mean that problems may not still exist, however if they do they will usually be as a result of unusual circumstances (eg maintenance). If the exposure data is below the exposure standard but approaching it, then the situation requires further evaluation and potentially the introduction of better controls. If however, the exposures are above or very close to the exposure standard then the process is probably out of control and a mitigation programme to control exposures should be developed.

- ***Non-Compliance Analysis***

  When considering monitoring programmes which are non-compliance dependent, the interpretation of the data is solely end use dependent. For example many large organisations require their business units to conduct routine monitoring programmes, the results of which may be used for different purposes. Increasingly, organisations are moving to statistical based programmes and are using statistical tools (see section 5.1.5) to assist in the evaluation of that data.

  Interestingly, there is no uniform approach within industry as to which statistical metric should be used, with some using the 95%ile, others the geometric mean and some the 95% upper confidence limit of the Minimum Variance Unbiased Estimate (MVUE). While these metrics will be discussed in section 5.1.5, it is useful to show the diversity of interpretation within the industrial environment.

  For epidemiological purposes, interpretation of the data usually involves placing exposures into broad groupings (eg high, medium and low) so that these can be linked to health effects. This usually involves complex statistical analysis on a group basis which can be distinctly different from interpreting individual exposures.

No matter what the situation, interpretation of exposure data is an important task and should only be undertaken by those qualified and experienced to do so. This does not mean that you should not do this task but merely suggests that if you don't have experience in this area then you should seek the input of someone who does.

5.1.5 Basic Statistical Analysis

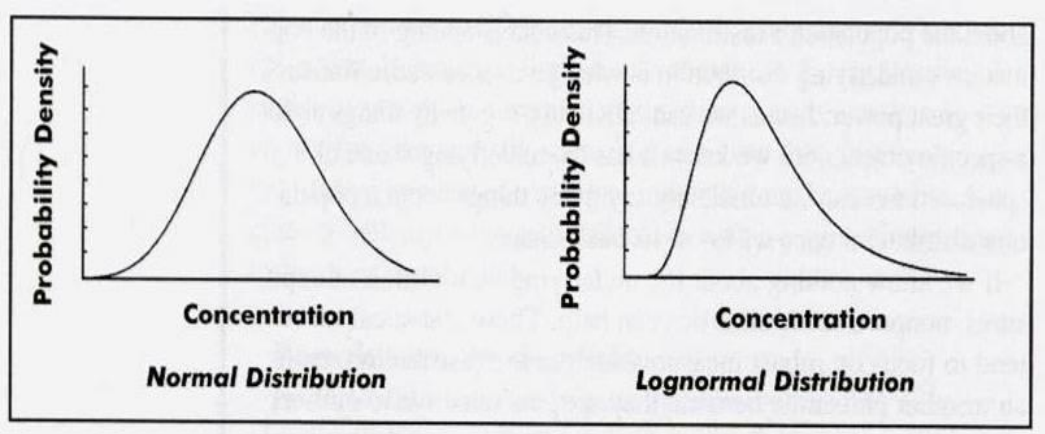
In the interpretation of data statistical tools provide a powerful option, however it is important that their theoretical basis and limitations are understood.

In many cases the rules for applying statistical analysis techniques to data are very rigid and in many real life cases may be difficult to meet. For example, the requirement for random sampling may present challenges, especially as few work processes are constant from day-to-day. Nevertheless, such requirements should be observed as much as is possible and in the end a degree of "professional judgement" will be required.

- ***Distribution of Data***

  A distribution is a description of the relative frequencies of the members of that population. In essence, a distribution of a dataset describes how the data is distributed about a central point.

  Two distributions are commonly encountered in reviewing occupational hygiene data. If the data is distributed equally around a simple central mean (ie about as many values are above the mean as below), this kind of distribution is referred to as a "normal" or Gaussian distribution. However, if the data is not symmetrical about a simple central mean but skewed to one side then this type of distribution is referred to as lognormal. Both these distributions are indicated in Figure 5.3.



(Source: AIHA 1998 – *Used with the permission of the American Industrial Hygiene Association 2007*)

Figure 5.3 – Normal and Lognormal Distributions

Each of these distributions can be described in statistical terms by the use of simple descriptors, eg arithmetic mean (AM) and standard deviation (SD or s) for a normal distribution and the geometric mean (GM) and geometric standard deviation (GSD) for a lognormal distribution. While the AM and GM tells us information about the central tendency of data, the SD and GSD tell us about the variability of the data.

Observations of many occupational hygiene datasets have shown that it is usually highly skewed to the right (but not always). One reason for this is that exposures cannot be less than zero so the left tail of the distribution is compressed whereas there is potentially no upper limit to exposure levels in a workplace.

Thus, it is reasonable to assume that the underlying distribution for workplace exposure data is the lognormal distribution unless there is a compelling reason to believe otherwise, however the assumption of lognormality of a dataset should be checked.

- ***Basic Statistical Formulae***

The following simple formulae are used to calculate the AM and SD for normal distributions and GM and GSD for lognormal distributions.

$$AM = \frac{\Sigma X_i}{n}$$

$$SD(s) = \sqrt{\frac{\Sigma (X_i - \bar{X})^2}{n - 1}}$$

Where Σ = sum of data items of X and n is the number of observations

$$GM = e^{\frac{\Sigma (\ell nX)}{n}}$$

$$GSD = e^{\sqrt{\frac{\Sigma (y_i - \bar{y})^2}{n - 1}}}$$

Where $y = \ell nX$ and n = number of observations

When interpreting data the following guidance is of value:

GSD	**Inference**
1.0	No variability. All readings have the same value
<1.44	Data approximates a normal distribution
1.5 - 2.0	Very little variability in data
2.0 – 3.5	Moderate variability in data
> 3.5	High variability in data

- ***Other Statistical Measures***

Other statistical measures in common use include:

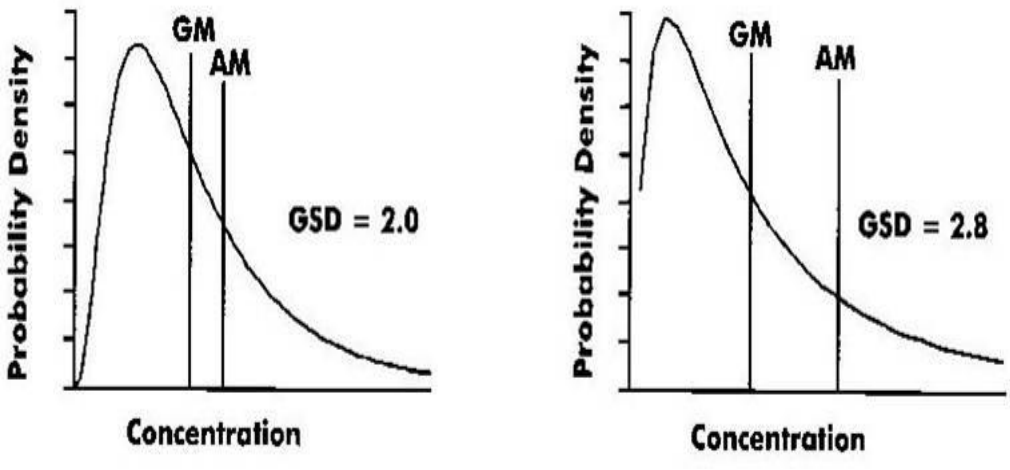
- Upper and lower confidence limits
- 95th percentile
- Minimum variance unbiased estimate

Confidence limits allow one to gauge the uncertainty in the parameter that we are estimating (AM or GM). For example the wider the confidence limits the less certain we are of the point estimate of the parameter (AM or GM). Confidence limits are usually calculated for the AM or GM in order to determine, with a specified degree of confidence (usually 95%), the range in which the true population parameter (AM or GM) is likely to lie.

Forming a “picture” of an exposure profile’s upper tail is especially important when evaluating the health hazards of agents with acute health effects. It is also useful when estimating the risk of non compliance to an exposure standard: usually the 95th percentile (95%ile) is used and can be calculated using statistical techniques or graphically (refer ***Log Probability Plots***).

The minimum variance unbiased estimate (MVUE) is especially useful in those cases when the data is heavily influenced by high results.

MVUE is simply (but difficult to calculate) an unbiased estimate of the true arithmetic mean of a lognormal dataset. When the data has little variability (GSD <2.0) the GM and MVUE (AM) will be close together, however as variability increases (GSD 2.0 – 3.5) the MVUE (AM) will give a better estimate of the central point of the exposure profile (Figure 5.4).



(Source: AIHA 1998 – *Used with the permission of the American Industrial Hygiene Association 2007*)

Figure 5.4 – AM and GM of Lognormal Distributions

- ***Log Probability Plots***

If data is expected to follow a lognormal distribution this can easily be proved via the use of a probability plot.

The process involves ranking the exposure data from the lowest to highest and assigning each a rank from 1 (lowest value) to the highest (n). The plotting position of each is calculated from the formula:

$$\text{plotting position (\%)} = \frac{\text{Rank}}{n+1} \times \frac{100}{1}$$

Each exposure is plotted against its plotting position (%) on special log probability paper and a line of best fit drawn. If it is indeed a lognormal distribution the data should fall on or near the straight line.

Log probability graphs are useful in that they provide a simple means of obtaining the GM and GSD. The GM is found by reading off the concentration at the 50%ile while the GSD is obtained by dividing the concentration at the 84%ile by the 50%ile. The 95%ile (used by some organisations as a measure of compliance) can also be read off the graph if required.

The above process is also useful when checking that persons have been assigned to the correct similar exposure group (SEG) as described in section 5.1.4. In such cases mixed SEGs will be indicated by groups of outlying data which also follows a straight line.

While undertaking a log probability plot is a valuable exercise to enshrine the concept in your memory, most computer packages available for use with occupational hygiene exposure data have this facility.

5.1.6 Quality Assurance

The degree of confidence one can have in workplace exposure data is dependent on two key criteria. These are:

a) An appropriately validated analytical method

b) The use of appropriate sampling methodology and practice

Having one of these factors in isolation does not guarantee that the results from a monitoring exercise will be appropriate.

While numerous quality assurance schemes operate throughout the world in respect to analytical methods and the performance of laboratories that use them, no such schemes have been developed to cover sampling methodology and practice in workplace monitoring.

Good occupational hygiene practice dictates that self-applied quality control processes should form part of any workplace monitoring exercise. For example, the measurement protocol should be evaluated and documented in advance and then adhered to during the exercise. Analytical variation can be assessed using blank or spiked samples.

Field quality control is generally limited to field and media blanks together with well-defined calibration practices.

Failure to follow such basic quality assurance practices could give rise to a lack of confidence in the results of a workplace evaluation and thus a waste of time and resources.

5.2 SURVEY DESIGN

5.2.1 Non-Sampling Approaches

In recent years the concept of “control banding” has achieved significant prominence, especially in Europe.

The concept of control banding was developed in the late 1980’s by occupational health experts in the pharmaceutical industry. This industry uses large numbers of new chemical compounds with limited toxicity data. The experts reasoned that such compounds could be classified into bands by their toxicity and by their need for restriction of exposure. Each band was aligned with a control scheme.

Control banding is a process in which a single control technology (such as *general ventilation* or *containment*) is applied to one range or band of exposures to a chemical (such as 1 – 10 mg/m^3) that falls within a given hazard group (such as *skin and eye irritants* or *severely irritating and corrosive*). Four main control bands have been developed for exposure to chemicals by inhalation:

- Band 1 – Use good industrial hygiene practice and general ventilation
- Band 2 – Use local exhaust ventilation
- Band 3 – Enclose the process
- Band 4 – Seek expert advice

For some activities, processes, tasks or jobs, experts can specify that respiratory protective equipment (in combination with other control approaches) is always necessary. The most developed model for control banding has been established by the HSE of the United Kingdom.

The control banding approach focuses resources on exposure controls and describes how strictly a risk needs to be managed. This qualitative risk assessment and management tool is intended to help small businesses by providing an easy-to-understand, practical approach to controlling hazardous exposures at work.

The principle of control banding was first applied to dangerous chemicals, chemical mixtures, and fumes. The control banding process emphasises the controls needed to prevent hazardous substances from causing harm to people at work. The greater the potential for harm, the greater the degree of control needed to manage the situation and make the risk “acceptable”.

The basis of these bands for exposures to chemicals by inhalation is detailed in Table 5.2.

Table 5.2 – Control Bands for Exposures to Chemicals by Inhalation

Band No.	Target Range of Exposure Concentration	Hazard Group	Control
1	>1 to 10 mg/m^3 dust >50 to 500 ppm vapour	Skin and eye irritants	Use good industrial hygiene practice and general ventilation
2	>0.11 to 1 mg/m^3 dust >5 to 50 ppm vapour	Harmful on single exposure	Use local exhaust ventilation
3	>0.01 to 0.1 mg/m^3 dust >0.5 to 5 ppm vapour	Severely irritating and corrosive	Enclose the process
4	<0.01 mg/m^3 dust <0.5 ppm vapour	Very toxic on single exposure, reproductive hazard, sensitiser*	Seek expert help

* Exposure to any concentration of a sensitiser requires expert advice

This approach has been developed into web based applications specifically to assist small and medium-sized enterprises to do risk assessments for chemicals and mixtures of chemicals.

The most developed of these is COSHH Essentials. COSHH Essentials (http://www.coshh-essentials.org.uk/) (accessed December 2006) is a control banding tool that helps small and medium-sized enterprises to do risk assessments for chemicals and mixtures of chemicals. This tool requires four pieces of information:

- The type of task (eg mixing liquids, sack filling, manually cleaning and disinfecting surfaces)
- The hazard classification from the material safety data sheet (MSDS) obtained from the chemical manufacturer or supplier
- The volatility or dustiness of the chemical or product
- The amount used in the task (small quantities = grams or millilitres; medium quantities = kilograms or litres; large quantities = tons or cubic metres)

The system then:

- Identifies the control band (control approach),
- produces advice on controlling risk from the chemical used in the specified task, and
- provides written guidance and documentation as a result of the assessment.

In British law, the duty to control risk remains with the employer. Both the web and paper versions of the COSHH Essentials tools are designed to assist the small or medium-sized employer meet regulatory requirements. COSHH Essentials is a free service and was developed by the HSE in collaboration with British industry and trade unions.

A similar approach to COSHH Essentials has been developed jointly by the ILO, WHO and United Nations Environment Programme and published as the ILO Chemical Control Toolkit http://www.ilo.org/public/english/protection/safework/ctrl_banding/toolkit/icct/index.htm (accessed 2006)

The ILO Toolkit has five (5) stages which need to be followed. These are:

Stage 1: Find the hazard classification and match it to a hazard group. For common solvents this has already been done and the information provided on the ILO website. For other substances there is a need to establish the risk phrases for the substance and then find the hazard group from the ILO website.

Stage 2: Establish the amount of substance to be used and use this to determine the scale of use from the table supplied by the ILO.

Stage 3: Establish how much of the substance will escape to the atmosphere. This is done via looking at the physical state of solids (eg pellets – low, crystalline – medium, fine powders – high) or via comparison of the boiling point of liquids to a table provided by the ILO.

Stage 4: Find the control approach by using a selection guide that has been prepared by the ILO.

Stage 5: Find the task-specific control guidance sheet(s) from a table which links the task description and the control approach.

Once the appropriate control approach has been determined it needs to be implemented and maintained.

Control banding approaches are also being developed in Belgium (REGETOX project), The Netherlands (Stoffenmanager), and Norway (KjemiRisk). The World Health Organisation is working with its Collaborating Centres to pilot control banding programmes in more than a dozen countries.

It is important to realise that non sampling approaches such as COSHH Essentials and the ILO Chemical Control Toolkit are not appropriate for many situations. Such situations are “hot” processes, open spray applications, gases, etc. However, the COSHH Essentials scheme is being progressively extended by the addition of industry and task-specific guidance on many situations; see http://www.hse.gov.uk/pubns/guidance/index.htm (accessed March 2007). Sheets are now available for welding, metalworking fluids, silica exposures and low-level asbestos work. Particular industries such as printing have developed customised sheets for their own specialised processes.

It should also be recognised that all such systems provide general guidance based on the most likely scenario and do not take account of individual process variations. While such systems are a useful tool for small businesses, assessment of a workplace by an experienced occupational hygienist may be (and in many cases is) required.

5.2.2 Sample Numbers

When developing any sampling strategy, one question which always arises is "how many samples do I need to collect to provide representative and useful information?" The answer depends on what information is required from the exercise. Some examples would be:

- ***Compliance*** – The number of samples is sometimes prescribed in legislation so the decision process may be straight forward. In other cases it is necessary to collect enough samples to be able to demonstrate compliance. For very low exposures this may be just a few samples but as exposures approach the exposure standard this will require many more samples.

- ***Epidemiology*** – Such exercises invariably involve collecting as much data as possible and is usually limited by time, budgets and resources.

- ***Corporate Requirements*** – Again, such programmes usually have specific requirements but in many organisations are based on one or more of the statistical monitoring approaches.

- ***Degree of Confidence*** – In such cases an increased level of confidence (99% as against 95%) will result in a significant increase in sample numbers.

Some general "rules of thumb" have been proposed (eg 1 in 10 workers should be sampled or a minimum of 3 samples with a spread of less than 25%), however such approaches should be used with care as they could significantly affect the quality of the data.

Grantham (2001) describes a number of other approaches. These include:

- ***Using rough estimates of the mean and the standard deviation***

  This approach requires some preliminary data and is represented by the formula

$$\text{Number of samples} = \left[t_{value} \cdot \frac{CV}{E} \right]^2$$

  Where t_{value} = t-statistic for degrees of freedom (number of samples -1)

  CV = Coefficient of variation $\left[\frac{\text{Rough standard deviation}}{\text{Rough mean}} \right]$

  E = Error that is acceptable

  For example:

  If five measurements have a rough mean of 60 ppm and standard deviation of 15 ppm then

$$CV = \frac{15}{60} = 0.25$$

  No. degrees of freedom = 5-1 = 4, so value of t - statistic (from reference tables) = 2.776 (95% confidence)

  If we assume the acceptable error is 15% (0.15)

$$\text{Number of Samples} = \left[2.776 \times \frac{0.25}{0.15} \right]^2$$

$$= 4.62^2$$

$$= 21.4$$

$$= 22 \text{ samples (approximately)}$$

- ***Method of Rappaport and Selvin (1987)***

  This process determines the number of samples needed to test the mean exposure of a lognormal distribution of exposures against an exposure standard. This approach also requires some preliminary data and is demonstrated in Table 5.3.

Table 5.3 – Rappaport and Selvin Sample Number Model ($\alpha = 0.05$, $\beta = 0.10$)

	GSD				
F	**1.5**	**2.0**	**2.5**	**3.0**	**3.5**
0.10	2	6	13	21	30
0.25	3	10	19	30	43
0.50	7	21	41	67	96
0.75	25	82	164	266	384
1.25	25	82	164	266	384
1.50	7	21	41	67	96
2.00	2	6	11	17	24
3.00	1	2	3	5	6

Where F = $\dfrac{\text{True sample mean of exposures}}{\text{Exposure Standard}}$

= $\dfrac{\text{Approximated arithmetic mean}}{\text{Exposure Standard}}$

GSD = Geometric standard deviation

α = 5% chance that it is claimed that the workplace complies with the exposure standard when in fact it does not

β = 10% chance that it is not claimed that the workplace complies with the Exposure Standard when in fact it did

Table 5 has been prepared from the equations developed by Rappaport and Selvin (1987) and clearly demonstrates the fact that as the mean of the exposures approaches the exposure standard, more samples are necessary to make an accurate judgement as to whether the exposure standard is exceeded. Clearly, if the mean of the exposures is well below or greatly above the exposure standard, few samples are required. Similarly, as the variability in the data increases (increasing GSD) then more samples are needed to make an accurate judgement. While the above may seem logical, it was not until Rappaport and Selvin proposed this approach that such simple logic evolved in respect to this matter.

Other approaches are:

- ***NIOSH Compliance Method***

  See section 5.1.3 for details.

- ***AIHA Approach***

  The AIHA (1998 and 2006) indicates that there is a point of diminishing returns in respect to the number of samples required to adequately define an exposure profile. Fewer than six (6) measurements leaves a great deal of uncertainty about the exposure profile, while more than ten (10) provides additional refinement in exposure estimates but the marginal improvement is rarely cost effective.

  While it is possible to obtain a reasonable approximation of an exposure distribution with 6-10 samples, as the exposures approach the exposure standard 30 or more measurements may be necessary to ensure the distribution of exposures is well defined.

5.2.3 Sampling Patterns

When designing a sampling strategy there are a number of different sampling approaches that can be adopted. These are usually based on the contaminant, type of survey, work patterns and process variability. These include:

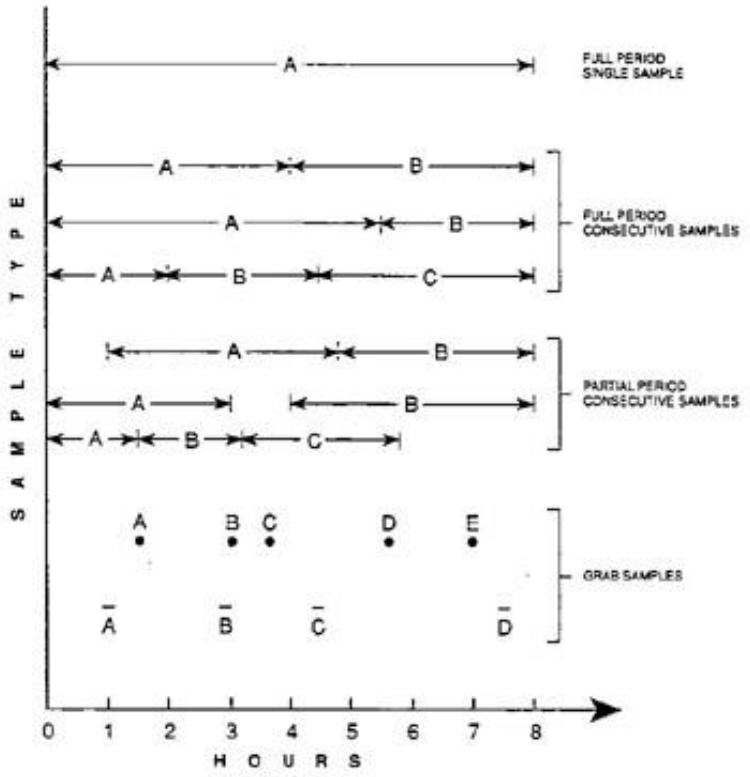
- Grab samples
- Partial period consecutive samples
- Full period consecutive samples
- Full period single samples

In some countries this is referred to as:

- Grab sampling
- Task duration sampling
- Short period sampling (less than the task duration and sometimes taken consecutively)
- Full shift sampling

Irrespective of the nomenclature used the fundamental concept is similar.

These different approaches are shown graphically in Figure 5.5.



(Source: NIOSH 1977)

Figure 5.5 – Sampling Patterns

What is important to appreciate is that the sampling approach adopted must take into account the exposure pattern of the person being sampled if representative data is to be obtained. In the following discussion "period of interest" can refer to either the period upon which the exposure standard is based (8 hours in many cases) but also in modern working patterns to the period of exposure while conducting a task. It is for the hygienist to make a judgement as to what is their "period of interest" for the exercise being conducted.

- ***Grab Samples*** – are samples lasting only a few minutes or seconds. They are usually taken using direct reading instrumentation during an initial survey (walkthrough survey) to highlight potential exposures or sources of exposure.

- ***Partial Period Consecutive Samples*** – consists of one or more samples of equal or unequal duration covering only a part of the period of interest. The major problem with this approach is how to estimate the exposure that occurred during the period not sampled. NIOSH (1977) recommend that at least 70-80% of the full period is sampled.

  Some international standards indicate that in situations where exposures are likely to be constant as little as 50% of the full period need be sampled. In all cases professional judgement plays a significant role in choosing the best approach.

- ***Full Period Consecutive Periods*** – these cover the full period of the relevant standard (eg 8 hours for an 8 hour TWA exposure standard or 15 minutes for a STEL). This approach is very useful in those situations where the process is intermittent, thus giving data not only on the TWA exposure but also the variation in exposures in relation to the process.

- ***Full Period Single Samples*** – are normally carried out to establish the average exposure of workers during their normal work day.

5.2.4 Sampling to Assess Acute or Chronic Effects

The toxicology of individual substances can have a significant influence on the design of sampling strategies. For example chronic acting substances such as crystalline silica (quartz) are sampled over an extended period (eg full shift duration) while acute acting substances should be sampled over a time period in accordance with the appropriate STEL or if the onset of an effect is rapid the appropriate use of alarmed direct reading instrumentation may be appropriate.

In some instances it may be appropriate to sample for both the full shift and over short periods as a substance may have both TWA and STEL exposure standards (eg trichloroethylene).

5.2.5 Practicalities of Sampling Programmes

While the previous sections (see also section 5.1.3) describe the various approaches to sampling and the number of samples to be collected, there are a number of practical issues that also need to be addressed.

The first of these is cost effectiveness. Large statistically-based monitoring programmes are very difficult to undertake in terms of the equipment required, the resources necessary to undertake the exercise and the ongoing disruption to the process. Consequently it is rare for such programmes to be implemented outside of multi-national corporations and thus the question arises “what can reasonably be done?”

For example, a single person operating without any assistance will find it difficult to calibrate, distribute, monitor and recalibrate more than five sample collection devices at one time. Given this, it is important that the quality of the monitoring be excellent, the persons and situations determined for monitoring be appropriate and the collection of data be such that any abnormalities in results can be explained.

Obviously, professional judgement and experience are major factors in this situation but provided the basics are clearly understood and correctly applied, a good assessment of worker exposure can be made.

The relationship between observations (work practices, control measures, dustiness of process, etc) and measurements cannot be over-stated; it is better to have fewer samples that can be clearly interpreted than a large number of samples with limited data which can't. The balance between what is reasonably possible to achieve and what is necessary to obtain a picture of exposure needs to be assessed for each and every exercise. If one person cannot achieve what is necessary to obtain an exposure profile, then extra resources will be required.

Unfortunately, there is a shortage of good quality well trained people to perform sampling exercises in the workplace, which may well limit what can be done.

The final limitation on sampling programmes, in many cases, is the process itself. In some situations the processes (eg batch process which occurs infrequently), do not lend themselves well to statistically-based random sampling monitoring exercises. An evaluation of each process is required before considering what can be reasonably achieved.

5.3 PERSONAL SAMPLING

5.3.1 Breathing Zone

As the main route of entry into the body for many substances is via inhalation, it is logical that any estimate of exposure of such substances should be conducted in a location consistent with normal inhalation patterns of workers. By convention, this has been deemed the "breathing zone" and is defined by some statutory authorities (eg AS2985) as:

"A hemisphere of 300 mm radius extending in front of the face and measured from the midpoint of a line joining the ears."

Samples collected in the breathing zone of a worker are termed “personal samples” and are directly linked to workplace exposure standards.

Research in wind tunnels has demonstrated that the location of the sampling head can result in significant concentration differences over short distances. To avoid such variations it is common practice to attach sampling heads in the area of the worker’s lapel but still within the breathing zone.

The other variable in the sampling head location equation is worker practices, which may have a significant influence on exposure. One such case occurs when a worker inserts his or her head into a reaction vessel to monitor the process.

Such actions may give rise to incredibly high exposures of short duration. The sampling device needs to be positioned in such a manner within the breathing zone to collect the contaminant of concern.

One approach to overcome (or at least minimise) some of the difficulties if factors are significantly influencing the exposure cloud, is the use of dual lapel sampling. This at least gives some estimate over the variation in the exposure profile over relatively short distances.

5.3.2 Operator Variability

The concentration of contaminants in the workplace is subject to both temporal and spatial variation and thus likely to be in a constant state of flux. This is not only due to changes in the process, but also ventilation rates, climatic conditions, etc.

For workers, the range of tasks undertaken during a work day can dramatically influence an exposure pattern and concentrations. In many cases individual approaches to performing the same task (eg left or right handed shovelling) may (and often does) result in significant exposure differences between workers performing the same task.

Such factors must be considered when designing a sampling strategy so as to ensure they are minimised.

5.4 AREA SAMPLING

5.4.1 General or Background Measurements

Samples which are not taken on the individual in the breathing zone are generally referred to as static (or area) samples. Such samples do not normally correlate well with actual personal exposures but they still do have a useful role. Static samples are useful for the following purposes:

- To check the performance of control devices.
- As a surrogate for personal exposures, when a clear correlation between the results from static samples and personal samples has been established.
- In identifying and quantifying contaminant sources in the workplace and in delineating areas of unacceptable contamination.
- As part of the process for assessing trends in baseline concentrations.
- Are sometimes the only realistic means of measurement when certain types of continuous monitoring are required.
- As the only realistic method of sampling high volumes of air (eg asbestos clearance monitoring).

It should be understood that workplace exposure standards are linked to personal sampling and the use of static or area samples for health assessment is not generally accepted.

5.4.2 Particle Size

The way in which aerosols distribute themselves in an airstream depends on the aerodynamic properties of the aerosol concerned. When applied to dust, larger particles tend to settle out of the air quite quickly due to gravitational forces and smaller particles tend to remain airborne for longer periods.

Such behaviour is directly attributable to the aerodynamic diameter of the particles. If a dust particle has the same settling velocity as a spherical particle of unit density (1 g/cm^3) and diameter of 1 µm, it is deemed to have an aerodynamic diameter of 1 µm. This is independent of the particle's size, shape, density and mass.

This concept is fundamental in our understanding of why particles deposit in the lungs and airways in the manner that they do.

Particle size also has an influence on contaminant concentration. If we have a mixed dust of varying particle size, upon settling it is not unusual to find one particular contaminant is highly concentrated in one size fraction. This could mean that close to a source concentrations of the contaminant are relatively low (on a mass/mass basis), however at a point where the finer particles have settled the concentration is significantly higher.

5.4.3 Breathing Air Quality

Air supplied or self-contained breathing apparatus relies on the use of air generated by air compressors to provide the air source. It is important to ensure that the quality of this air is assessed at regular intervals to check for contaminants such as carbon monoxide and oil mist, which may have been inadvertently generated by the compressor. If significant pipework is used to direct the breathing air around a plant, it is not uncommon for condensation to occur in the pipes, leading to corrosion. Under some circumstances such corrosion can give rise to an astringent taste in the air.

In most commercial systems filters are installed to control moisture, oil mist and carbon monoxide, but these have a finite life and need to be changed when expended.

There are varying approaches to monitoring these contaminants in the air but the advent of direct reading devices has made the inline analysis of carbon monoxide on site relatively easy.

In modern systems continuous monitoring instrumentation for carbon monoxide and built-in filtration are common. For older systems it may be necessary to sample the breathing air using external procedures. In such cases air is drawn into a gas sampling bag from which it is extracted and presented to the instrument (carbon monoxide monitor or indicator tube) for measurement. Oil mist is usually sampled by passing a known volume of air through a small pore size filter. The collect oil is either analysed gravimetrically or more accurately by infra-red or gas chromatographic means.

5.5 SURFACE AND OTHER MEASUREMENTS

5.5.1 Surface Contamination Measurements

If a comprehensive risk assessment for exposure to contaminants in the workplace is to be developed, it is essential that any contribution from surfaces be evaluated. This will always be dependent on the toxicological properties of the substance and is common practice in the nuclear industry.

There are various methods used for evaluating surface contamination, such as micro vacuuming, disposable paper towels and manual wipe methods. The manual wipe method (also called smear and wipe) is the most commonly used and involves a filter paper being drawn over a known area of contaminated surface and then being analysed to produce an assessment of the level and nature of the deposit.

Another method which has shown good results in laboratory trials (Wheeler & Stancliffe 1998) is the use of adhesive tape, more specifically forensic tape. Such tapes are constructed of a clear plastic top coat, a sticky middle layer and a base layer. By removing the clear plastic top coat the sticky layer can be pressed into a surface thus collecting what contaminants are present. In general samples (both wipe and adhesive tape) are treated with acid to dissolve any contaminants present, followed by atomic absorption spectrophotometry, or the samples can be analysed without any acid digestion by X-ray fluorescence spectrometry (XRF).

Other approaches to assessing contaminated surfaces involve the use of pH sticks or colorimetric pads (acids and alkalis) or instrumentation such as mercury sniffers (the high vapour pressure of mercury makes this a particularly effective technique).

The question as to why you would undertake surface contamination invariably arises. Such sampling (especially during evaluation of contaminated waste sites) improves the characterisation of what hazards may be present and allows for better decision-making.

Surface contamination samples can indicate sources of leakage and help to track the spread of contamination. They can give an indication of how and where skin contact might occur. However, they are not a direct measure of exposure and cannot readily be compared with any exposure limits.

5.5.2 In-situ XRF Metal Analysis

An XRF spectrometer uses primary radiation from an X-ray tube to excite secondary emission from a sample. The radiation emerging from the sample includes the characteristic X-ray peaks of major and trace elements present in the sample. Dispersion of these secondary X-rays into a spectrum, usually by X-ray diffraction, allows identification of the elements present. The height of each characteristic X-ray peak relates to the concentration of the corresponding element in the sample, allowing quantitative analysis of samples for most elements in the concentration range 1 ppm to 100%.

In recent years small hand-held XRF analysers have been developed which are extremely useful for measurements of samples within the field. One such application is their use to measure elements in contaminated soils and unknown bulk materials. This is particularly useful for metal analysis.

It should be noted that particle size and surface preparation can influence results. Improved analysis can be achieved if the sample is dried, sieved, ground or pressed.

Dost (1996) evaluated a field XRF unit in relation to the measurement of dusts from surfaces in workplaces and commented on the ease with which the elemental nature and level of contamination in the workplace could be determined. Dost also concluded that the XRF technique had a distinct advantage over the traditional wipe method where the contaminant material was on a rough and porous surface (eg concrete). Conversely, it was not suitable on surfaces such as steel as it picked up the elements of this surface as well as the overlaying contaminant material.

A common use for XRF instruments is in the evaluation of coatings for the likely presence of significant amounts of lead.

5.5.3 Bulk Sampling

In many instances it will be necessary to collect some bulk samples to identify which contaminants are likely to be present in the workplace. This is commonly the case in regard to asbestos identification where bulk samples are collected and the presence and type of asbestos identified by dispersion staining or other confirmatory techniques.

The same principles can be applied to other unknown substances found in workplaces. Before developing a monitoring programme, bulk samples of an unknown material can be sent to a laboratory for analysis to check on the specific contaminants present and to check for any contaminants which may interfere with some sampling methods.

The results will guide what type of monitoring strategy is required and thus it is very useful in the overall process.

5.5.4 Skin Exposure

Dermal exposure can present a significant pathway for some contaminants to enter the body. This is especially the case with pesticides, but other compounds can be absorbed this way.

Dermal exposure evaluation methods have been broadly categorised into direct and indirect methods.

- ***Direct***

  Direct means assessing what is deposited onto the skin; indirect means estimating dermal dose either as attributable to some biologic indicator that is actually measured or that which could potentially result from a contaminant measured on an accessible surface.

  The most common direct method is the use of dermal dosimeters in the form of patches. Other direct evaluation methods include skin washes and wipes, and the video detection of fluorescent tracers.

- ***Indirect***

  Indirect methods refer primarily to measuring a biologic response such as cholinesterase activity in blood or urinary excretion, but also include measuring surface contamination.

In comparison to air sampling and even biological monitoring, dermal dosimetry is not a simple or routine procedure.

An individual applying dermal dosimeters should be thoroughly trained regarding the placement and retrieval of the dosimeters and recording of observations and other information about the activity.

In addition to objective parameters, observed work practices can also have statistically significant important influences on dermal exposure.

Each patch dosimeter is a sandwich holding a passive matrix (like a cotton gauze sponge) flat and to protect it from skin perspiration. Either one or two sets of patch dermal dosimeters can be used. The most important is the set placed against the skin under the clothing. It is believed that errors will result from using patch dosimeters attached to the inside of clothing that is free to move relative to the skin; such dosimeters will neither collect contaminants reaching the skin via penetration through openings (such as the neck, sleeves, or cuffs) nor be affected by the air motion carrying contaminant through the weave of the fabric. A second set of dosimeters may be placed outside of any clothing; it is also important that no inner dosimeter is placed beneath an outer dosimeter.

After dosimeters have been in place throughout an activity involving exposure, they are carefully removed, prepared for extraction (the quantitative removal of the chemical from the collection matrix), and the extract is analysed for the mass of chemical.

Whole body dosimeters are typically a set of long cotton underwear that minimises the effect of non-uniform depositions within a body part, but suffers from the lack of a barrier between the skin and dosimeter and may add heat stress to the wearer. After use, the whole body dosimeter may still be dissected into portions covering individual body parts.

As with all other approaches to assessing dermal exposures, there are limitations to the use of dermal dosimeters. Among the most important of these limitations (not restricted to dermal dosimeters) is the difficulty in accurately collecting depositions of volatile chemicals.

Biological monitoring to assess dermal exposure is a common technique (eg cholinesterase activity in blood for pesticides); however it may be invasive and unless correct sample collection techniques are observed may grossly underestimate exposure. In such cases dermal dosimetry (patches) may be a good alternative.

In other cases (Tetraethyl lead) where skin absorption is a significant exposure pathway, a combination of environmental monitoring and biological monitoring may give the most accurate picture of employee exposure.

Irrespective of the circumstance, dermal monitoring should only be undertaken by persons trained and experienced in the appropriate monitoring techniques.

Tool kit for Dermal Risk Assessment and Management - RISKOFDERM

The European Research Project RISKOFDERM – Risk Assessment of Occupational Dermal Exposure – has developed a conceptual model for dermal risk assessment and a simple to use tool kit for assessment and management of health risks from dermal exposures and is currently undergoing final evaluation. The tool kit can be downloaded at:

http://www.eurofins.com/research-development/occupational_hygiene/risofderm.asp

The tool kit was constructed by analysing the major determinants of dermal hazard and control exposure. The results were combined in the form of a decision tree. The tool kit does not show all the details behind the assessment, but asks the user a series of questions that are translated by the system into hazard and exposure categories that lead to an estimate of health risk from dermal exposure together with suggested control strategies.

Hazard

The user is asked to enter the identification of the chemical and the risk phrases and any additional information such as pH and the physical state of the chemical.

The information is translated into two hazard categories – one concerning local effects, the other systemic effects after uptake through the skin. The hazards are rated – negligible, low, moderate high very high or extreme.

Exposure

User asked to enter information to identify the workplace or process that is assessed and which one of the Dermal Exposure Operational units best fits with the sub category of exposure to solid or liquid:

- Handling of contaminated objects – solid or liquid
- Manual dispersion – solid or liquid
- Hand tool dispersion – solid or liquid
- Spray dispersion – solid or liquid
- Immersion – solid or liquid
- Mechanical treatment – solid or liquid

From the information the tool kit will apply a default exposure rates, take into account duration and the exposed body areas and the actual exposure score from local effects and the internal exposure score from systemic effects are then calculated separately and ranked as health risk scores with suggested controls ranging from no action required up to substitute in either case and stop working.

The toolkit is an attempt to adapt elements of exact science to a situation where the necessary input data are of limited quality and are only estimates. The purpose is to enable the user to estimate the order of magnitude of hazard, exposure and risk and to encourage the user to deal with issues of dermal hazard, exposure and control.

The RISKOFDERM project has been the subject of significant controversy and more detail can be found in an overview by Oppl et al (2003).

5.6 CONFINED SPACES

5.6.1 Identification and Nature of Hazards

Confined spaces have various legal definitions in different parts of the world and while a full list of such definitions is not appropriate for this course, all contain the same (or similar) key elements. These include:

- They are enclosed or partially enclosed spaces at atmospheric pressure during occupancy.
- May have a deficiency or an excess of oxygen.
- May have an atmosphere which has potentially harmful levels of contaminants.
- May contain a product which could cause engulfment.
- Could have restricted means of entry and exit.

Examples of confined spaces include:

- Storage tanks, boilers, silos, pressure vessels, etc
- Pits, pipes, sewers, ducts, etc

A confined space is determined in part by the hazards associated with entry into such a space and not just work performed in a physically restrictive location.

The presence of chemical agents (alone or in combination) may present a risk to personnel in a confined space that would not otherwise occur in the general atmosphere.

Some of the hazards that may be associated with work in confined spaces are:

- ***Hazardous Substances***

  This includes the use of chemicals, previously stored substances or their by-products (eg H_2S from decomposing plant material), fumes from welding, painting, etc.

- ***Flammable Atmospheres***

  This includes gases, vapours and dusts which are present in the explosive range.

- ***Unsafe Oxygen Level***

  This includes oxygen deficient atmospheres as a result of oxidation, combustion, displacement, absorption, consumption by some process and, excess oxygen as a result of a leaking oxygen supply fitting, oxy-propane cutting, oxygen injection and the use of chemicals that liberate oxygen (eg hydrogen peroxide).

- ***Engulfment***

  Asphyxiation caused by a stored supply of material immersing workers within the confined space.

- ***Physical and Other Factors***

  This includes manual handling, ignition hazards, electrical hazards, mechanical hazards, noise, radiation, biological hazards and heat stress.

5.6.2 Monitoring in Confined Spaces

The human senses should <u>never</u> be trusted to determine if the atmosphere within a confined space is safe. Many toxic gases and vapours (such as carbon monoxide) cannot be seen or smelt, nor can the level of oxygen be established accurately without appropriate instrumentation.

As permit to enter procedures for confined spaces invariably involve a risk assessment, this process should ensure that appropriate arrangements are put in place to test the atmosphere within the confined space.

Where appropriate the atmosphere should be tested for:

- Oxygen content; and/or
- airborne concentration of flammable contaminants; and/or
- airborne concentration of potential harmful contaminants.

The common means of sampling the air to assess the risk of adverse health effects is to test for specific materials with a suitable portable analyser. There are many different kinds of analysers available but the results are only as good as the operator's skill and the state of analyser maintenance. An explosimeter, used for measuring the percent Lower Explosive Limit (LEL) in a confined space, should be tested against a known standard gas, both before and after a test for vessel entry, to ensure that an accurate reading is obtained. It should be noted that a reading below the LEL could still mean that hundreds or even thousands of ppm of contaminants are present in the atmosphere.

Instruments used for testing the atmosphere in a confined space should be selected for their ability to measure hazardous concentrations and should be calibrated in accordance with the manufacturer's guidelines or manuals.

If atmospheres that are to be sampled are potentially explosive, intrinsically safe monitoring equipment will be necessary. Initial monitoring should be performed from outside the confined space by inserting a sample probe at appropriately selected openings. Telescopic extension probes or probes attached to a line can be used to reach remote regions.

Some gases or vapours are heavier than air (for example, hydrogen sulphide) and in unventilated areas will settle to the bottom of a confined space. Also, some gases are lighter than air (for example, methane) and will be found around the top of the confined space. As it is possible for contaminants to settle at different levels, the top, middle and bottom of a space should be sampled. Horizontal spaces should also be sampled at representative intervals along their length. Sampling should be such as to reflect accurately the conditions within the confined space.

When considering the appropriate time to monitor the atmosphere, it should be understood that unless monitoring is undertaken immediately prior to entry, the results may not be relevant and an unsafe condition may potentially exist.

While pre-entry testing indicates whether the atmosphere in the confined space is acceptable for entry, atmospheric conditions in the confined space can change, therefore the atmosphere should be re-tested during the work day.

Testing the atmosphere within the confined space while work is in progress will indicate whether or not the ventilation system is adequate or if the work processes are making the atmosphere unsafe.

Continuous monitors provide constant surveillance of atmospheric conditions in a confined space. Personal direct reading monitors can be used to initially test the space, and then can be worn by an employee during work to detect atmospheric changes during entry. These monitors should be fitted with visual and audible alarms to warn employees of the hazard and the need for further action as set out in the entry procedure and permit.

Re-testing and continuous monitoring of the atmosphere may be necessary:

- if determined under the risk assessment;
- as indicated from the initial testing of the atmosphere;

- because of the potential for later release or disturbance of hazardous material. Such material includes sludge, scale or other deposits, brickwork and liquid traps. The hazardous material may be released if disturbed or if heat is applied. Where harmful contaminants are released, control measures should be based on the assumption that any further disturbance of the sludge will release more vapour; or

- because of the work undertaken in the space. For example, heat or fumes from processes such as welding can build up rapidly in a confined space.

No matter what type of instrumentation is used to assess a confined space (or any other workplace), it is important that the operator clearly understands the limitations of that equipment. For example, an explosimeter exhibits different sensitivities towards different flammable gases or vapours and thus to give accurate results it should be calibrated with known concentrations of the gas or vapour likely to be present in the atmosphere being assessed.

Moreover, most chemical sensors used for the measurement of contaminant gases are fitted with filters to minimise cross sensitivity from other contaminants. These filters need to be replaced according to the manufacturer's instructions and the potential problems of cross sensitivity well understood by the instrument operator.

It should also be noted that monitoring is never a substitute for the systematic and verified isolation of the confined space from any outside source of hazardous material.

6. BIOLOGICAL MONITORING

6.1 FUNDAMENTALS OF BIOLOGICAL MONITORING

Workplace air monitoring and comparison of the results with exposure standards provides information about the probable exposure of workers to inhalation hazards. It does not provide information about the other exposure routes of skin absorption, ingestion and non work related exposures.

Biological exposure monitoring, or biological testing, is a way in which you can determine how much of a particular contaminant has actually entered and has been taken up by the body from all these routes. A number of substances can be measured in this way. The advantages of such an approach include:

- It provides additional information where there is a respiratory hazard
- It can be used where the main route of exposure is not inhalation
- It can highlight deficiencies in the wearing of personal protective equipment, ie respirators and gloves and/or clothing
- It provides evidence for medical assessment

Biological monitoring is one of the three tools used in the prevention of disease from hazardous substances in the work environment, the other two being occupational hygiene or environmental monitoring and health surveillance.

Biological monitoring means the assessment of exposure to chemicals (substances) that are present in the workplace, through the measurement of appropriate determinants in biological specimens from exposed workers. In most cases, the specimen used for biological monitoring is urine, blood or exhaled air.

The risks associated with the obtaining and handling of bodily fluids, in terms of potential exposure to possible pathogens, ie HIV, Hepatitis, viruses etc have to be considered.

In many countries only a qualified doctor or nurse can obtain such samples. Local advice must be sought before such work is to be carried out.

Biological monitoring can be divided into:

- Direct biological monitoring also referred to as biological monitoring of exposure
- Biological effect monitoring

6.2 DIRECT BIOLOGICAL MONITORING

The purpose of direct monitoring is to assess the health risk through the evaluation of internal dose of the chemical in question with the aim of ensuring the exposure does not reach levels that can cause adverse effects.

The direct analysis of the contaminant is undertaken in the specimen:

Blood – eg for lead and mercury

Urine – eg for cadmium and MOCA (methylene bis-orthochloroaniline)

Hair and nails - eg for arsenic

Breast milk and body fats – eg for pesticides and Polychlorinated Biphenyls (PCBs)

Expired air – eg for carbon monoxide and organic solvents – eg benzene

OR analysis of its metabolites

Blood – carboxyhaemoglobin from carbon monoxide

Urine – mandelic acid from styrene

6.3 BIOLOGICAL EFFECT MONITORING

Biological effect monitoring is aimed at identifying early and reversible biochemical changes resulting from exposures, ie no detrimental effect has occurred but one or more measurable biochemical changes has occurred. The degree of change is less than that which leads to injury and is not associated with a known irreversible pathological effect.

Some examples of biological effect monitoring are:

- Zinc protoporphyrin in blood – these levels increase with exposure to lead, because lead inhibits the biosynthesis of heme.
- Cholinesterase activity in red blood cells and plasma – exposure to organophosphate pesticides depresses cholinesterase activities.

Biological effect monitoring is not health surveillance through which individuals with early signs of adverse health effects are identified.

6.4 GENERAL CONSIDERATIONS

The extent and rate of absorption of a chemical after exposure depend on the properties of the chemical, especially its solubility in lipids and water, and the route of exposure. Once absorbed a chemical is distributed and spreads into various tissues depending on the susceptibility of the tissue due to variations in pH, permeability etc. Very water soluble chemicals may be distributed throughout the total body water, while lipophilic (attract non polar organics such as fats and oils) may concentrate in the body fat or other lipid tissues such as the brain.

The loss of chemical from the body or elimination depends on metabolism and excretion. Chemicals may be eliminated by numerous routes including faecal, urinary, exhalation, perspiration and lactation.

A chemical may be excreted from the body without metabolism, ie the particular chemical can be measured directly. In other cases, the chemical may be metabolised through oxidation, reduction, hydrolysis or combination of these followed by often very complex biochemical reaction in the body. Hence the choice of the indicator of exposure and even the timing of when to take a sample is critical.

6.5 BIOLOGICAL HALF-LIFE

The biological half-life of a substance is the time required for half of that substance to be removed from the body by either a physical or a chemical process. The half lives for different substances vary significantly and hence the importance of the correct sampling time cannot be over emphasised.

6.6 SAMPLING TIME

The timing of biological samples can be very important. Substances absorbed into the body are removed at different excretion rates. The concentration of some determinants can change rapidly, so in these cases sampling time must be observed and recorded carefully. On the other hand, a determinant that accumulates slowly may not need a specific sampling time.

Practical guidance on the interpretation of sampling times is given by the ACGIH (2007). While the ACGIH provides the recommendations as listed in Table 6.1, it is important to understand that this information is for guidance only and an understanding of the substance being monitored is critical if accurate results are to be achieved.

Table 6.1 – Recommended Sampling Times

Sampling Time	**Recommended Collection**
Prior to shift	16 hours after exposure ceases
During the shift	Anytime after 2 hours of exposure
End of shift	As soon as possible after exposure ceases
End of the work week	After 4 or 5 consecutive working days with exposure
Discretionary	At any time

The UK Health & Safety Executive (HSE) in the Guidance Note EH56 “Biological Monitoring for Chemical Exposures in the Workplace” (HSE 1992) uses the following (Table 6.2) to provide advice on the timing of sample collection.

Table 6.2 – Optimum Time for Collecting Samples

Half Life	**Optimum Time for Taking Samples**
<2 hours	Concentration changes too fast – not suitable
2 to 10 hours	End of shift or next morning
10 to 100 hours	End of shift at end of week
>100 hours	Random sampling acceptable

(Source*:* HSE – *Reproduced with permission*)

6.7 URINE SPECIMEN ACCEPTABILITY

The concentration of urine can have a marked effect on the results of the analysis of the contaminant. Sample results can be corrected for urine concentration in one of two ways: by adjusting for the specific gravity of the sample or by correcting for the creatinine level in the urine as creatinine excretion from the body occurs naturally at a nearly constant rate. The World Health Organisation has adopted the following guidelines for acceptable limits to assist in overcoming the issues associated with highly diluted and highly concentrated urine samples:

Creatinine concentration: >0.3 g/L and <3 g/L

or

Specific Gravity: >1.010 and <1.030

Samples outside these guidelines should be discarded and another sample collected.

Some BEIs® for determinants whose concentrations is dependent on urine output are expressed as relative to creatinine concentration. For other determinants correction for urine output is not appropriate.

6.8 BIOLOGICAL STANDARDS

6.8.1 Biological Exposure Indices

Similarly to TLVs®, the results of biological monitoring are compared against Biological Exposure Indices or BEIs®. The main source of BEIs® is from the ACGIH in their handbook *Threshold Limit Values and for Chemical Substances and Physical Agents and Biological Exposure Indices* (ACGIH 2006).

Biological Exposure Indices (BEIs®) are guidance values for assessing biological monitoring results. BEIs® represent the levels of determinants that are most likely observed in specimens collected from healthy workers who have been exposed to chemicals to the same extent as workers with inhalation exposure at the TLV®.

In a similar fashion to TLVs®, BEIs® are to be used as guidelines in the evaluation of occupational hygiene health hazards. BEIs® do not indicate a sharp distinction between hazardous and non hazardous exposures. Due to the often varied nature of concentration in biological specimens great care and caution must be exercised in the interpretation of the results from a single specimen.

BEIs® apply to 8-hour exposures, 5 days per week. Although modified, altered and extended shifts are often used across industry the BEI® Committee does NOT recommend the adjustment or use of a correction factor be applied to the BEIs®.

Use of BEIs® should only be done by experienced occupational health professionals in consultation with the associated documentation for them. The BEI® is a guideline for the control of potential health hazards for workers and the values are inappropriate for use for the general public and for non occupational exposures. In the application of BEIs® reference must be made to the current edition of the Documentation of the Threshold Limit Values and Biological Indices from the ACGIH®.

6.8.2 Notations

A notation is a designation that appears as a component of the adopted BEI® value to provide additional information with respect to the particular chemical:

"B" = Background

The determinant may be present in biological specimens collected from subjects who have not been occupationally exposed, at a concentration which could affect the interpretation of the result.

"Nq" = Nonquantitative

Biological monitoring should be considered for this compound based on the review; however a specific BEI® could not be determined due to insufficient data.

"Ns" = Nonspecific

The determinant is nonspecific, since it is also observed after exposure to other chemicals.

"Sq" = Semi-quantitative

The biological determinant is an indicator of exposure to the chemical, but the quantitative interpretation of the measurement is ambiguous.

These determinants should be used as a screening test if a quantitative test is not practical or as a confirmatory test if the quantitative test is not specific and the origin of the determinant is in question.

6.8.3 UK Limits

In the UK the HSE has established a system of non-statutory biological monitoring guidance values as an aid in the interpretation of biological monitoring data.

Biological Monitoring Guidance Values (BMGVs) are set where they are likely to be of practical value, suitable monitoring methods exist and there are sufficient data available. The type of data that are available will vary between substances and therefore the route taken to deriving the BMGV will vary between substances. BMGVs are either based on a relationship between biological concentrations and health effects, between biological concentrations and exposure at the level of the WEL or are based on data collected from a representative sample of workplaces correctly applying the principles of good occupational hygiene practice. The technical basis for each BMGV will be clearly described in supporting documentation such as an EH64 summary or other guidance.

BMGVs are non-statutory and any biological monitoring undertaken in association with a guidance value needs to be conducted on a voluntary basis (ie with the fully informed consent of all concerned). BMGVs are intended to be used as tools in meeting the employer's primary duty to ensure adequate control under COSHH. Where a BMGV is exceeded it does not necessarily mean that any corresponding airborne standard has been exceeded nor that ill health will occur. It is intended that where they are exceeded this will give an indication that investigation into current control measures and work practices is necessary.

Of course, that is not necessarily to say that because biological monitoring results are below a particular guidance value an employer need take no further action to reduce exposure; but it should be noted that BMGVs are not an alternative or replacement for airborne occupational exposure limits.

6.9 CONFIDENTIALITY

There are several ethical and confidentiality issues that must be considered and implemented before commencing a biological monitoring programme.

- The method should be appropriate for the requirements of the investigation.
- The procedures should not threaten the health of the participant.
- The risk of using invasive methods must be justified by the benefits.
- The informed consent from the participants is needed. This consent must only be given when the participant feels no fear of reprisals if their consent is not given.
- Results of the monitoring should be kept confidential and shared only with the occupational health professional and the participant.

7. SAMPLE ANALYSIS

7.1 INTRODUCTION

Analysis of occupational hygiene samples may be done on the job using some form of direct reading device or instrument. Alternatively, a sample is often collected at the workplace and sent to a laboratory for analysis. This analysis could vary from a relatively simple weighing of the contaminant on a filter to the determination of a metal using an inductively coupled plasma (ICP) spectrometer or the use of a gas chromatograph linked to a mass spectrometer for the determination of an organic solvent.

In most cases the hygienist does not perform the laboratory analysis, but an understanding of some of the basics is required to:

- Select an appropriate monitoring and analytical method
- Communicate with the analytical laboratory
- Understand the principles of the direct reading instrument
- Make an assessment of the reliability of the results

7.2 ANALYTICAL METHODS

Most methods currently employed for occupational hygiene sample analysis are instrumental rather than the classical “wet chemical methods” common prior to the 1960’s.

The types of analysis can typically be divided into two main types

- Spectroscopy
  - Atomic
  - Molecular
- Chromatography

7.2.1 Spectroscopy

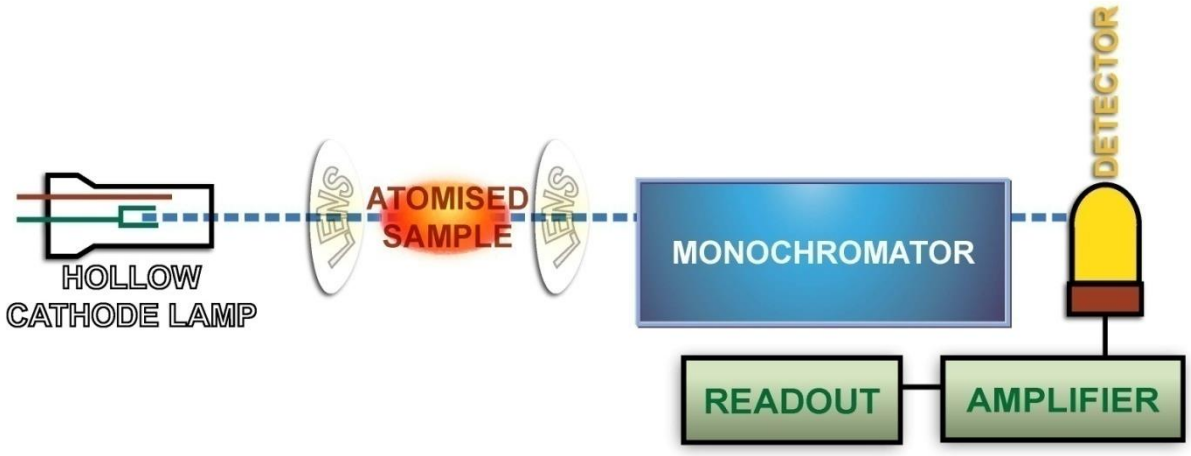
The basic underlying principle of spectroscopy is that all elements or chemical compounds absorb or emit electromagnetic radiation at specific frequencies. If a sample is radiated at a specific frequency for a particular element, if that element is present the amount of radiation absorbed or emitted is proportional to the concentration of that element in the sample.

a) ***Atomic Spectrometry***

Typically used for the analysis of the metallic elements. Samples usually collected using conventional sampling methods onto filters, impingement into liquids or adsorption onto a solid. Samples then prepared by appropriate method for subsequent analysis.

- *Flame Atomic Absorption Spectrometry (AAS)*

  The sample in solution is atomised by flame and the absorption of a specific wavelength of light from the hollow cathode lamp in the flame is measured to quantify the element. This technique typically used for the analysis of approximately 60 metals.



(Source: BP International)

Figure 7.1 – Schematic of an Atomic-Absorption Spectrometer

(Source: University of Wollongong)

Figure 7.2 – Atomic Absorption Spectrometer

- *Hydride Generation*

  Arsenic and selenium have poor sensitivity using conventional Flame AAS because their spectral lines are in the far UV. Hydride generation overcomes this issue. As and Se are converted to their respective hydrides AsH_3 and H_2Se. When these hydrides are swept through the flame or a through a heated quartz cell a larger proportion of the element reaches the light path resulting in increased sensitivity.

b) ***Flameless Atomic Absorption***

AAS is not sensitive enough for analysis of low concentration of metals in biological samples such as blood. During AAS there is a high flow rate of sample through the flame and a more sensitive method where less material is used is required.

- *Graphite Furnace*

  Atomisation of elements without the use of a flame can be achieved with the use of electricity (electrothermal atomisation). The sample is placed inside a hollow graphite tube and rapid heating of the tube using a high electric current causes the sample to atomise.

(Source: University of Wollongong)

Figure 7.3 – Graphite Furnace AAS

- *Cold vapour generation*

  This technique is used for the analysis of mercury because of the volatility of mercury at room temperature. Mercury compounds are reduced to metallic mercury and the mercury vapour is transported to the absorption cell by a stream of gas for determination.

c) ***Atomic Emission Spectrometry***

This technique is also based on the flame excitation of an element, but is looking at the emission of energy when the excited element is returned to its ground state.

- *Flame Emission*

  Atomic absorption spectrometers can be operated in the emission mode or a separate instrument, a flame photometer can be used. Typically the elements where this technique is used are the alkali and some alkaline earth metals eg Sodium and Potassium.

- *Inductively Coupled Plasma Spectrometry*

  An extension of atomic emission spectrometry is inductively coupled plasma spectrometry (ICP). By using gas plasma temperatures up to 10,000°C can be obtained resulting in a large increase in excited atoms and hence sensitivity. Plasma is a cloud of highly ionised gas comprising ions, electrons and neutral particles. In ICP the gas used is usually argon because it is easily ionised with radio frequency electromagnetic fields.

  Since all elements in a sample emit their characteristic wavelengths simultaneously it is possible to measure a large number of elements, up to 60, simultaneously or sequentially.

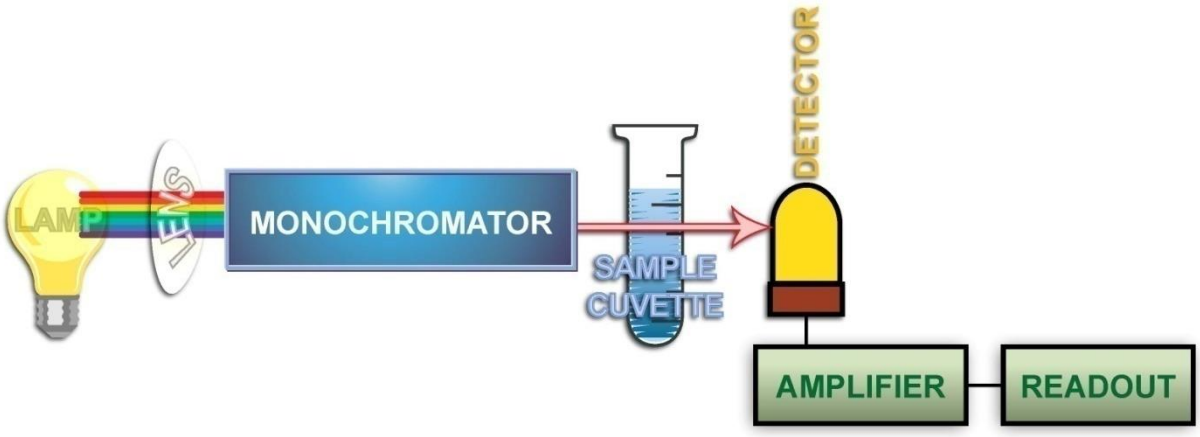
  The scanning ICP has a distinct advantage over AAS in that a separate lamp for each specific element is used in AAS but up to 60 elements can be analysed by ICP on the same sample.

d) ***Molecular Spectrophotometry***

- *UV-Visible Spectrophotometry*

  This technique is used for metals or organic compounds. Samples are collected by conventional sampling methods onto filters or by impingement into solutions.

  The principle of the method is based on the absorption of ultraviolet and visible radiation by the excitation of bonding electrons in molecules.



(Source: BP International)

Figure 7.4 - Schematic of a Single Beam UV-Vis Spectrophotometer

Most chemicals species absorb UV or Visible radiation and thus can be quantified, eg oil. For non absorbing compounds a reaction with a colour producing reagent (a chromophore) may allow its quantification.

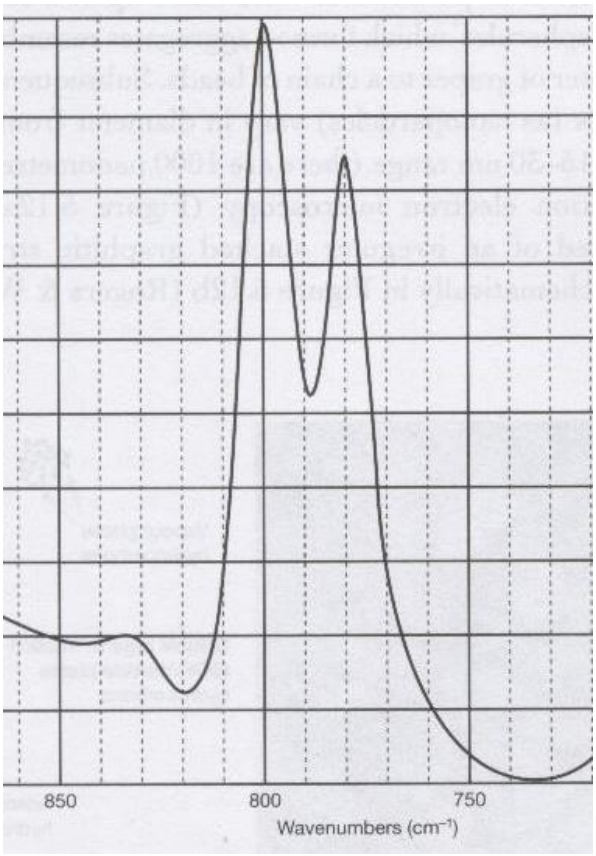
Eg the reaction of hexavalent chromium with s-diphenyl carbazide to produce a red complex with an absorption peak at 540 nm.

- *IR Spectrophotometry*

  Infra-red spectrometry provides a way of identifying pure species as each molecular species has its own unique absorption spectrum, ie fingerprint.

  Absorption or emission of infra-red radiation results in the change in vibration or rotation of a molecule. The number of ways a molecule can absorb energy is related to the number of atoms and the number of bonds it contains. IR is particularly applicable to organics and covalently bonded metal complexes.

  The IR spectrum for quartz is provided in Figure 7.5. Note the distinctive quartz "doublet" at 798 and 779 cm^{-1} wavenumbers.



(Source: University of Wollongong)

Figure 7.5 – IR Spectrum for Quartz

The main application of infra-red spectrophotometry is identification of compounds and in occupational hygiene is also used for direct gas and vapour monitoring using portable instruments and for the measurement of quartz in dust.

- *Molecular Fluorescence*

  Fluorescence is one of the ways a molecule returns to its ground state after excitation. It involves the emission of radiation at characteristic wavelengths of the molecule and different from the exciting wavelengths. Fluorescence can be used to measure compound which fluoresce such as aromatic hydrocarbons.

7.2.2 Chromatography

Chromatography is a separating method that relies on differences in partitioning behaviour between a flowing mobile phase and a stationary phase to separate the components in a mixture.

A column or other support holds the stationary phase and the mobile phase carries the sample through it. Sample components that partition strongly into the stationary phase spend a greater amount of time in the column and are separated from components that stay predominantly in the mobile phase and pass through the column faster.

There are a number of different chromatography techniques and include:

- ***Gas chromatography (GC)***

  Applied to volatile organic compounds. The mobile phase is a gas and the stationary phase is usually a liquid on a solid support or sometimes a solid adsorbent.

- ***High-performance liquid chromatography (HPLC)***

  A variation of liquid chromatography that utilizes high-pressure pumps to increase the efficiency of the separation.

As the components elute from the column they can be quantified by a detector and or collected for further analysis. An analytical instrument can be coupled with a separation method for on line analysis and includes gas and liquid chromatography with mass spectrometry.

(Source: University of Wollongong)

Figure 7.6 – Gas Chromatograph

(Source: University of Wollongong)

Figure 7.7 – Gas Chromatograph Mass Spectrometer

7.2.3 Other Analytical Techniques

- ***X-Ray Diffraction***

  X-Ray diffraction (XRD) can help identify and quantify crystalline substances. However it cannot give information on the elements present in the sample. An example where XRD is used is in the analysis of materials containing silicon and oxygen:

  - Quartz (SiO_2) has a TLV of 0.1 mg/m^3 (respirable)
  - Kaolin is a hydrated aluminium silicate $Al_2Si_2O_5(OH_4)$ has a TLV of 10 mg/m^3 (inhalable)
  - Amorphous Silica has a TLV of 10 mg/m^3

  Conventional analysis only showing the amounts of silica and oxygen is not helpful in this situation; we need to know the form that the silica and oxygen is in. XRD is able to both identify and quantify the different crystalline phases that have quite different potential health effects.

- ***X-ray Fluorescence***

  X-ray fluorescence (XRF) is widely used for the identification of elements. The absorption of x-rays produces an excited atom that returns to its ground state via a series of electronic transitions. These transitions are accompanied by an emission (fluorescence) of X radiation which is characteristic of the element.

  Multi channel instruments permit up to 24 elements to be analysed simultaneously for samples such as ashes, ores, minerals, ceramics, alloys and metals.

- ***Mass Spectroscopy***

  This technique is based on the conversion of a sample into gaseous ions and their separation on the basis of charge to mass ratios. This provides both qualitative and quantitative information.

The spectra obtained are relatively easy to interpret since they provide information based on the mass of structural components and the total molecular weight of the compound.

Its critical that BEFORE sampling is carried the occupational hygienist talks to the laboratory who will undertake the analysis.

7.2.4 Detection Limits, Sensitivity, Chemical Interferences

- ***Detection Limits***

The occupational hygienist should talk to the laboratory BEFORE undertaking sampling. One of the most important things is to know what the limit of detection (LOD) of the method is as this dictates the minimum sampling volume and therefore the length of sampling time required. It may be impossible to collect enough of the material in a 15 minute period for subsequent analysis. Ideally the limit of detection should be lower than $1/10^{th}$ of the exposure standard.

Example

Sampling rate 2 L/min
Limit of Detection 10 µg

If the TLV is 0.1 mg/m^3

$$\text{Minimum sampling time} = \frac{10 \times \text{analytical limit of detection}}{\text{Exp standard} \times \text{flow rate}}$$

$$= \frac{10 \times 10\ \mu g}{}$$

$$= 100\ \mu g/m^3 \times 2 \times 10^{-3}\ m^3/min$$

$$= 500 \text{ mins}$$

ie full shift sample required

In a similar fashion each laboratory analytical method also has its own limit of detection that must be considered before sampling.

- ***Method Sensitivity***

  Does the analytical method cover the concentration range of interest? Some analytical methods may not have sufficiently low limits of detection to measure short term exposures. Is there another method that could be used to get better sensitivity eg the use of ICP rather than AAS for the analysis of metals.

- ***Chemical Interferences***

  What other substances are likely to be present in the sample and are they likely to interfere with the proposed analytical method?

  For example if a welder is being sampled for "welding fumes" the gravimetric determination, ie the filter weighing, will be adversely affected if "grinding dusts" have also been sampled during the fume collection period. This is especially a problem if chemical speciation of individual contaminants is required.

7.2.5 Sources of Analytical Methods

There are a number of recognised sources of standard and recognised methods that are used for occupational hygiene analysis. These include:

- NIOSH Manual of Analytical Methods (NMAM) – a collection of over 1,700 methods for sampling and analysis of contaminants in workplace air, and in the blood. Available on line at: www.cdc.gov/niosh.nmam (accessed December 2006)

- UK HSE Methods for the determination of hazardous substances (MDHS Series) more than 100 methods available on line at: www.hse.gov/uk/pubns/mdhsindex.htm (accessed December 2006)

- OSHA – Standard methods for sampling www.osha.gov/dts/osta/otm/otm_toc.html (accessed December 2006)

- ISO – Standard methods for sampling and analysis www.iso.org/iso/en/ISOOnline.frontpage (accessed December 2006)

- National Standard – A number of standards including the sampling for respirable and inspirable dust, welding fumes and organic vapours are available through the National Standards organisations of a number of countries.

- SKC Inc Comprehensive Catalog and Sampling Guide – annual publication and also on their website www.skcinc.com (accessed December 2006) provides references to the method, sampling parameter, analysis and equipment for over 2,500 specific compounds.

7.3 FILTERS

Many analytical methods used in workplace monitoring require the use of some form of filtration, usually to extract the contaminant of interest from the air being sampled.

The choice of collection media will normally be dictated by the choice of sampling instrument and by analytical considerations. In general there are three types of mechanisms which capture particles during filtration. These are:

- Interception (impingement) – This occurs when the particle is smaller than the pore of the filter.
- Inertial Impaction – This occurs with a change in direction of airflow and requires high velocities and dense fibre packing of filters.
- Diffusion – This occurs with very fine particles and occurs at low flow rates and is assisted by electrostatic forces.

There are a number of properties that are desirable (but not always present) in filter media. These include:

- High collection efficiency that is known
- Manageable resistance (particularly as the load on the filter increases)
- Low moisture pick up or loss

- Low electrostatic properties
- Compatibility with the selected analytical technique
- Low cost

Not all these properties are achievable in one filter so the selection of a particular filter media for a particular measurement becomes one of compromise.

The filter selection guide below provides assistance on which filters can be used for particular contaminants but local or statutory requirements may necessitate using an alternative.

Table 7.1 – Filter Selection Guide

Material	Main Properties	Air Sampling Applications
Mixed Cellulose Ester	Hydrophilic Readily soluble for atomic absorption analysis Readily rendered transparent for transmitted light microscopy Dissolve and clear easily	Metal dust analysis Asbestos and man-made fibres
Polyvinyl Chloride (Pure Homopolymer)	Hydrophobic Non-oxidising surface Silica-free Low ash Low tare weight for gravimetric analysis	Gravimetric analysis of dusts Hexavalent chromium Quartz analysis by IR spectrophotometry
Polytetrafluoroethylene (Teflon)	Hydrophobic Inert to solvents, acids and bases Autoclavable	Alkaline dusts Polynuclear aromatics Pesticides Isocyanates

Material	Main Properties	Air Sampling Applications
Polycarbonate	Hydrophobic Microscopically smooth surface Straight-through pores Extremely thin (10 – 20 µm) and transparent Autoclavable	Scanning electron microscopy Asbestos fibres
Silver	Wide solvent compatibility Higher temperature tolerance Autoclavable Uniform porosity and thickness	Bromine Asbestos by TEM Silica by x-ray diffraction
Glass Fibre (MMMF)	Partially hydrophobic Higher temperature tolerance Autoclavable High particulate retention	Pesticides Coarse gravimetric analysis Isocyanates Ethylene glycol
Quartz	Low level metals content High temperature 300°C Autoclavable	PM10 Diesel particulates
Cellulose	Autoclavable Uniform strength Ashless (Type 40)	AA HPCL

(Source: SKC Inc – *Reproduced with permission*)

Notwithstanding the information provided above, many Occupational Hygienists choose not to use mixed cellulose ester filters for metal fume – metal dust analysis due to the poor electrostatic properties which make them difficult to weigh. Alternatives commonly used include glass fibre or polyvinyl chloride.

One aspect of filter selection that is sometimes confusing concerns pore size. When sampling for respirable dust (50% cut at 4 µm), it is not uncommon to use a filter (PVC) of nominal pore size 5 µm. This seems illogical but it is possible due to the fact that the construction of most membrane filters is such that the airways follow a torturous path and thus collection of aerosols well below 1 µm is common. The only exception to this is polycarbonate filters, which has drilled holes straight through the filter rather than a torturous pathway.

For some contaminants it may be necessary to use a filter impregnated with a stabilising agent or a backing pad treated with a collection media where the contaminant may be present in the gaseous form or in both the particulate and gaseous form.

Examples of this are:

Glutaraldehyde - Glass fibre (MMMF) filter impregnated with 2,4 – dinitrophenylhydrazine

Fluoride - PTFE (Teflon) membrane filter with sodium carbonate treated cellulose backing pad

These examples demonstrate the need for close communication with the laboratory conducting any analysis before sampling.

Two other features of filters are critical and can cause significant errors in gravimetric analysis if not considered. These are moisture and electrostatic charge. In the case of some filters (especially membrane filters), moisture pick-up or loss can be significant. This can be corrected for by the process of “equilibration”. This process requires that sample filters and a suitable number of blanks be placed in clean containers with the lids slightly ajar, in the balance room where they are to be weighed. They are then left for a suitable time to come to equilibrium with the balance room atmosphere (overnight, but this may depend on the filter type) before weighing.

At the end of the sampling exercise the process is repeated and a correction made for any gain or loss of mass in the blank filters (this should be minimal if the balance room atmosphere is well controlled).

The other critical issue is electrostatic charge. This can be overcome by the use of a static eliminator (usually an Americium 241 or Polonium 210 source). A high voltage static eliminator may be used but it should be checked to ensure that it does not punch holes through the filter.

One final aspect needs to be considered and that is the transportation of dust-laden filters after collection. Experience has shown that the layer of dust on the filter is fragile and any shocks or vibration may cause loss of material unless precautions are taken.

The best method is delivery by hand, but if this is not possible the filters should be packed in such a way that normal transportation shocks do not cause loss of material.

7.4 LABORATORY BALANCES

While weighing is often considered the simplest of the analytical tools, there are a number of sources of error that must be considered.

The analyst is often weighing sub milligram quantities of material and greater care has to be taken during both filter/sample head preparation and filter reweighing after sampling.

Insufficient sampling time may mean not enough material is collected and cannot be detected unless an appropriate laboratory balance is used.

Calibration of the microbalance is a key aspect and the following extract from AS3640 can be used as a guide to what is required.

"The accuracy of the microbalance used in the gravimetric measurements shall be checked in the following manner:

a) *Repeatability*

Every 6 monthly, an appropriate repeatability test shall be conducted on the microbalance.

b) *Before every weighing session*

Before weighing the filters –

i) check the balance with a reference weight at or near to full electrical capacity; and

ii) check the linearity of the balance inside or near to the working range.

c) *During every weighing session*

When weighing filters –

i) conduct a zero check after each sample/blank filter weight determination; and

ii) verify that electrostatic effects are insignificant by repeat sample weighing.

d) *After every weighing session*

Check the calibration of the balance with a reference weight at or near to full electrical capacity.

e) *Long weighing sessions*

If a series of filters is being weighed the microbalance accuracy shall be checked at appropriate intervals during the procedure."

7.5 MICROSCOPY

Microscopy or to be more correct polarised light microscopy together with dispersion staining is the technique is used for the identification and phase contrast microscopy for counting of fibres.

Fibres are particles that have a needle-like or thread-like appearance with a specific length to width ratio. Some examples of fibres include asbestos, fibreglass, rockwool and ceramic fibres.

Monitoring for asbestos fibres is carried out following the appropriate Standards methods such as:

- Determination of Airborne Fibre Number Concentrations: A recommended method by phase contrast optical microscopy (membrane filter method) published by the WHO (1997)
- NIOSH Method 7400 Asbestos and other fibres by PCM
- HSG 248 – Appendix 1: Fibres in air: Sampling and evaluation by Phase Contrast Microscopy (UK)
- NOHSC Code Asbestos: Code of Practice and Guidance Note or the Membrane Filter Method for Estimating Airborne Asbestos Dust (Australia)

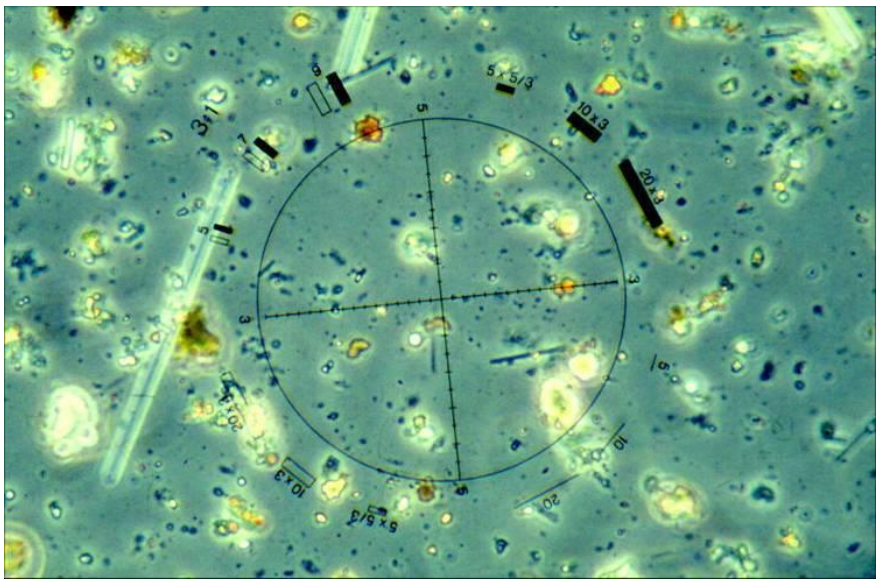
Microscopy should only be performed by a trained and certified person. Typically such persons routinely participate in an inter laboratory system to maintain their skills and validate their consistency with international standards.

The principle of the method is air samples are collected on a grided mixed cellulose ester or cellulose nitrate filter mounted in a cowled asbestos sampling head.

After sampling the filters are mounted on a microscope slide by collapsing the membrane using acetone vapour making it transparent. Glyceryl triacetate is added to the slide to provide a suitable medium for seeing the fibres.

(Source: University of Wollongong)

Figure 7.8 – Sampling Head for Asbestos Fibres

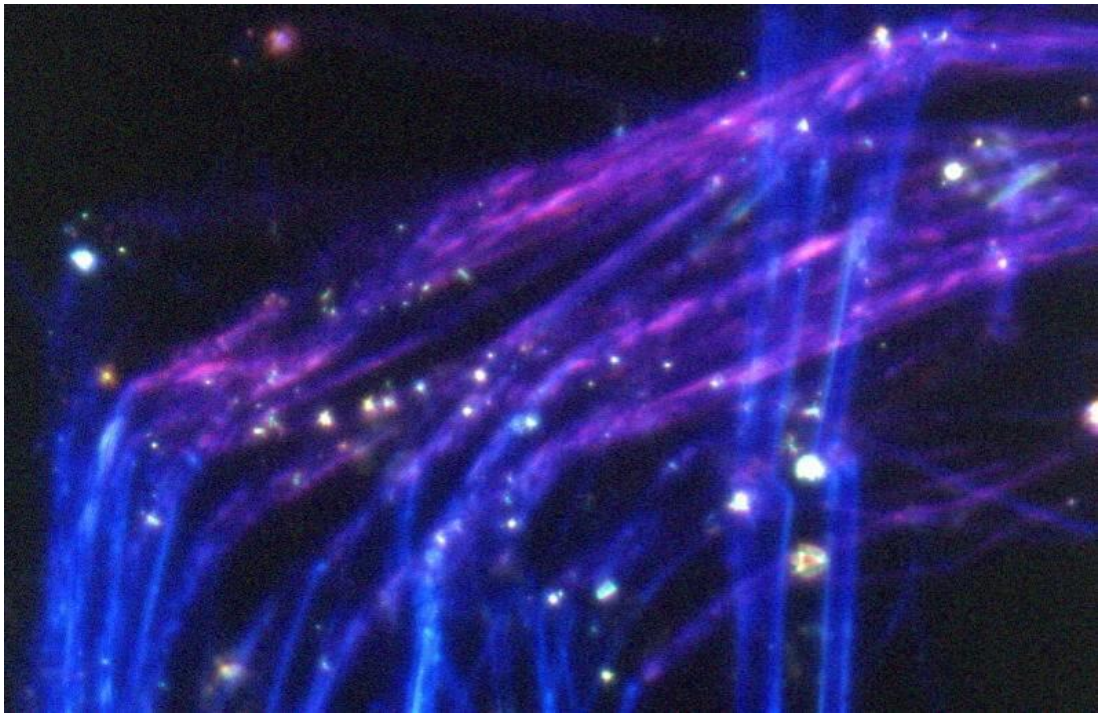


(Source: A Rogers – *Reproduced with permission*)

Figure 7.9 – Phase Contrast Microscopy – Amosite Fibres & Synthetic Mineral Fibres

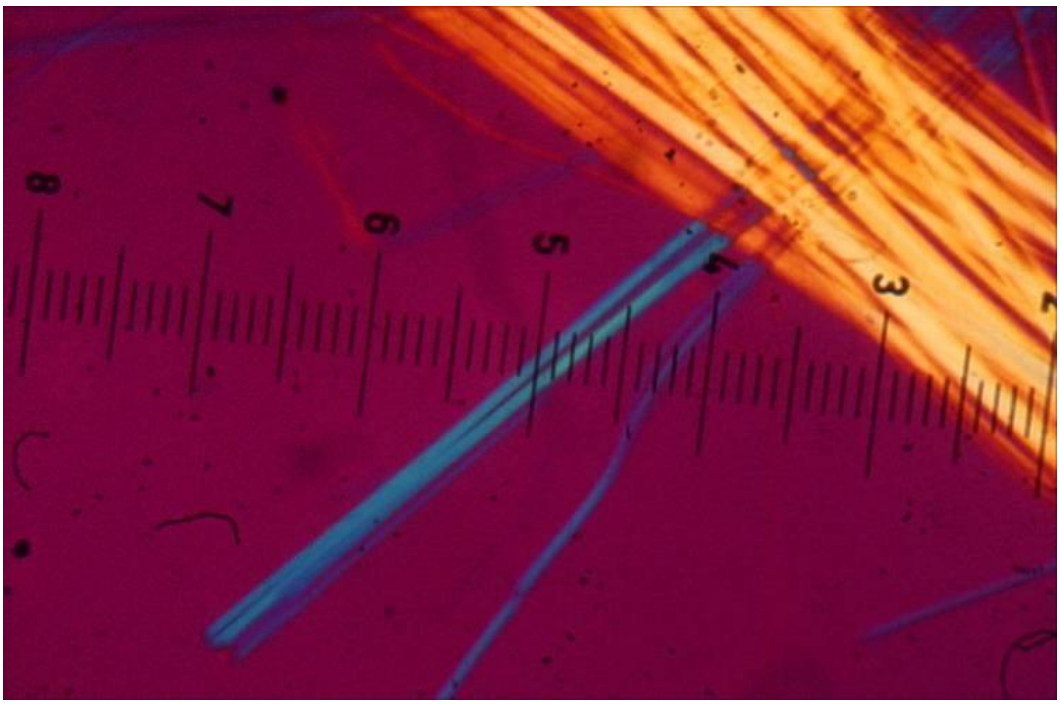
The fibres are then counted using phase contrast microscopy following standards fibre counting rules. Results are expressed as numbers of fibres/ml of air.

The other area of analysis in regard to asbestos fibres is that of identification in bulk materials. This involves the suspension of fibres in liquids of known refractive indices and observation of the colours displayed under polarised light at different orientations of the fibres. A variety of microscope configurations can be used, including dispersion staining and crossed polars with first order red compensator plate. This technique is both rapid and sensitive in the hands of a trained operator. Figure 7.10 shows chrysotile using dispersion staining, while Figure 7.11 shows amosite but with 1st order red retardation.



(Source: A Rogers – *Reproduced with permission*)

Figure 7.10 – Chrysotile



(Source: A Rogers – *Reproduced with permission*)

Figure 7.11 – Amosite (1st Order Red Retardation)

7.6 QUALITY ASSURANCE OF ANALYSIS

7.6.1 Internal Quality Control

The internal quality control process is the set of procedures adopted by a laboratory to assess whether the results from each set of tests are consistent. Occupational hygiene samples can often pose quality control concerns including the very low levels being measured, matrix effects from the sampling medium, interfering substances, incomplete recoveries, degradation in storage or transport etc. The procedures typically used include method validation, the use of standards, blanks and controls, recoveries and quality control charts.

- ***Method validation***

  Before use an analytical method must be validated to ensure it is sufficiently accurate and precise.

Its accuracy may be tested by analysing known concentrations of the analyte. For example, by adding known amounts of solvent to charcoal tubes, desorbing it and analysing it by gas chromatography; or by spiking blood or urine samples with lead for example and analysing by atomic absorption. The recovery of the analyte is the percentage of added analyte recovered, ie measured in the analysis.

Precision is determined by analysing enough replicate samples to enable the calculation of the standard deviation or coefficient of variation. Several different concentrations over the range should be selected.

The measurement range is a guide as to the usual operating range of the method. At the lower end this involves an estimate of the limit of detection (LOD) and the limit of quantitation (LOQ).

Other factors to be evaluated include:

- Interfering substances
- Capacity of the collection media (eg breakthrough volume for sorbent tubes)
- Stability of samples
- Critical steps in the analysis where special care must be taken

There are well established and validated methods for many common chemicals.

- ***Standards***

Standard reagents: are chemicals of known purity and composition. These materials are often available from external agencies eg Standard Reference Materials from the US National Bureau of Standards.

Calibration standards: these are reference standards against which all test and control samples are compared.

Where standard calibration curves are prepared at least 5 points should be used and appropriate regression analysis should be undertaken to ensure the viability of the calibration curve.

- ***Blanks***

  Field sampling blanks should be submitted with field samples to determine if there has been contamination during sample handling and storage. The blank is treated in the same manner as the field sample but with no air being drawn through it.

  Reagent blanks are used in the laboratory to correct for any contribution made by the laboratory reagents used in the analysis.

- ***Control Materials***

  These have been previously analysed and are analysed with the test samples so that a comparison between actual and expected result can be made.

- ***Recoveries***

  Recoveries should be assessed both as part of the method validation process, but also on an ongoing basis as part of the quality control process.

- ***Duplicates***

  Duplicate samples, ie from the field are more useful in assessing the reproducibility of the sampling or analysis than are duplicate analysis, ie two chromatograph injection from the one air sample.

- ***Quality Control Charts***

  These can provide a means of showing the reliability of each method and to identify trends or cyclical changes in laboratory performance.

7.6.2 External Quality Assurance

- ***Proficiency Testing Schemes***

  Many countries run inter-laboratory testing schemes and some of these are International:

  - NIOSH - Proficiency Analytical Testing (PAT) – solvents on charcoal, asbestos, silica and metals on filters
  - UK HSE – Workplace Analysis Scheme for Proficiency (WASP) – solvents on charcoal, metals on filters

  They involve the distribution of control samples to laboratories by an outside agency. The material is analysed and the results returned to the coordinating body for statistical analysis.

- ***Laboratory Accreditation***

  The purpose of accreditation is to ensure a laboratory's results are reliable. A laboratory applying for accreditation is visited by assessors, who examine all aspects of the laboratory's operations including the qualifications and experience of staff, quality, calibration and maintenance of instruments, accommodation, laboratory practice including sample handling, quality control, recording and reporting, and the test methods used. If satisfied, the appropriate approval to undertake the type of analysis being sought is granted.

  Similar schemes, eg UKAS in the UK, AIHA programme in the USA, NATA in Australia, all follow the principles outlined above.

8. AIR SAMPLING EQUIPMENT – DUSTS, FUMES & FIBRES

8.1 INTRODUCTION

Dust, including fumes and fibres, in the occupational environment can be described as airborne particles that can be hazardous to health and is one of the common issues found in workplaces. Dust usually comprises solid particles generally greater than 0.5 µm in size, formed by crushing or other forces on a parent material (which may be natural or synthetic). Fume is produced from the condensation of vapourised materials (usually metals) and consists of particles typically less than 0.05 µm in size that have a tendency to agglomerate. Fibres are either natural (eg asbestos) or synthetic materials (eg glass wool) of thread-like characteristics which is three or more times longer than its width.

Particulates is a generic term used to refer to particulate aerosols such as dust, fumes, mists and smoke.

From a health perspective the two key factors which are important when assessing exposure from dusts, fumes or fibres are the chemical composition of the material (toxic effect) and particle size (where it deposits in the body).

When assessing worker exposure to dusts, fumes or fibres two different approaches can be adopted in the majority of cases. These are filtration samplers and direct reading instruments; both of which have advantages and disadvantages. However the most common approach in workplace exposure assessment is the use of filtration samplers.

8.2 SAMPLING PUMPS

There are many sampling pumps commercially available that are designed for use with appropriate capture devices to collect dust, fumes and fibres in the workplace environment. Some operate from mains power but most are small battery-powered pumps which can be worn by the person being sampled.

These pumps can operate at flowrates between 0.5 to 5 litres/minute (L/min), however most particulate sampling is carried out at flowrates between 1.0 to 2.5 L/min.

While there is no defined list of requirements for a sampling pump, the following list gives a number of features which have been found to be very useful when sampling particulates.

- *Automatic flow control:* A stable airflow is important as this value in the calculation of exposure. Automatic flow control ensures that the flow rate remains constant as the sample builds up on the filter thus creating backpressure on the pump.

- *Pulsation dampening:* This is critical when sampling using a size selection device (eg miniature cyclone) as variations in the flow alter the cut off point of the sampling device. Pulsation dampening is needed on reciprocating pumps but is not necessary on rotary vane pumps (Table 8.1).

- *Capacity to operate at a reasonable backpressure:* As material builds up on the capture filter the backpressure on the sampling pump will also increase.

- *Ability to set flowrates over a reasonable flow range:* Necessary as not all capture devices operate at the same flowrate.

- *Good battery capacity:* This allows continuous operation for the full duration of a work shift.

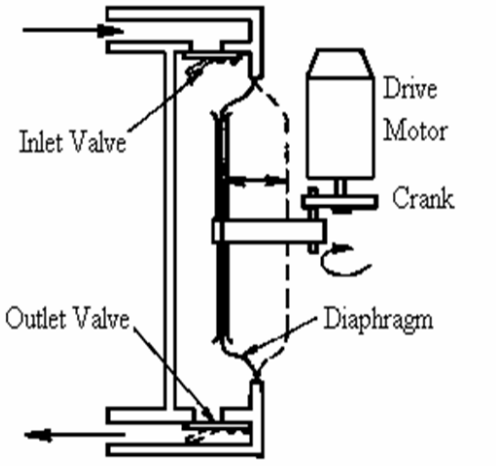
- *Intrinsically safe:* This is a mandatory requirement for those pumps that are used in workplaces where the risk of an explosion may be high (eg coal mines, oil refineries).

Historically three different types of operating systems have been used in sampling pumps (diaphragm, piston and rotary vane), all of which have advantages and disadvantages (Table 8.1).

Table 8.1 – Advantages & Disadvantages of Various Pump Operating Systems

	Diaphragm	Piston	Rotary Vane
Power Consumption	Low	Medium	High
Battery Size	Small	Medium	Large
Weight	Low	Medium	High
Repair	Simple	Difficult	Moderate
Cost	Cheap	High	Medium
Flow Smoothness	Strongly pulsating	Mildly pulsating	Smooth
Pressure Drop Limits	About 5 kPa	None	None
Valve Problems	Can leak	Can leak	None (no valves)

Over the past 10 years, diaphragm operated sampling pumps have become the most common and they operate as indicated in Figure 8.1.



(Source: BOHS – *Reproduced with permission*)

Figure 8.1 – Schematic of a Diaphragm Sampling Pump

No matter which sampling pump is used, there are several factors that need to be considered and appropriately managed if accurate results are to be obtained. These are:

- *Maintenance:* All sampling pumps need to be kept in good operating order. This includes ensuring that the automatic flow compensation system is operating correctly and that the internal inline filters (to protect the diaphragm) are not placing an excessive backpressure on the system. The manufacturer's instructions should have guidance on the appropriate maintenance to be carried out and at what frequency.

- *Battery charge:* Some battery types (eg Nickel-Cadmium) have an unusual characteristic in that if they are operated for short periods and recharged, they will develop a "memory effect" and thus only operate for a short period. This can be overcome by "cycling" the battery by operating it until it is nearly exhausted and then recharging. This should be repeated several times. If after this process the battery still has a "memory effect" a new battery should be installed. This effect is less common with Nickel Metal Hydride batteries.

  Modern chargers are designed to adjust the flow of current to the battery so that they are not overcharged but maintained on "trickle" charge so that they are ready for instant use. Some also have a discharge/recharge facility which makes cycling of batteries very simple.

- *Internal flowmeters:* Most sampling pumps which have built-in flowmeters suffer a serious design flaw and should not be considered as an accurate measure of flow. Calibration with an appropriate flowmeter is necessary at all times.

8.3 CAPTURE DEVICES

8.3.1 Deposition Curves

The fraction of airborne particles which can be inhaled by the human body is dependent upon the properties of the particles, the speed and direction of air movement near the body, the rate of breathing and whether breathing is through the nose or mouth. Inhaled particles can subsequently then deposit somewhere in the respiratory tract (depending on size) or can be exhaled.

The International Standards Organisation (ISO 1995) has defined sampling conventions for use in assessing the possible health effects of airborne particles in the workplace. Conventions are defined for the inhalable, thoracic and respirable fractions. These are:

- *Inhalable fraction:* The mass fraction of total airborne particles which is inhaled through the nose and mouth.

  In general terms the inhalable fraction includes all particles <100 µm, however it may include some larger particles but experimental data does not exist to confirm this statement.

- *Thoracic fraction:* The mass fraction of inhaled particles which penetrate beyond the larynx.

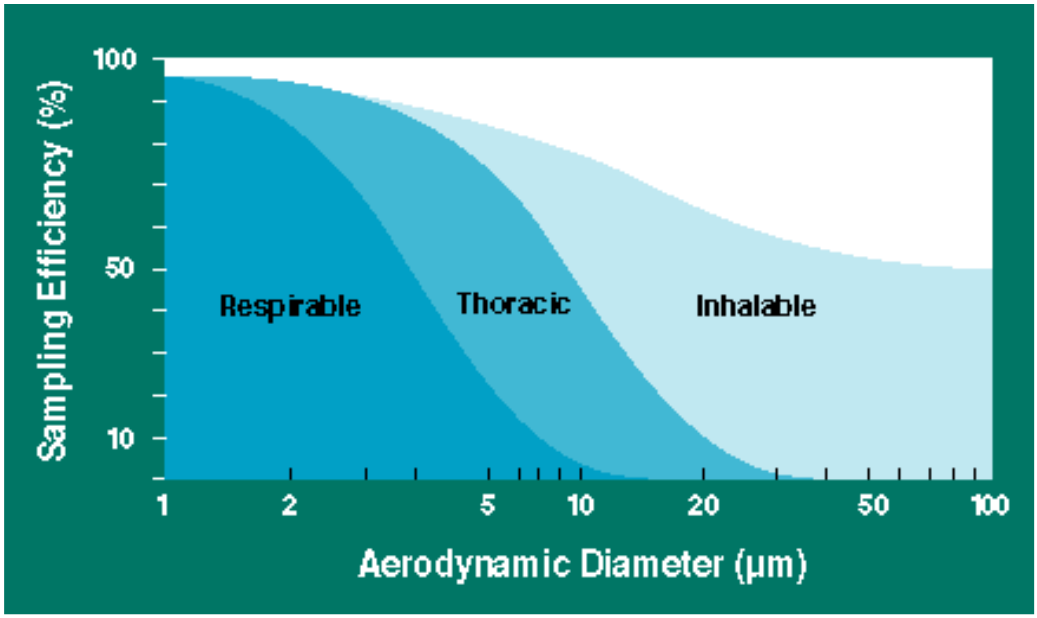
  In general terms the thoracic fraction includes all particles <50 µm and having a 50% cut (of total airborne particles) of about 10 µm.

- *Respirable fraction:* The mass fraction of inhaled particles which penetrate to the unciliated airways (alveoli).

  In general terms the respirable fraction includes all particles <16 µm (majority <10 µm) and having a 50% cut at about 4 µm.

Over the years, various terminology has crept into the literature (eg inspirable, total inhalable, total) and while this may still persist in some countries, there is general consensus that the ISO nomenclature (ISO 1995) is the most appropriate.

The interactions of the various size fractions are best described graphically, as can be observed in Figure 8.2.



(Source: TSI Inc – *Reproduced with permission*)

Figure 8.2 – ISO Size Fractions for Particles

The importance of the above definitions of the deposition curves cannot be overstated as this links the potential health effect with the sampling device necessary to assess the potential health risk.

For example, let's consider two dusts common in the international mining environment, coal and lead dust. If we first consider the health effect of each:

- *Coal dust:* Gives rise to the respiratory disease "pneumoconiosis" whereby normal lung tissue is replaced by fibrous scar issue due to the long term inhalation of coal dust.

- *Lead dust:* Lead is a systemic poison which has been associated with kidney dysfunction, increased blood pressure and sperm abnormalities. Historically the major toxic effect of lead has been on the blood system, resulting in anaemia.

Clearly these two dusts are operating on two separate target organs (lungs and blood), hence it is appropriate to sample each accordingly.

For coal dust, collection of the respirable fraction is important and for lead dust collection of the inhalable fraction is important.

8.3.2 Sampling Heads

As a result of the various size fractions definitions, a number of sampling devices (heads) have been developed and are commercially available. These, when operated at a particular flowrate, collect one or more of the size fractions indicated in section 8.3.1.

Typical sampling heads are:

- ***Inhalable Dust***

  - *IOM Sampling Head:* This device (Figure 8.3) was developed by the UK Institute of Occupational Medicine (IOM) and consists of a single orifice entry and a filter contained within a cassette. The sampler requires a sampling pump operating at 2 L/min and an appropriate filter.

  - *United Kingdom Atomic Energy Authority* (*UKAEA) 7 hole Sampling Head:* This device (Figure 8.4) comprises a filter holder with a multi-orifice entry (7 holes) and requires a sampling pump operating at 2 L/min.

  - *Conical Inhalable Sampler (CIS):* This device (Figure 8.5) was developed in Germany and is known as either the CIS or GSP sampler. It requires a sampling pump operating at 3.5 L/min. This device can also be used with porous foam plugs and specific cassettes so as to sample the respirable or thoracic fractions.

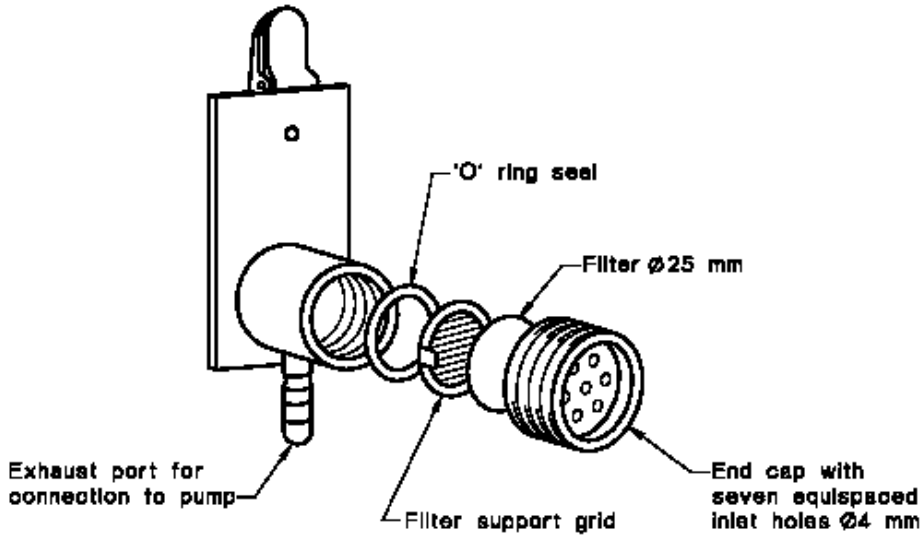
  - *SKC Button Aerosol Sampler:* This device (Figure 8.6) was originally developed for the collection of inhalable bioaerosols but has been found to closely follow the ISO sampling criteria for inhalable dust when operated at a flowrate of 4 L/min.

- *Pre-Loaded Cassettes:* The approach common in the USA is to use 37 mm membrane filter loaded into a plastic cassette (Figure 8.7) to measure “total inhalable dust”. It should be understood that this does not equate to the ISO definition and thus this device should not be used to sample in accordance with the ISO criteria.

Over the years a number of comparative studies have been undertaken involving all or some of the instruments listed above. In general, the IOM sampler has been shown to give the best agreement to the ISO criteria for inhalable dust under the widest range of workplace conditions and is therefore the preferred method of sampling inhalable dust in many (but not all) countries.

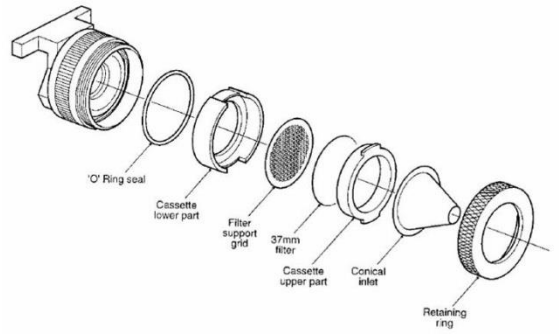
(Source: University of Wollongong)

Figure 8.3 – IOM Sampler



(Source: HSE – *Reproduced with permission*)

Figure 8.4 – UKAEA 7-Hole Sampler



(Source: HSE – *Reproduced with permission*)

Figure 8.5 – CIS Sampler

(Source: SKC – *Reproduced with permission*)

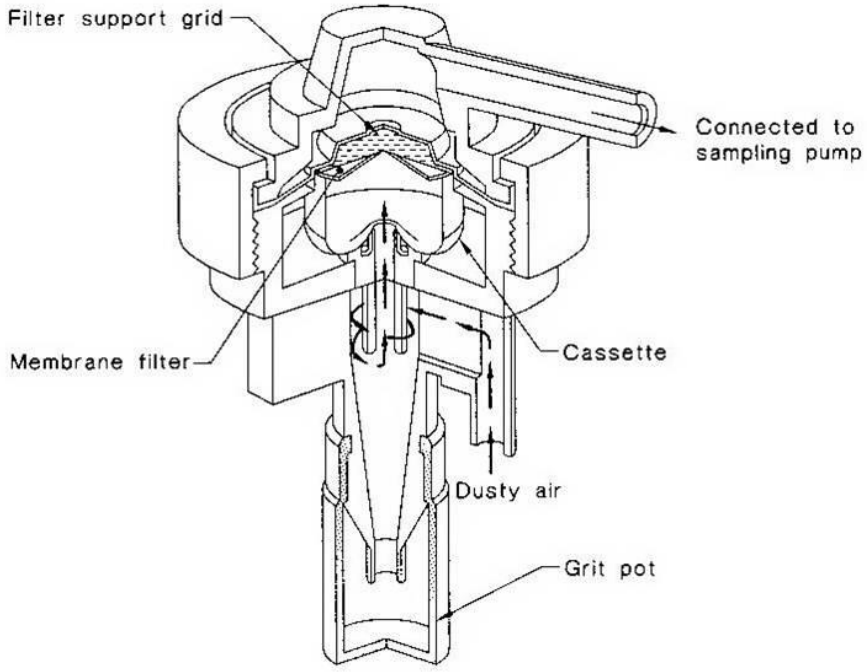
Figure 8.6 – SKC Button Sampler

(Source: University of Wollongong)

Figure 8.7 – Pre-Loaded Plastic Cassettes

- ***Respirable Dust***

  - *Miniature Cyclone:* A number of miniature cyclones have been developed over the past 30+ years (BCIRA, SIMPEDS, Dorr-Oliver, Aluminium), all of which operate under the same principle (Figure 8.8), albeit at different flowrates. In all cases (no matter what the flowrate) a steady flowrate is required if the cyclone is to selectively size the sampled aerosol into the correct fraction (ie 50% cut at 4 µm). The flowrates of the commonly used cyclones are listed in Table 8.2.



(Source: HSE – *Reproduced with permission*)

Figure 8.8 – Operation of a Miniature Cyclone

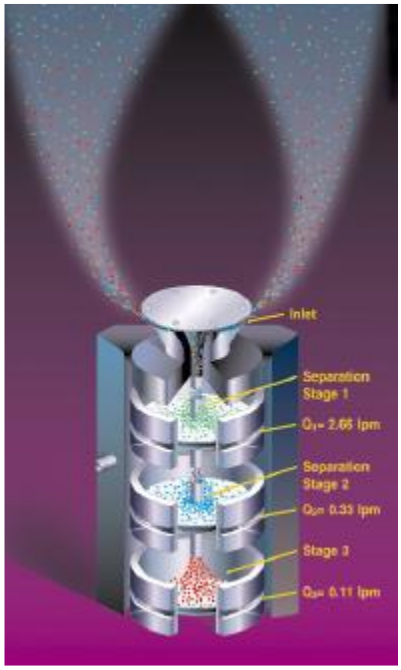
Table 8.2 – Designated Flowrates for Size Selective Samplers

Size-Selective Sampler	Designated Flowrate (L/min)
BCIRA Cyclone	2.2
SIMPEDS Cyclone	2.2
Aluminium Cyclone	2.5
10 mm Nylon Cyclone (Dorr-Oliver)	1.7

- ***Thoracic Dust:*** Several different approaches have been taken in an attempt to measure the thoracic fraction of a dust cloud. One device, the “Respicon” (Figure 8.9) is a multistage virtual impactor that traps the various size fractions onto individual collection filters of 37 mm diameter (Figure 8.10). A sampling pump operating at 3.1 L/min is required as is a 4 µm stage 1 cut module.

(Source: TSI Inc – *Reproduced with permission*)

Figure 8.9 – Respicon Sampler



(Source: TSI Inc – *Reproduced with permission*)

Figure 8.10 – Schematic of Respicon Stage Impaction

The other approach to measuring the thoracic fraction is the use of polyurethane foam filters which are specifically designed to separate the individual fractions. These foam filters can be inserted into either the CIS or IOM sampling head to act as size selection devices, with the individual dust fractions being collected on membrane filters.

A third device called the CIP 10 has been developed in France by the French National Institute for Research and Safety. The apparatus is based on the novel method of separation using annular impaction within a rotating housing containing a miniature filter made of polyurethane foam. The device comes in three versions depending on the inter-connectable selector that is installed. Both the respirable and inhalable versions operate at a flowrate of 10 L/min but the thoracic version operates at 7 L/min.

8.3.3 Special Sampling Heads

For some particular aerosols, specific sampling heads have either evolved or have been specially developed. These include:

- ***Asbestos and Synthetic Fibres***

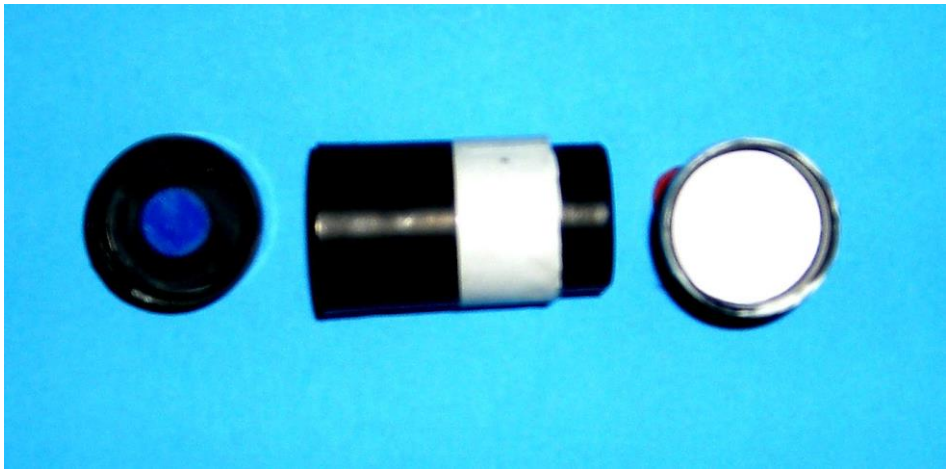
  Sampling for asbestos or synthetic mineral fibres is usually performed using an open faced cassette with an electrically conductive cowl.

  The original design was made of metal (Figure 8.11) but in recent years the three-piece graphite impregnated plastic cassette (Figure 8.12) has become common. A 0.8 µm (1.2 µm used in some countries) mixed cellulose ester membrane filter is used to collect the fibres as this has the advantage of being able to be destroyed with acetone vapour at a later stage during the analysis process.

Sampling rates of between 1 to 4 L/min are commonly used (in some countries rates of 8 or 15 L/min are used), depending on the type of sampling being undertaken (workplace exposure assessment or control monitoring after removal).

(Source: Gully Howard Technical – *Reproduced with permission*)

Figure 8.11 – Metal Cowl and Sampling Head for Fibre Sampling



(Source: University of Wollongong)

Figure 8.12 – Three-Piece Conductive Plastic Cassette for Fibre Sampling

- ***Diesel Particulate***

  The development of a commercial specialised sampling head for diesel particulate has only occurred within the past 10 years. Prior to this, all sampling for this contaminant was via the use of research samplers which were expensive and complex.

  The current commercial device (Figure 8.13) uses a cassette containing an integral precision-jewelled impactor which screens out particles >1 µm. In situations where diesel particulate is the only contaminant present such separation is not important, however in many workplaces other contaminant dusts may be present. This is especially the case in coal mines where the coal dust in the sample needs to be separated from the diesel particulate before analysis. The cassettes also contain a heat treated quartz filter which assists in the analysis process. The cassette can either be used with or without a cyclone, the cyclone being necessary when high dust loads are present which could overload the impactor.

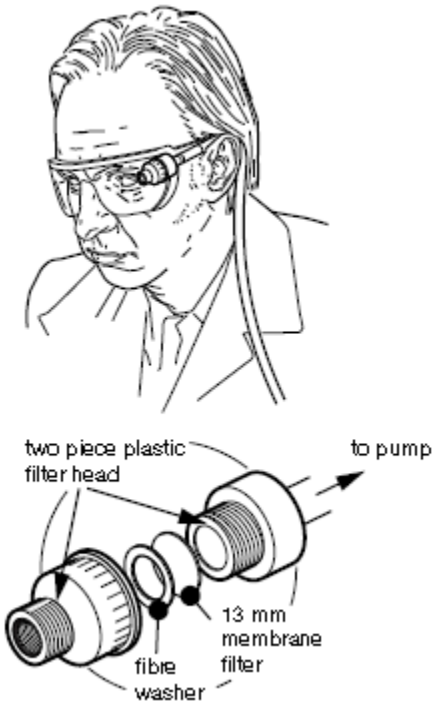
(Source: SKC Inc – *Reproduced with permission*)

Figure 8.13– Diesel Particulate Cassette

- ***Rosin-based Solder Flux Fume***

  One unique approach is prescribed by the UK Health & Safety Executive for the sampling of rosin acids in rosin (colophony) solder flux fume (MDHS 83/2).

Sampling in this case is performed by using a 13 mm Millipore Swinnex type sampling head containing a 5 µm pore size mixed cellulose ester filter. Sample rates of between 1 and 2 L/min are recommended, depending on the fume load in the atmosphere. The sampling head is attached to the worker's safety glasses as indicated in Figure 8.14.



(Source: HSE – *Reproduced with permission)*

Figure 8.14 – Sampling for Rosin-based Solder Flux Fume

There are no doubt many more specific sampling heads in use throughout the world, however their use is likely to be localised due to historic or statutory requirements. Consequently, there is a need for practising occupational hygienists to familiarise themselves with any such local requirements.

8.4 SAMPLING TRAINS

After the selection of the most appropriate sampling head, sample pump and filter (section 7.3.1), the time has come to link all these components together into what has become known as a "sampling train".

The individual components of a sampling train for respirable dust using a miniature cyclone are shown in Figure 8.15.

(Source: University of Wollongong)

Figure 8.15 – Respirable Dust Sampling Train

Similar sampling trains can be constructed for inhalable dust, diesel particulate and organic vapours using the appropriate components for each. Connection of the sampling train to a worker usually involves placing the pump on the worker's belt (or in a pocket if it is a miniature pump) and then connecting the sampling head in the breathing zone of the worker (Figure 8.16). If a belt is not available, a suitable harness can be worn by the worker to support the equipment.

(Source: University of Wollongong)

Figure 8.16 – Sampling Train Connected to a Worker

In some cases special care needs to be exercised when attaching the sampling head. One such case is when sampling for welding fume where the sampling head must be placed under the welder's protective face shield. This is because the level of contaminant exposure outside the shield is significantly higher than inside.

Once the sample train is attached to the worker, note the time and any other relevant data (see section 8.5 with regard to calibrating pumps before use). Check the sampling head and pump periodically during sampling to ensure that the equipment is still operating, and if necessary re-measure and adjust the flowrate (this should not be necessary with good quality well-maintained sampling pumps). At the end of the sampling period, carefully remove the sampling equipment (recording the time) and in a dust-free area re-calibrate the sampling pump. The sample should be considered invalid if the pre and post sampling rates vary by more than ±5%. Some international standards suggest pre and post sampling rates may vary by ±10%, however this is considered too high by most hygienists. The collection filter (or filter cassette) should then be removed from the sampling head and either re-weighed on site or transported to a laboratory for re-weighing (see Sections 7.3 and 7.4).

Once all the information is available (eg mass of dust on filter, flowrate of pump and sample duration) the actual concentration in the workplace can be calculated (section 8.6).

8.5 CALIBRATION OF SAMPLING EQUIPMENT FOR DUSTS, FUMES & FIBRES

The accurate analysis of atmospheric dust concentrations is dependent on the determination of the mass of dust, fume or fibre on the collection media (either gravimetrically, chemical analysis or microscopy) and the total volume of air sampled (ie total number of m^3 of air sampled).

When calibrating sampling pumps (and other sampling equipment), it is important that a path of traceability is established and maintained.

This is usually performed via the use of a primary and secondary standard. A primary standard is one which is directly traceable to a national standard and a secondary standard is one which has to be calibrated at regular intervals against a primary standard. Examples of such standards commonly used in occupational hygiene monitoring are:

- ***Primary Standards***

  Soap film meters

  Wet-test gas meter

  Bell spirometer

- ***Secondary Standard***

  Electronic meters*

  Rotameters

  Magnehelic gauges

  * In some countries some particular types of electronic meters are considered primary standards (eg BIOS frictionless piston), however third party accreditation bodies in other countries do not agree.

Primary standards are usually not suitable for field measurements and thus it is common practice to use a calibrated secondary standard.

Examples of primary and secondary standards for airflow measurement are shown in Figures 8.17 – 8.19.

(Source: SKC – *Reproduced with permission*)

Figure 8.17 – Soap Film Meter

(Source: University of Wollongong)

Figure 8.18 – Electronic Meter

(Source: SKC – *Reproduced with permission*)

Figure 8.19 – Rotameter

When measuring airflow, the following points should be considered.

1. Always calibrate a sampling pump using a sample head identical to that used in the field.

2. Allow the sample pump to stabilise for at least 5 minutes after it has been switched on and adjust the flow to the required flowrate.

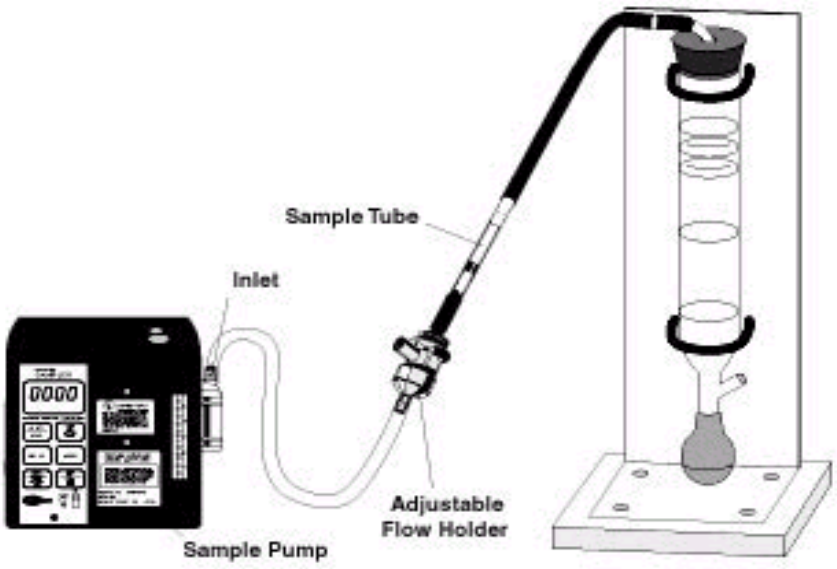
3. Measure the flowrate of the pump until three consecutive results are within ±1% of the mean (this may not be possible if using rotameters but easily achievable with electronic or soap film meters). Calculate the mean value of the three consecutive results and use this in the total airflow calculation (section 8.6).

4. It is also important to appreciate changes in environmental conditions which can adversely affect the accuracy of a calibration device. Such factors can be:

    - Flowrate determinations are made at altitudes differing by more than 500 m from the previous calibration.

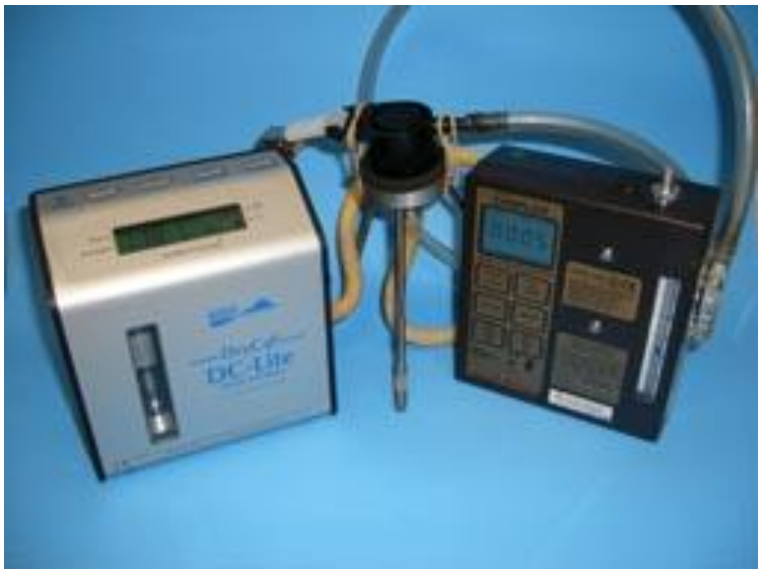
    - Temperature differing by more than 15°C from that at the previous calibration.

Examples of a sampling train being calibrated with a soap film meter and an electronic meter are provided in Figures 8.20 and 8.21.



(Source: SKC – *Reproduced with permission*)

Figure 8.20 – Calibration Using a Soap Film Meter



(Source: University of Wollongong)

Figure 8.21 – Calibration Using an Electronic Meter

The following suggested calibration schedule for sampling equipment is provided as guidance only and reference should be made to national standards or local statutory authorities.

Item	Maximum Period Between Successive Calibrations	Comments
Pumps	On use	Before and after measurement
Pumps - Direct Automatic Flow Control	Initially 12 months but after three consecutive tests (ie two years) showing results within ±5% of the expected result, the interval can be lengthened to three years	Constant flow compensation
- Indirect Automatic Flow Control	Initially six months, but after three consecutive tests (ie 12 months) showing results within ±5% of the expected result, the interval can be extended to 12 months	Constant flow compensation
Rotameters	Monthly for three months then if measurements are within ±3% of expected result, the interval can be extended (one year small bore and two years large bore)	Calibrated against a primary flowmeter over range of use
Soap Film Meter	On commissioning	Check volume marks
Electronic Meters	Monthly for three months then if measurements are within ±3% of expected results, the interval can be extended to six months	Calibrated against a primary flowmeter over range of use
Stop Watch	Six monthly	Against a national time system (speaking clock) over at least one hour
Balances (Electronic)	One month Six months 12 months 36 months	One point check Repeatability check Service Full range calibration by external accredited calibration authority

While the above recommendations may appear overly conservative they represent best practice as detailed by a group of experienced occupational hygienists. Observance of the indicated calibration schedule should meet the majority of statutory requirements.

8.6 CALCULATION OF RESULTS

As indicated in section 8.5, two components are necessary to establish the atmospheric concentration of dust, fume or fibre in the atmosphere of a workplace. These are the quantity of contaminant on the collection media (filter) and the total volume of air sampled.

The calculation of fibre results is complex and beyond the scope of this course, but the calculation of dust and fume concentrations are provided below.

- ***Calculation of Total Volume of Air Sampled***

  If we know the flowrate of a sampling pump (as detailed in section 8.5) and the time that sampling was undertaken, we can calculate the total volume of air sampled. For example, if the flowrate was 2.2 L/min and sampling was performed for 7 hours 42 minutes, we can make the following calculation.

  Volume (Litres) = 2.2 x 462
  = 1,016.4

  $$\text{Volume } (m^3) = \frac{1{,}016.4}{1{,}000}$$

  = 1.0164 (Note: 1 m^3 = 1000 L)

- ***Calculation of Mass on Filter***

If, for example, we are sampling for respirable or inhalable dust and analysing by gravimetric means, we need to establish the total amount of dust on the filter (usually in mg). This is done by subtracting the pre weight of the filter from the post weight of the filter and correcting for moisture pick-up or loss via a blank correction. Thus the weight of the dust on the filter is:

Mass (mg) = post – pre weight of filter (mg) – blank correction (mg)

Thus, if the pre weight of the filter was 5.76 mg and the post weight of the filter was 7.84 mg and the blank was -0.01 mg, then:

Corrected Mass on Filter (mg) = 7.84 – 5.76 – (-0.01)
= 2.08 – (-0.01)
= 2.08 + 0.01
= 2.09

and the concentration of dust in the atmosphere would therefore be:

$$\text{Concentration (mg/m}^3\text{)} = \frac{2.09}{1.0164}$$

$$= 2.056$$

$$= 2.1^*$$

* (Rounded depending on the uncertainty of the balance used as per AS 3640 - which was a 5 place microbalance in this case)

If subsequent analysis for some specific contaminant was undertaken, then the calculation is dependent on the concentration of that contaminant on the filter.

For example if an inhalable dust sample was analysed for zinc (Zn) and the amount on the filter was found to be 256 µg (ie 0.256 mg), then the concentration of Zn in the sample would be:

$$\text{Zn (mg/m}^3\text{)} = \frac{0.256}{1.0164}$$

$$= 0.252$$

$$= 0.25^*$$

* (Rounded based on the accuracy of the analytical method)

8.7 DIRECT READING INSTRUMENTS

While the use of direct reading instrumentation for measuring gases and vapours is common, the case is not the same in respect to dust monitoring. Over the past 40 years numerous devices have been released onto the market, however they have only attracted limited use, usually in very specific situations.

One type of direct reading device which has some success is based on the principle of a laser photometer which detects light scattered by the presence of dust particles. One such device is shown in Figure 8.22 and this particular instrument can be very useful in evaluating control procedures within a workplace and for pinpointing sources of emissions. Unfortunately, most optical-based instruments over-respond in locations where high moisture is present (eg sprays, water mist), making their application very limited in many situations.

(Source: TSI Inc – *Reproduced with permission*)

Figure 8.22 – Dust Trak

The response of a laser scattering instrument depends on the size, shape and reflectivity of the airborne particles rather than on their mass. Some instruments can give a mass readout, but this is only accurate if calibrated for the specific dust in question.

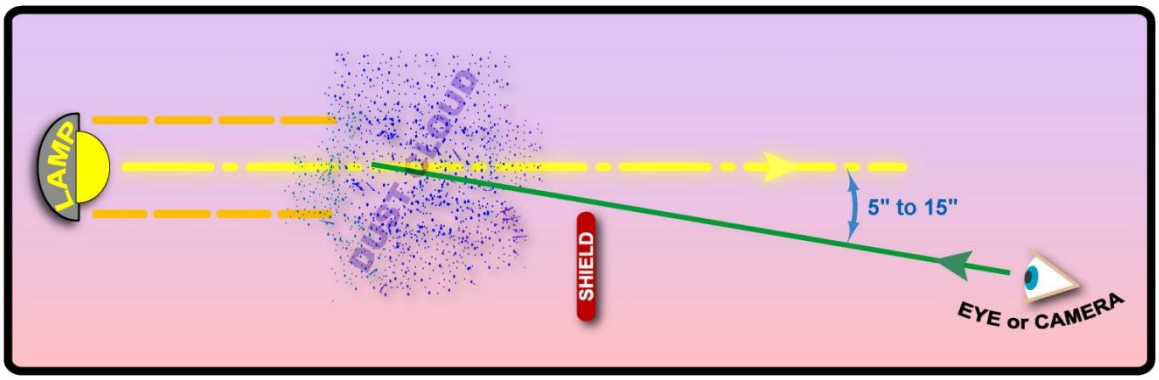
In recent years one development has the potential to alter this situation. This is the Personal Dust Monitor (PDM) currently being developed for the US coal mining industry. This device (Figure 8.23) is based on the principle of the tapered element oscillating microbalance (TEOM) and has an internal heater to overcome moisture issues. Testing to date has demonstrated comparable results to current sampling practices and appears to be a significant breakthrough.

(Source: Thermo Fisher Scientific – *Reproduced with permission*)

Figure 8.23 – Personal Dust Monitor

One device that is not a direct reading instrument but has value in highlighting the presence of dust particles is the "Dust Lamp". The application of this device is adequately explained in MDHS 82 and is based on the "Tyndall effect" discovered by John Tyndall in the mid 1800's.

Essentially, a bright beam of light is shone through the area where it is thought a particle cloud may be present. The particles present diffract the incident light and an observer looking up the beam to the source of the illumination (at an angle of about 5 – 15°) can see the dust particles. The process is described schematically in Figure 8.24 and can be a powerful tool if linked to photography or digital video equipment.



(Source: HSE – *Reproduced with permission*)

Figure 8.24 – Principle of the Dust Lamp

This device has been included to demonstrate how a simple beam of light can be used to investigate possible sources of dust exposure but as with most things some level of knowledge and skill is required to achieve good results (see MDHS 82).

8.8 SELECTION GUIDE

The following information has been included to provide basic guidance on the selection of the appropriate sampling head, capture mechanism and flowrate for a range of contaminants. It is based on the experience of the authors and may not reflect local statutory requirements.

Contaminant	Sampling Head	Collection Medium	Typical Flowrate (L/min)
Asbestos and synthetic mineral fibres	Open faced filter with conductive cowl (3-piece cassette)	Mixed cellulose ester membrane filter (0.8 µm pore size)	1 – 4 (8 – 16 used in UK)
Respirable dust (including respirable silica)	Miniature cyclone	PVC (5.0 µm pore size)	1.7 – 2.5 depending on type of cyclone
Inhalable dust	IOM (or equivalent)	PVC (5.0 µm pore size) or glass fibre	2 (can be subsequently analysed for metals, etc)
Welding and other metal fumes	IOM (or equivalent)	PVC (0.8 µm pore size)	2
Rosin solder flux fume	Millipore, Swinnex	Mixed cellulose ester membrane filter (5.0 µm pore size)	1 - 2 depending on fume load in atmosphere

9. AIR SAMPLING EQUIPMENT – VAPOURS & GASES

9.1 INTRODUCTION

A simple definition of gases and vapours is:

Gas – a substance which is airlike. It is neither solid nor liquid at room temperature.

Vapour – the gaseous form of a substance which is a solid or liquid at room temperature.

Gases are formless fluids that expand to occupy the space or enclosure in which they are confined. Examples are nitrogen, oxygen, chlorine and ammonia. Vapours are the gaseous form of a substance that is normally a solid or liquid at room temperature and pressure. Example: organic solvents give rise to vapours in the air by their evaporation, heating or spraying.

Sampling or monitoring can be undertaken by two main approaches:

- sample collection with subsequent laboratory analysis
- direct reading instruments for use in the workplace

9.2 WHOLE OF AIR SAMPLING OR "GRAB SAMPLING"

The air can be collected in a container passively (ie by evacuating the container prior to sampling) or actively (ie by using a pump). The container is subsequently sealed and transported to the laboratory for analysis. The sample is referred to as a "whole air sample" or "grab sampling" and the compounds remain in the ambient air inside the container. The method is often used when the concentration of the contaminant is constant or where peak concentrations need to be measured. The method can also be used for the identification of unknowns and to evaluate contaminant sources. The samples are typically collected over a short period of time from a few seconds to several minutes.

As a general rule whole air sampling is best done when the target compounds are chemically stable and have vapour pressures greater than 0.1 torr at 25 degrees C and 760 mmHg. Recoveries are very much dependent on the humidity of the sample, the chemical activity of the sample matrix and the inertness of the container.

The common types of containers used for whole air sampling are stainless steel canisters, air sample bags, gas bottles or even gas syringes.

- **Canisters**

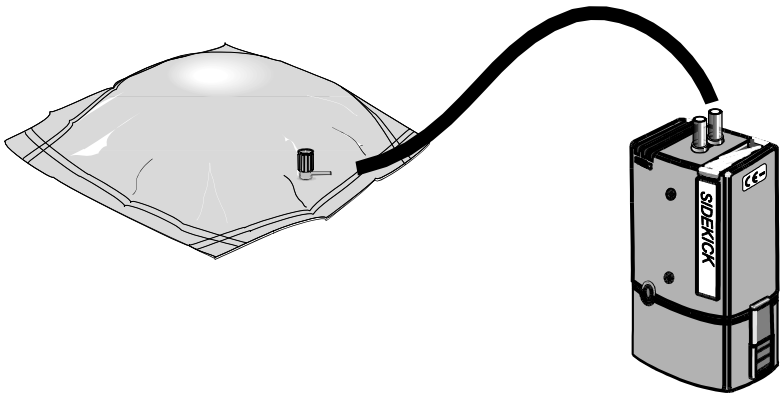
  Canisters can be spherical or cylindrical and are typically made from stainless steel, have superior inertness, hold time to analysis and ruggedness for field use and do not require the use of a sampling pump. A Summa canister is a stainless steel container that has the internal surfaces specially treated using a “summa” process. This process combines an electro polishing step with a chemical deactivation step to produce a surface that is nearly chemically inert. The degree of chemical inertness of a whole of air container is critical to minimising reactions with the sample and maximizing recoveries of the collected material.

  The canister is evacuated by vacuum prior to use. Opening of the valve allows the air to enter and fill the container, the valve is then closed and canister returned to the laboratory for analysis. Canisters range in volume from less than 1 litre to about 10 litres. Canisters need to be cleaned prior to use and the degree of cleaning (10% or 100%) required is dependent on the analytical requirements for the sampling and as a rule of thumb can be used down to the ppb range.

- **Gas Sampling Bags**

  Gas bags are relatively inexpensive, can be carried to site in a brief case, filled in seconds and shipped easily to the laboratory for analysis.

Gas bags come in different sizes up to 250 litres but typically for occupational hygiene sampling purposes bags are typically between 5-15 litres. The bags are constructed from a number of materials including polyester, polyvinylene chloride, Teflon (polytetrafluoroethylene), and tedlar (polyvinyl fluoride). They often comprise of two films or are laminated with aluminium to reduce permeation through the walls. Sample loss and adsorption on to the bag material are concerns and samples should be analysed as soon as possible after collection. Levels down to the ppm range can be measured using gas sampling bags.



(Source: SKC Inc – *Reproduced with permission*)

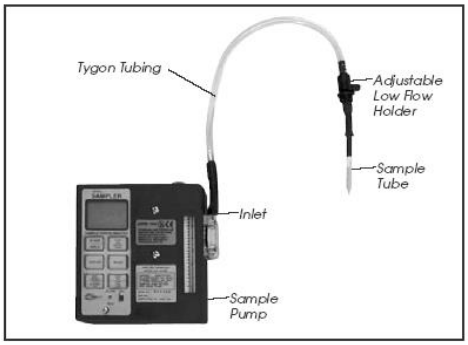
Figure 9.1 – Air Sampling Bag Being Filled by Pump

Gas bottles or gas syringes have also been used in the past, but their use has generally been replaced by other sampling methods.

9.3 ACTIVE SAMPLING

Active sampling occurs when air is drawn through an absorbing medium and the contaminants are collected / “scrubbed out”. Active sampling usually employs a calibrated, battery powered sampling pump that is connected by flexible tubing to a solid sorbent tube or to a reagent-solution in an impinger or other similar collection device. A known volume of air is then drawn through the tube or collection device and contaminants collected or removed by the sampling medium.

If the final flowrate differs from the initial flowrate by greater than ±10% (Australia), ±5% (UK) the sample should be discarded and sampling repeated. The flowrate variation used in Australian Standards (10%) is considered too high by many occupational hygienists and a value of 5% would represent best practice.



(Source: SKC Inc – *Reproduced with permission)*

Figure 9.2 – Sampling Train Using Adjustable Low Flow Holder

(Source: 3M Australia – *Reproduced with permission*)

Figure 9.3 – Personal Sampling With Sorbent Tube Collection

This removal process can be achieved by both absorption/derivatisation and adsorption techniques as described below:

- **Absorption/Derivatisation**

  Absorption (or solvation) is the technique whereby the gas or vapour is collected by passing it through a liquid where it is collected by dissolution in the liquid. There are a number of mechanisms whereby the gas or vapour is collected by a reaction with the liquid and can include derivatisation, oxidation, neutralisation and several others.

  Typically the gas is drawn through the collection device(s), Figure 9.4, by use of a sampling pump connected to:

  - a midget impinger
  - gas wash bottle or
  - fritted glass bubbler

The collection efficiencies of the three different devices rely on the size and number of bubbles ie the surface area produced in the liquid, the volume of liquid, the sampling flow rate and the reaction rate. Sometimes bubblers are connected in series to increase efficiencies and to collect any liquid carryover.

(Source: University of Wollongong)

Figure 9.4 – Midget Impingers

The devices suffer from a number of disadvantages including the need to keep the device upright to prevent loss of the liquid into both the atmosphere and also loss into the pump. This can make personal sampling quite difficult, but the technique can be used for a number of contaminants including:

- Formaldehyde collected in water or bisulphate solution
- Oxides of nitrogen collected in sulphanilic acid
- Ozone collected in potassium iodine solution
- Toluene diisocyanate collected in 1-(2-methoxyphenyl) - piperazine in toluene

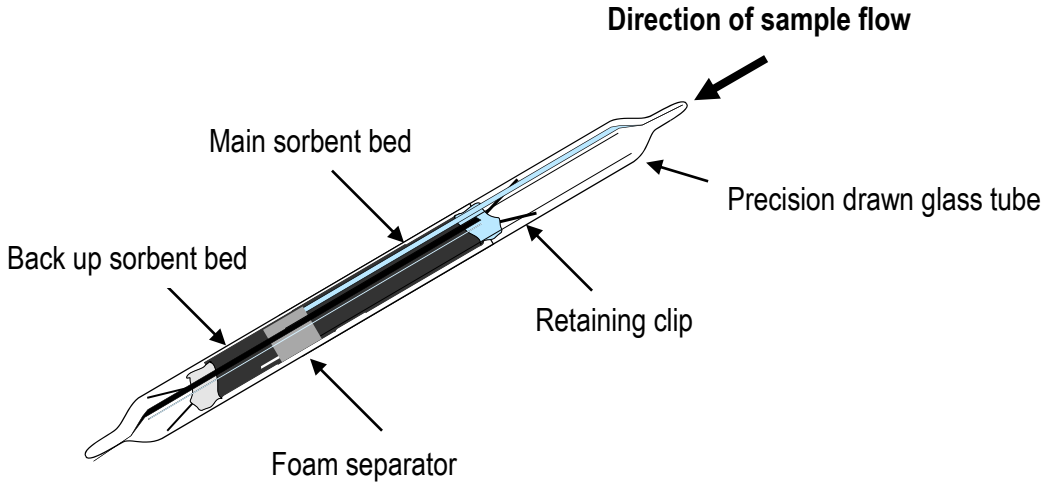
NB: The use of liquid collection methods have largely been superseded by the use of treated or impregnated filters, eg for isocyanates.

- **Adsorption**

  Adsorption is the technique whereby the gas or vapour is collected by passing it over and retained on the surface of the solid sorbent media such as activated charcoal, silica gel, porous polymers and molecular sieves.

  The adsorbent material is usually packed in a glass tube as shown in Figure 9.5. Immediately prior to use both ends of the glass tube are carefully broken off and the tube connected into the sampling train. The printed arrow on the sampling tube shows the direction of the airflow and should point towards the pump. If there is no arrow on the tube, insert the tube with the smallest sorbent section (ie the back up section) into the tube holder thus allowing the air flow to be through the main bed first.

  After sampling the tubes are capped and sent to the laboratory for analysis. Migration of the contaminant from the main sorbent bed section to the back up section can occur at room temperature. Field samples should also be kept under cold conditions eg use of dry ice in an insulated container and then stored under refrigeration in the laboratory. The collected material is desorbed in the laboratory using solvents such as carbon disulphide, or by vacuum or by thermal desorption prior to analysis



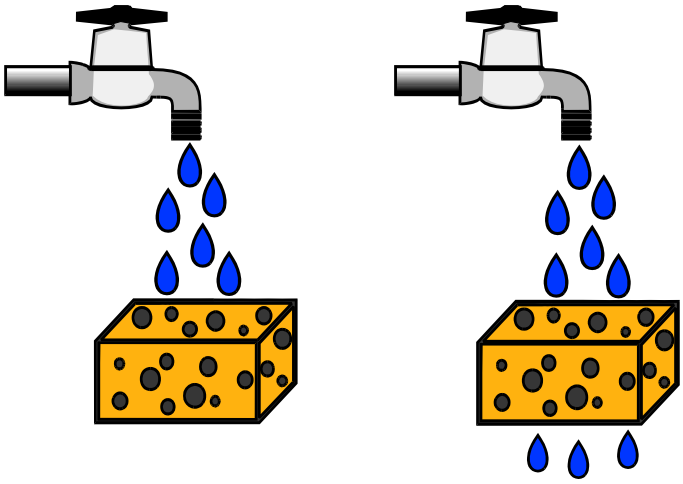
(Source: SKC Inc – *Reproduced with permission*)

Figure 9.5 – Sorbent Tube

Collection efficiencies are affected by temperature, humidity, sampling rate, the presence of other contaminants and breakthrough.

- ***Breakthrough***

  When a sorbent is full to capacity, breakthrough occurs. Breakthrough is when the tube becomes full and releases the collected material and is lost in the air leaving the tube. Breakthrough of contaminants through the sorbent bed can occur if the sample flow rates are too high, if the concentrations are such that the sample volume collected is too high or if the contaminant is not retained effectively on the collection media. Breakthrough can be checked for by using a glass tube with two sorbent beds, the main sorbent trapping bed and a back up bed. Breakthrough of a substance through a sorbent is said to occur in the NIOSH air sampling methods when the concentration in the back up section exceeds 20 % of the concentration in the front section.



(Source: SKC Inc – *Reproduced with permission*)

Figure 9.6 – Breakthrough

9.3.1 Types of Adsorbent Tubes

- **Activated Charcoal**

  Activated charcoal (carbon) is usually derived from coconut shells or coal. It is crushed and conditioned at high temperatures and low oxygen levels creating an extensive network of internal pores with a very large surface area. It is non polar and preferentially adsorbs organic vapours rather than polar molecules. It is therefore an excellent sorbent for a wide range of common industrial organic compounds such as hydrocarbons, chlorinated hydrocarbons, ketones, esters and ethers.

  However activated carbon has poor recovery capabilities for reactive compounds, some polar compounds such as amines, phenols, aldehydes, low molecular weight alcohols, low boiling point compounds such as ammonia, ethylene and methylene chloride and other sorbents must therefore be used.

- **Silica Gel**

  Silica gel is typically used for polar substances such as glutaraldehyde, amines and some inorganic substances which are difficult to desorb from charcoal. A disadvantage of silica gel is its affinity for water vapour which can displace other polar substances from its surface.

Sample volumes may therefore have to be reduced when sampling in high humidity environments. When using silica gel polar solvents such as water and methanol are used for desorption of the collected material.

- **Porous Polymers**

  There are a number of commercial porous polymers that are used for where the gas and vapour are either not collected effectively from activated charcoal or where there are poor recoveries. Examples include:

  Tenax – for low level contaminants
  XAD 2 – for pesticides
  Chromosorb - pesticides
  Porapaks – has polar characteristics

  Other solid sampling media for gases and vapours also include:

  Molecular sieves
  Florisil for PCBs
  Polyurethane foam (PUF) for pesticides, PNAs

  Specific advice should be sought from the Standard Air Sampling Methods from the Internationally recognised testing authorities such as NIOSH, OSHA, HSE or the local standards organisation and industry guides (SKC 2006) for the contaminant of interest.

- **Thermal Desorption**

  Use of pumped sampling onto glass tubes packed with charcoal, followed by carbon disulphide (CS_2) extraction and gas chromatography (GC) analysis was developed for volatile organic compounds in the 1970's.

It is still used for personal exposure assessment ie occupational hygiene and stack emission testing, but is fundamentally limited with respect to sensitivity and has been superseded to a degree, especially in Europe, by thermal desorption for the following reasons:

- ***Sensitivity***

  Solvent extraction requires dilution with at least 1 to 2 ml of CS_2 followed by injection of only 1µl of extract into the GC, thus giving a 10^3 dilution of the sample right at the start of the process. Other factors limiting sensitivity include: solvent artifacts, interferences from the solvent itself (masking volatile target analytes) and low desorption efficiencies. Conversely TD allows complete transfer of all target analytes to the analytical system with no dilution or solvent interference. Detection limits offered by TD are typically 10^3 to 10^4 higher than equivalent solvent extraction methods facilitating ambient monitoring at ppt/ppb levels as well as higher ppm (and % level) concentrations.

  By comparison, charcoal / CS_2 methods are invariably limited to concentrations >0.1ppm.

- ***Desorption Efficiency***

  Thermal desorption efficiency is readily validated and is always above 95%, independent of ambient conditions and the nature of the target analytes – polar/apolar, volatile/semi-volatile etc. The desorption efficiency of charcoal/CS_2 extraction methods is typically in the order of 80% under best conditions. Additionally charcoal is hydrophilic and adsorbs water from humid air. The presence of water can reduce desorption efficiencies (eg 20-30%), especially in the case of polar compounds.

- ***Reproducibility***

  As described above, the desorption efficiency of solvent extraction is usually lower than that of TD and can vary from 20 to 80% depending on target analyte and atmospheric humidity. This significantly comprises reproducibility. Other issues include the evaporation of CS_2 during sample preparation and its absorption into the rubber septa of autosampler vial caps.

- ***Analytical Performance***

  Originally, charcoal/CS_2 methods were intended for used with packed column GC technology and FID detection. In this case, the limitations of CS_2 are minimised by its very low response on FID. However even under these conditions, impurities in the solvent, solvent related baseline disturbances and the large dilution factor all contributed to limit method sensitivity to ppm level atmospheric concentrations. With the modern preference for GC's configured with mass spectrometer (MS) detectors, CS_2 brings additional limitations. It generates a large response on the MS, often requiring deactivation of the detector ionisers until after the solvent has completely passed through the system. This means that target compounds co-eluting with the solvent will not be measured at all.

- ***Thermal Desorption Tubes***

  The "industry standard" for TD tubes is ¼ inch (6.4 mm) OD x 3½ inch (88.9 mm) long stainless steel sorbent tube pre-packed with the sorbent of choice. In addition, a ¼ inch brass SwageLok type storage cap (fitted with a PTFE ferrule) for the non sampling end of the tube, and a diffusion cap at the end of the tube is normal practice.

A suitable sorbent must be selected for the compound or mixture to be sampled. If more than one sorbent is required (due to the different volatilities of the compounds in question), two or more samplers packed with different sorbents should be exposed simultaneously.

It is essential that tubes are conditioned before they are used for sample collection. Once sampling or analysis is completed, tubes should be recapped with the brass storage caps as soon as possible and returned to a clean environment for storage.

Specific details including the general handling of TD tubes, selection of the sorbent, conditioning of tubes, short and long term storage of tubes after sampling should be obtained from the manufacturer prior to use.

(Source: Markes International Ltd – *Reproduced with permission*)

Figure 9.7 – General Thermal Desorption Tubes

(Source: Markes International Ltd – *Reproduced with permission*)

Figure 9.8– Thermal Desorption Unit with GC/MS

9.3.2 Collection Efficiency of Adsorption Tubes

Factors that can affect the collection efficiency of adsorption tubes include:

Temperature – adsorption is an exothermic process and is reduced at higher temperatures. Some compounds can migrate through the sorbent bed and should be stored after sampling by keeping them cool/cold in a coolbox, fridge or freezer.

Humidity – charcoal has a great affinity for water vapour and hence reduces its collection of other contaminants

Sampling flow rate - if sampling pump flow rates are too high contaminants do not have sufficient residence time to be removed by the sorbent resulting in collection losses.

Channeling – if the sorbent tube is incorrectly packed, channels or gaps in the bed can be formed through which the gases flow and hence are not in contact and not adsorbed on to the surface of the sorbent.

Overloading of sorbent tubes can occur if concentrations/sampling times are too long or by the presence of other contaminants including water vapour that preferentially occupy the adsorption sites.

The manufacturers' information and standard sampling methods eg NIOSH, OSHA, HSE, ISO Standards Australia etc should be referred to for specific details pertaining to the sampling for the particular contaminant.

9.3.3 Desorption Efficiencies

While adsorption of a contaminant from the atmosphere onto a tube of some specific type is a very effective way of collecting the contaminant, difficulties arise during the laboratory analysis in the recovery of that analyte from the tube.

In essence, some of the material that has been collected from the atmosphere cannot be recovered from the tube and thus, if this is not accounted for in the calculation of an exposure, will lead to errors. To overcome this, a "desorption efficiency" for each batch of tubes must be established. There are varying methods for doing this but the general approach is to load a number of tubes from a batch with varying amounts of the contaminant of interest and then process the tubes as normal. The percentage recovered (eg 80% or 0.8) is deemed the desorption efficiency for that particular batch of tubes and for that particular contaminant.

It is important that the laboratory understand the reasons for this process and be familiar with the appropriate methods to establish such values. In some circumstances manufacturers publish a list of typical desorption efficiencies for common contaminants which can be a useful guide to the laboratory.

9.4 SAMPLING PUMPS

The operation of the various types of sampling pumps is discussed in section 8.2. The major difference between sampling pumps used for dust and vapour sampling is the operating flowrate. For most organic vapour sampling the required flowrate is typically 20-200 mL/minute, thus giving rise to the generally used terminology "low flow" pumps.

The other main difference is in respect to flow pulsation. In organic vapour sampling it is the total volume of air collected which is important not the need to maintain a low pulsation flow; hence some low flow pumps do not have as sophisticated flow control systems as dust sampling pumps. Pre and post sampling rates should not vary by more than ±5%. If outside this recommended range the sample should be considered invalid.

For the collection of gases, flowrates of about one litre/minute are usually required and this can be achieved by “throttling down” a dust sampling pump, provided it has an exhaust port for the collection of the gas into a Tedlar bag, etc.

9.5 MIXED EXPOSURE TO SOLID/LIQUID/AEROSOL/GASES/VAPOURS

Where contaminates are present in a mix of solid, liquid, aerosol and gas or vapour phases particular care must be taken to ensure that levels are not underestimated. Three examples highlight issues for mixed phase sampling:

Example 1

The “traditional method” for sampling and measurement of coke oven emissions was to collect and analyse the “Benzene Soluble Fraction of the Total Particulate Matter” collected on a membrane filter. However it has been shown that the polyaromatic hydrocarbons emitted from coke ovens are present in a mix of a particulate phase and a vapour phase and hence sampling for just the particulate phase was an underestimation of the concentration of coke oven emissions.

Samplers have now been developed which include a sorbent layer behind the particulate membrane filter to collect the vapour phase which passes through the membrane filter.

Example 2

Practical difficulties associated with the use of impingers (eg liquid loss due volatilisation of solvents, sample carry over and liquid spillage, the need to keep sampler upright and breakage of the glass components) led to the development of impregnated filters to assist in overcoming these issues for contaminants such as isocyanates, formaldehyde and glutaraldehyde.

However, during the spraying of “two pack” isocyanate containing paints, the isocyanates may be present in both the particulate and vapour phase. Particles may not react completely with the impregnated filter. Similarly, if just using an impinger small particles may not be collected efficiently. To overcome these potential under sampling issues a sampling train comprising of an impinger followed by an impregnated filter can be used

Example 3

In the smelting of aluminium for example, fluorides can exist as a particulate, as a hydrofluoric acid mist or as gaseous hydrofluoric acid and need to be sampled separately when determining hydrogen fluoride and fluorides in air, HSE MDHS 35/2.

Samples are taken by drawing a measured volume of air through a PTFE (Teflon) membrane filter and a sodium carbonate impregnated paper pad mounted in an inhalable sampler. The PTFE filter removes the particulate fluorides, whilst the sodium carbonate impregnated pad collects the hydrogen fluoride. Hydrofluoric acid mist is not retained on the filter so it is also collected on the sodium carbonated impregnated paper pad.

9.6 DIFFUSION OR PASSIVE SAMPLERS

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

Diffusion is the natural process by which gases and vapours flow from a higher concentration to a lower concentration in the absence of bulk flow. Most diffusion or passive samplers operate on the principle of gaseous diffusion across a permeable membrane (AS 2986). Fick's first law of diffusion can be applied to the mass uptake rate:

$$\frac{m}{t} = \frac{AD}{L}(c - c_0)$$

where m = mass of adsorbate collected in grams

t = sampling time in seconds

A = cross sectional area of the diffusion path in square cm

D = diffusion coefficient for the adsorbate in air in square cm per second – available from manufacturer of the sampler for a given chemical

L = length of the diffusion path in cm (from porous membrane to sampler)

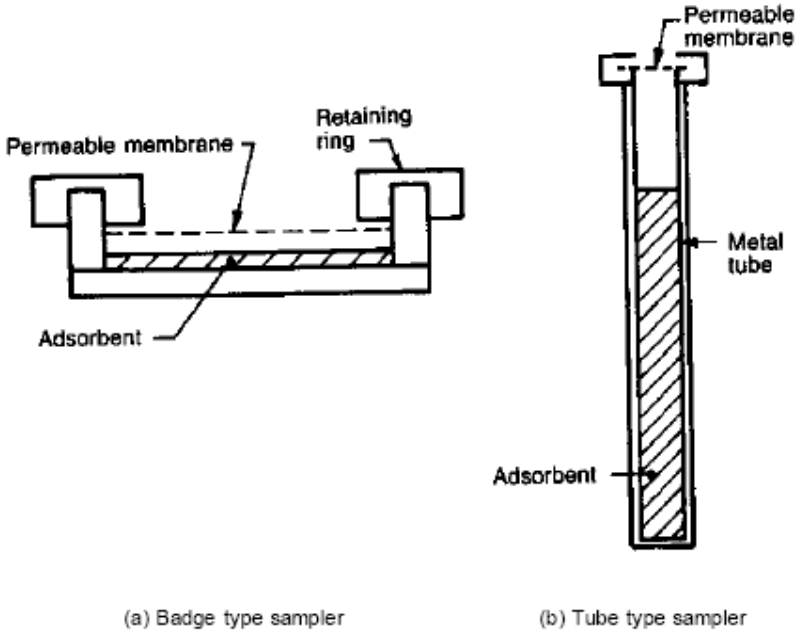
c = concentration of contaminant in ambient air in gram per cubic cm

c_0 = concentration of contaminant just above the adsorbent surface in gram per cubic cm

From the above equation, if c_0 is zero (ie the collection medium is effective) the mass transfer or collection rate is proportional to the ambient concentration c.

The sampling rate of a diffusion monitor is dependent on the diffusion coefficient of the contaminant and the geometry of the monitor. The 3M and SKC badge monitors and Dräger ORSA monitors have the diffusion path axial to the sorbent while the diffusion path to the Radiello is radial to the sorbent surface. Therefore, every contaminant on every brand of monitor has its own unique, fixed sampling rate.

The sampling rate remains constant as long as the sorbent media does not reach its capacity and as long as adequate airflow is maintained across the face of the monitor. The manufacturers of the monitors supply the sampling rate and capacity information.



(Source: HSE – *Reproduced with permission*)

Figure 9.9 – Typical Passive Samplers

(Source: 3M Australia – *Reproduced with permission*)

Figure 9.10 – 3M Diffusion Monitor

Organic vapour diffusion monitors are typically loaded with activated charcoal and contaminants that can be actively sampled with a charcoal tube can generally be sampled with a diffusion monitor as well.

Similarly charcoal and other sorbents can be treated with chemical impregnants that rely on chemisorption to collect materials that have poor capture, retention and recovery with activated charcoal. For example, a solid sorbent can be treated with 2-(hyroxymethyl) piperidine and used to collect formaldehyde, or activated charcoal can be treated with a bromine compound and used to collect ethylene oxide. Other diffusion monitors have been developed for inorganic mercury and more recently for amines.

Diffusion monitors meet or exceed an accuracy of ± 25% at 95% confidence for many workplace contaminants. They are simple and easy to use and do not require the use of sampling pumps, tubing, and batteries or air flow calibration. They are light weight and can be simply clipped on to the collar of the worker for personal sampling (TWA or STEL) or can be used for area monitoring as long as there is sufficient airflow.

If used for area monitoring or static sampling they should be placed in the open away from corners and where the air movement is at least 25 ft/min or 0.13 m/sec in any orientation.

Some of the disadvantages of diffusion monitors are that they cannot be used to sample everything, eg they cannot sample low vapour pressure organics such as glutaraldehyde, reactive compounds such as phenols and aldehydes. Diffusion badges using charcoal suffer from the same moisture and recovery issues associated with the use of active sampling tubes. Additionally, with some diffusive samplers (depending on design) inaccuracies can occur at wind speeds >2.5 m/s. The “sampling rate” is supplied by the manufacturer and is different for each compound. While some diffusion monitors have a back up section most do not making it difficult to know if breakthrough has occurred especially for the more volatile compounds such as methylene chloride.

The manufacturers' information and standard sampling methods eg NIOSH, OSHA, HSE, ISO Standards Australia etc should be referred to for specific details pertaining to the sampling for the particular contaminant.

9.7 CALCULATION OF RESULTS

9.7.1 Active Sampling

Two components are necessary to establish the atmospheric concentration of gas and vapour in the atmosphere of a workplace. These are the concentration of contaminant on the collection media and the total volume of air sampled.

- **Calculation of Total Volume of Air Sampled**

  If we know the flowrate of a sampling pump (as detailed in section 8.5) and the time that sampling was undertaken, we can calculate the total volume of air sampled. For example, if the flowrate was 100 mL/min and sampling was performed for 5 hours, we can make the following calculation.

  Volume (Litres) = 5 x 60 x 100 / 1,000
  = 30

  Volume (m^3) = 0.030
  ($1m^3$ = 1,000 L)

- **Calculation of Mass on Sample Media**

  If the laboratory analysis resulted in 6.3 µg of toluene being measured on the charcoal tube with an assumed desorption efficiency of 100% and zero breakthrough and zero blank, then

  Mass (mg) of toluene = $\frac{6.3}{1000}$
  = 0.0063

- **Calculation of Concentration**

Using the formula

$$\text{Conc (mg/m}^3\text{)} = \frac{M_F + M_R - M_B}{D \times V}$$

Where M_F = mass of analyte in front section (mg)

M_R = mass of analyte in backup section (mg)

M_B = mass of blank

D = desorption efficiency (as a fraction)

V = volume in m^3

$$\text{Concentration of toluene mg/m}^3 = \frac{0.0063}{1 \times 0.03}$$

$$= 0.21$$

9.7.2 Diffusion/Passive Sampling

The time weighted average concentration of the environment sampled can be calculated by knowing the length of the sampling period, the contaminant weight determined by the laboratory, the recovery coefficient and the calculation constant either A or B. The calculation constant “A” is used to calculate the concentration when expressed in units of milligram per cubic metre (mg/m^3) and the constant “B” when expressed in units of parts per million (ppm).

NB These calculation constants are determined and supplied by the particular manufacturer for use with certain contaminants sampled using their particular monitor.

$$A = \frac{1000}{\text{Sampling Rate}}$$

$$B = \frac{1000 \times 24.45}{\text{Sampling Rate} \times \text{Molecular Weight}}$$

Air temperature will slightly influence the sampling rate of the diffusion monitor. The expressions can be multiplied by a temperature correction factor for samples collected at other than 25°C. No correction is needed for differences in pressure

Table 9.1 – Sampling Temperature Correction Factors

(C)	(F)	Correction factor
44	111	0.97
37	99	0.98
31	88	0.99
25	77	1.00
19	66	1.01
13	55	1.02
7	45	1.03
2	36	1.04
-3	27	1.05
-8	18	1.06

(Source: 3M – *Reproduced with permission*)

Example - Procedure for the 3M Organic Vapour Monitor

The time weighted average concentration of contaminant in mg/m^3 can be calculated from the following expression:

$$C\ (mg/m^3) = \frac{W\ (micrograms) \times A}{r \times t\ (minutes)}$$

The time weighted average concentration of contaminant in ppm can be calculated from the following expression:

$$C\ (ppm) = \frac{W\ (micrograms) \times B}{r \times t\ (minutes)}$$

Example Calculations

Contaminant:		Benzene
Length of sampling time (t)		420 minute
Temperature (T)		75 °F
Calculation Constant	A	28.2
	B	8.82
Contaminant weight (W)		27.2µg
Recovery coefficient (r)		0.97

$$C\ (mg/m^3) = \frac{27.2 \times 28.2}{0.97 \times 420}$$

$$= 1.88\ mg/m^3$$

$$C\ (ppm) = \frac{27.2 \times 8.82}{0.97 \times 420}$$

$$= 0.59\ ppm$$

9.8 DIRECT READING INSTRUMENTS

9.8.1 Introduction

Significant advances in this area of occupational hygiene monitoring over the last 10 to 20 years. Often in the past they were large bulky instruments unsuitable for personal monitoring, but with advances in the technology they can now be worn as personal sampling devices for an ever increasing number of gases and vapours.

Direct reading instruments allow real time measurements of gases and vapours and aerosols. Many are available with data logging capability that allows analysis of instantaneous (seconds), short term 15 minute STEL concentrations and 8 hour TWA concentrations of the particular contaminant.

Gas or vapour monitors can measure:

- Single gas or vapour
- Specific multiple gases and vapours
- Multiple gases and vapours without differentiating between them

The uses of these direct reading instruments include:

- Where immediate data is needed
- Personal exposure monitoring
- Help develop comprehensive evaluation programmes
- Evaluate effectiveness of controls
- Emergency response
- Confined spaces
- For difficult to sample chemicals
- Multi sensors/multi alarms
- Stationary installations for both a record of exposure levels and when connected to an alarm to indicate hazardous levels
- Fit testing
- Video monitoring etc

Some of the types of commonly used direct reading instruments are listed in Table 9.2. A discussion of some of the instruments will be made during the practical session.

Table 9.2 – Commonly Used Direct Reading Instruments for Gases and Vapours

Instrument	Uses	Principle of Operation	Range
Combustible gas detectors	Combustible gases and vapours – non specific.	Hot wire – test gas is passed over a heated wire (sometimes in the presence of a catalyst). The test gas burns changing the temperature of the filament and the electrical resistance is measured.	Usually measured in percentage of lower explosive limit. Some models measure down to ppm.
Colorimetric detectors	Various gases and vapours including formaldehyde, hydrogen sulphide, sulphur dioxide, toluene diisocyanate – specific.	Reaction of the test gas with a chemical reagent (either as a liquid or in some cases an impregnated paper or tape) and measurement of the colour produced.	Variable
Electrochemical sensors	Carbon monoxide, nitric oxide, nitrogen dioxide, hydrogen sulphide, sulphur dioxide, - specific.	Chemical oxidation of test gas	1 to 3,000 ppm
Infrared gas analysers	Organic and inorganic gases and vapours – specific.	Measures infrared absorbance of test gas.	Sub ppm to low percentage levels.
Metal oxide sensors	Hydrogen sulphide; nitro, amino, alcohol and halogenated hydrocarbons.	Metal oxide sensor is chemically reduced by the test gas increasing its electrical resistance.	1 to 50 ppm
Thermal conductivity sensors	Carbon monoxide, carbon dioxide, nitrogen, oxygen, methane, ethane, propane and butane.	Uses specific heat of combustion of a gas or vapour	Percentage
Portable gas chromatographs	Organic and inorganic gases and vapours – specific.	Uses a packed column to separate complex mixture of gases. Detectors available include flame ionization, electron capture, thermal conductivity, flame photometric and photoionisation.	0.1 to 10,000 ppm

9.8.2 Limitations

The disadvantages and/or limitations of direct reading instruments include:

- Often costly to purchase
- Need for frequent and regular calibration
- Lack of specificity
- Effect of interferences
- Cross sensitivity
- Need for intrinsically safe instruments in many situations
- Battery life
- Sensors (finite life, poisoning, lack of range)

The advantages and disadvantages for each type of instrument must be assessed for the particular needs in relation to the measurement of particular gases and vapours in the workplace.

An appreciation of the issues that arise from the cross sensitivity of sensors can be gained from the following example.

If, for example, we have an electrochemical cell designed to measure carbon monoxide and apply 100 ppm of the following gases across the cell we will typically obtain the following carbon monoxide readings on the instrument:

Hydrogen Sulphide	≈ 315 ppm
Sulphur Dioxide	≈ 50 ppm
Nitric Oxide	≈ 30 ppm
Nitrogen Dioxide	≈ -55 ppm
Chlorine	≈ -30 ppm
Hydrogen	<40 ppm
Hydrogen Cyanide	≈ 40 ppm
Ethane	≈ 90 ppm

Such false positive or false negative readings can give rise to a lack of confidence in the instrument to the point that alarms are ignored when they should not be.

To overcome this problem, manufacturers fit a filter to the sensor which typically results in the following changes:

	Unfiltered	**Filtered**
Hydrogen Sulphide	≈ 315 ppm	<10 ppm
Sulphur Dioxide	≈ 50 ppm	<5 ppm
Nitric Oxide	≈ 30 ppm	<10 ppm
Nitrogen Dioxide	≈ -55 ppm	-15 ppm
Chlorine	≈ -30 ppm	<-5 ppm
Hydrogen	<40 ppm	<40 ppm
Hydrogen Cyanide	≈ 40 ppm	<15 ppm
Ethane	≈ 90 ppm	<50 ppm

Obviously, it is important that these filters are maintained and that the limitations of the device are well understood by those using it in the workplace.

9.8.3 Maintenance and Calibration

Readings obtained from direct reading instruments are only as good and are a reflection of both the maintenance and calibration of the equipment. One approach used in the mining industry and has also found use in general industry is to set out the requirements and responsibilities for the examination and calibration of different classes of equipment based on their use.

Group I All equipment which is hand held or portable

Ia – provides a scaled output indication of actual gas concentration

Ib – provides an alarm output indication of actual gas concentration

Group II Severe use conditions of equipment eg mounted on operating equipment and can include vibration and high levels of dust and water vibration.

Group III Equipment installed at a fixed location for appreciable periods of time with a local read out of concentration

Group IV Equipment permanently installed with remote readout of concentration

Table 9.3 – Suggested Examination Schedules

Group	Group Type	Suggested Examination & Maintenance Schedule*
Ia	Handheld/portable	Shift / or before use Weekly Calibration 6 Monthly Service
Ib	Handheld/ portable with alarms	Shift / or before use Weekly Calibration 6 Monthly Service
II	Machine mounted	Shift / or before use Zero – Weekly Calibration – Weekly Alarm - Weekly Switching – Weekly 6 Monthly Service Overhaul - 4 Yearly
III	Underground fixed	Status – Daily System – Daily After relocation Switching – Monthly Yearly Service
IVa	Surface fixed	Status - Daily System – Monthly Yearly Service

Group	Group Type	Suggested Examination & Maintenance Schedule*
IVb, IVc	Surface fixed	Status – Daily System – Monthly Line Integrity – Monthly Yearly Service

* Daily – typically by user
Weekly – typically by maintenance person / department
Monthly – typically by maintenance person / department
Yearly – typically by external authority

The standard also sets out the requirements for a Certificate of Compliance, recordkeeping, accuracy requirements and the minimum competencies for persons and accredited authorities engaged in the examination, maintenance and testing of equipment covered by the standard.

Advice is also provided for the technique and equipment guidelines for carrying out span and zero tests on gas detecting equipment. Span test is the test of response to certified test gas(es). Zero test is test of response to zero gas conditions.

The test equipment and techniques described below are considered suitable for carrying out span and zero checks on gas detecting equipment.

Suitable test equipment for carrying out single point span checks consists of a cylinder containing the certified test gas fitted with either a calibrated flow meter with a precision regulator or a flow restrictor and pressure gauge.

For equipment in which the external atmosphere reaches the sensor or detector by diffusion, the test procedure usually involves dispensing the certified test gas to the sensor or detector of the equipment via a gas line and suitable calibration cup. Calibration cups conforming to the design of the manufacturer of the equipment under test, or supplied by that manufacturer should be used at all times.

For sample-draw equipment containing an integral pump or hand held aspirator, the sample inlet is connected to a gas line containing a plastic bag reservoir pre-flushed and filled with the certified test gas.

9.8.4 Intrinsic Safety of Instruments

The International Electrotechnical Commission Scheme for standards relating equipment for use in explosive atmospheres is known as IECEx.

Across the world there has been a general move towards the adoption of IECEx Standards and in particular the 60079 Series for Gases and Vapours and the 61241 Series for dusts by the different Standard setting organisations including those from Europe, United Kingdom, South Africa, USA, Canada, Asia and Australia and New Zealand.

The modern day automation of industry has meant an increased need to use equipment in Explosive or Ex areas. Such equipment is termed “Ex equipment” and is found in areas such as:

- Automotive refueling stations or petrol stations
- Oil refineries, rigs and processing plants
- Chemical processing plants
- Printing industries, paper and textiles
- Hospital operating theatres
- Aircraft refueling and hangars
- Surface coating industries
- Underground coalmines
- Sewerage treatment plants
- Gas pipelines and distribution centres
- Grain handling and storage
- Woodworking areas
- Sugar refineries
- Metal surface grinding, especially aluminium dusts and particles

An explosion can only take place if the following three factors are present:

- A flammable substance
- Oxygen
- An ignition source

An explosion only occurs if the substance-air mixture lies within a certain concentration range – the explosive limits.

Explosion Protection

The hierarchy for explosion protection are:

- Reduce or avoid the use of flammable substances
- Do not allow any releases of flammable substances to form potentially explosive atmospheres
- Remove sources of ignition from the potentially explosive atmosphere
- Use adequately designed equipment that reduces the probability of causing an explosion
- Provide measure to reduce the effects of explosions

Guidance is provided in the IECEx Standards to enable the choice of suitable equipment based on the following processes.

Classifications of Zones

It is necessary to firstly identify the likelihood of an explosive atmosphere being present. The explosive atmosphere may be caused by the presence of a flammable liquid, gas or vapour or by the presence of combustible dust in suspension or layers or a combination of dust and gas explosive atmospheres.

Gases, Vapours, Mists	Dusts	Explosive Atmosphere is Present
Zone 0	Zone 20	Most of the time
Zone 1	Zone 21	Some time
Zone 2	Zone 22	Seldom or short term

(Source: TestSafe – *Reproduced with permission*)

The area may also be classified as “Safe Area” if the explosive material or air is not expected to be available in quantities that would allow it to be explosive.

Explosion Groups

When the zone classification takes place, the explosive materials are examined and the explosion protected electrical equipment is divided into two groups depending on where it is used:

I equipment used in underground mining – explosive materials being mainly methane and coal dust

II equipment used in other hazardous areas ie other industries with additional subgroups for Group II according to the nature of the explosive gas atmosphere for which is intended:

IIA – least readily ignited gases such as propane and benzene
IIB – more readily ignited gases such as ethylene and diethyl ether
IIC – most readily ignited gases such as hydrogen and acetylene

Temperature Classes

To prevent the hot surfaces of electrical equipment from creating ignition the maximum surface temperature of electrical equipment exposed to gas must not exceed the ignition temperature of gases that may be in the area.

Group I electrical equipment requires the temperature of the components and surfaces exposed to dust and methane to be limited to less than 150°C.

In case the components and surfaces are protected from the ingress of dust, the maximum temperature of such components may be higher, but must be less than 450°C.

For Group II electrical apparatus the maximum surface temperature must not exceed the values in the Table 9.4 which corresponds to the temperature class of the equipment. For convenience, a temperature class may be assigned to a gas or vapour based on its ignition temperature.

Table 9.4 – Maximum Surface Temperature / Ignition Temperature

Temp Class	Maximum Permissible Surface Temp of the Equipment (°C)
T1	450
T2	300
T3	200
T4	135
T5	100
T6	85

(Source: TestSafe – *Reproduced with permission*)

Levels of Protection and Zones of Application

Intrinsic Safety has 3 levels of protection:

“ia” – means that the type of protection ‘intrinsic safety” (no release of spark energy or thermal energy that can cause ignition) is maintained with up to two faults.

“ib” – means intrinsic safety is maintained with up to one fault

“ic” – means intrinsic safety is maintained, but no requirement to apply faults.

Safety factors are applied and the equipment evaluated for spark and thermal ignition energy after the application of faults

Level of Protection	Suitable for
“ia”	Zones 0, 20
“ib”	Zones 1, 21
“ic”	Zones 2, 22

(Source: TestSafe – *Reproduced with permission*)

In areas where explosive atmospheres can occur despite the explosive protective measures employed, only explosive protected equipment can be used.

Explosive protective equipment can be manufactured to IEC protection type levels which are subject to the requirements of their own specific standards. Intrinsic safety, Flameproof, Increased Safety, Encapsulation etc are some of the common types of protection used for explosion protected electrical equipment.

The Ex marking label

Only appropriate certified and marked electrical equipment may be used in hazardous areas. Users of electrical equipment must ensure that the equipment complies with the relevant regulations and local standards.

The information of the name of the manufacturer, model number, Ex code and certificate number are attached to the equipment.

An example is:

Smith Electronics
Model TRE
Ex ia IIC T4
Cert 098X
Serial No 8765

“ia” equipment is suitable for zone 0 application

IIC the equipment is suitable for Groups IIA, IIB, IIC

T4 the equipment is suitable for gases with auto ignition temperature greater than 135°C.

Further and much more detailed information for the use of gas detection equipment in potentially explosive atmospheres including the Classification of Zones, Explosion Groups, Temperature Classes, the Types of Protection provided by equipment, the requirements for Certification and Marking is available from the different National Standards and Certification bodies.

9.8.5 Detector Tubes (Colorimetric Tubes)

Colorimetric tubes are often widely used to provide an initial and convenient gas and vapour assessment in a workplace.

The use of colorimetric tubes is based on the change in colour of a specific reactant when it comes in contact with a particular gas. The most commonly used are tubes that contain a solid reactant and a known volume of air is drawn through the tube using a manual pump and the concentration of the particular contaminant, if present, is able to be determined

(Source: Dräger Safety – *Reproduced with permission*)

Figure 9.11 – Gas Detector Pump

The substance conversion in the tube is proportional to the mass of reacting gas. Generally it is possible to indicate the substance as a length of stain indication. When a length of stain indication is not practical the indication is based on the interpretation of colour intensity according to a given reference standard or set of standards.

The accuracy of colorimetric tubes is dependent on a number of factors including sample pump volume, efficiency of the chemical reaction, humidity, temperature, manufacturer's calibration of the graduations and interpretation of the length or colour of the stain and is typically quoted as being 10 – 30%.

(Source: Dräger Safety – *Reproduced with permission*)

Figure 9.12 – New and Used Colorimetric Detector Tube

Direct reading colorimetric tubes are available from a number of different manufacturers including Dräger, Kitagawa, Gastech and MSA for grab or short term (seconds to minutes) measurement of approximately 300 gases. It must be noted that tubes from one manufacturer CANNOT be used with the pump from another manufacturer.

Also available are direct reading long term colorimetric tubes utilizing low flow battery operated pumps or diffusion type badges for long term measurements of 1 to 4 hours.

Some of the advantages of direct reading colorimetric tubes include:

- Relatively inexpensive and cheap to use
- Wide range of gases and vapours
- Immediate results
- No expensive laboratory costs
- Can be used for spot checks
- No need for calibration (tubes are pre-calibrated)
- No need for charging or electric power during operation

The limitation of such devices must also be noted and include:

- Interferences from other contaminants (cross sensitivities)
- Need to select correct tube and correct range of tube
- Results should not be compared to TWA
- Correct storage requirements
- Limited shelf life of tubes

Before selecting and or using any colorimetric tube the particular manufactures' instructions for that tube must be read to ensure the correct tube is both chosen and used correctly and the effect of any interference are known and understood before any measurement is carried out.

10. PRESENTATION OF RESULTS

Reporting of data in an appropriate format is of equal importance to collecting the actual results. As part of the reporting process it is important to identify at an early stage the stakeholders who require a report. In general, stakeholders would include:

a) The individual who was sampled (if this was the case) – If any person is required to wear a sample collection device then they are entitled to be told the results of that sampling. How this process is accomplished can take several forms but experience has shown that just sending an individual a document with results without any explanation can result in misinterpretation and unnecessary anxiety. If it is possible the results should be presented in person by someone familiar with their interpretation so that any questions can be addressed.

b) Management or person/group requesting the survey.

c) Statutory authorities – if involved in the exercise.

d) Workforce representatives (unions) – if involved in the process.

A review of some national standards (eg BSEN689, AS2985) presents slightly different approaches to the information required in a report.

BSEN689 requires the following:

“Reports shall be written of the occupational exposure assessment and of any periodic measurement. Each report should give reasons for the procedures adopted in the particular workplace.

The report has to contain

- the name of the person(s) or institutions undertaking the assessment and the measurements;
- the name of the substances considered;

- name and address of company;
- the description of the workplace factors including the working conditions during the measurements;
- the purpose of the measurement procedure;
- the measuring procedure;
- the time schedule (date, beginning and end of sampling);
- the occupational exposure concentrations;
- all events or factors liable to influence appreciably the results;
- details of quality assurance if any;
- results of the comparison with the limit value."

AS2985 requires the following:

"The test report shall include:

a) Identification of sample either as name of person wearing sample or sampler location.

b) Activities being conducted during sampling.

c) Any personal protective equipment worn.

d) Name of laboratory or authority which performed the test.

e) Date on which the test was carried out and sampling duration.

f) If uncertainties are not formally derived, for sampling periods greater than 60 minutes the concentration should be reported to two decimal places and three significant figures for six place microbalances, and to one decimal place and two significant figures for five-place microbalances.

g) Net weight of dust on filter.

h) The identity of any reference material used to assist in the validation of the test results.

i) Any observation, in relation to either the test sample or the performance of the test, which may assist in the correct interpretation of the test results.

j) References to the test method used."

While each of these provides a "laboratory style" report on the samples collected, they do not provide sufficient information to be considered appropriate occupational hygiene reports.

A well-based occupational hygiene report should be written in easy-to-read language, address all questions raised in the original scope of work and be able to satisfy an experienced occupational hygienist that the work was properly conducted and appropriate conclusions drawn.

One national professional occupational hygiene association has produced a guideline (AIOH 2006) for its members and suggests that a typical report should have the following contents:

- Executive summary
- Title
- Introduction
- Process description
- Methods and measurements
- Results and discussion
- Conclusions and recommendations

The difference between this approach and that of the two standards associations is the added focus on:

a) Process description
b) Results and discussion
c) Conclusions and recommendations

The AIOH (2006) describes the requirements for each of these sections, which have been produced with permission, below:

Process Description

Where a survey of an area, plant or process is conducted, the following should be described:

- Area/plant/process surveyed, eg*"a survey of the area known as cold press or CP was conducted".*

- Conditions at the time (ie personnel, process conditions, risk controls in place) eg *"usual operator unavailable", "shutdown", "worst case situation, with no controls", "as normal, believed to be a representative working day", "only Blender No.2 was operating", "protective equipment worn other than overalls".*

- Identify any items examined, eg *"Toolmaster serial number 123", "machine called the hot block curer".*

- Number of employees, duration of workshift(s) and task frequency and duration, eg *"9 employees work an 8 hour day, 5 day week with 2 hours overtime worked infrequently", "it takes about 30 minutes for 5 bags to be opened and poured daily".*

Diagrams and photographs are useful for clarifying sampling locations and conditions

Results and Discussion

- Results may be presented in the body of the report or as appendices. The level of information, considering the complexity of the processes, tasks and risks, should satisfy the technical reader but not unnecessarily complicate the report. Results should be traceable to the original field notes to enable verification of supporting data (eg identity of equipment used, calibration, etc) should this be needed.

- Results of personal sampling should be compared with the relevant exposure standard. If there is no relevant exposure standard, it will be necessary to either modify or adapt an existing guideline or develop a guideline. The rationale justifying the guideline used should be provided.

  eg for airborne contaminants

  a) time weighted average (TWA) and short term excursions limits (STEL), or

  b) TWA and general excursions limits (if no STEL is set), or

  c) peak/ceiling limits.

  - Results should be compared with any previous surveys at the premises and data from similar premises if available, eg *"…. The process produced results that are similar to other coating operations.* An explanation of general trends and unusual high or low trends should be included.

  - The level of risk should be determined (preferably quantitatively) to allow for the adequacy of controls to be assessed and the prioritisation of control options.

Conclusions and Recommendations

Conclusions should be drawn about whether or not the relevant exposure standard(s) have been exceeded and if the work could harm employee health, eg *"Exposure is likely to approach and may exceed the exposure standard and there is a significant risk", "It is believed that exposures are unlikely to approach the exposure standard and the risk is not significant", "The risk is uncertain due to the state of knowledge (or level of exposure)".*

Conclusions should also be drawn about adequacy of control and any further practical actions to eliminate or reduce the assessed risk so far as is practicable, eg *"existing controls adequate if maintained"…"existing controls not adequate and need to be upgraded".*

Recommendations should be selected using the hierarchy of control approach (personal protective equipment being the last resort) and guidance on an appropriate implementation time frame (eg urgent, short, medium or long term) should be provided. eg *"Temporarily cease work on No.123 process until corrective actions (see below) have been implemented", "Personal protection is a short term interim control. In the longer term engineering controls…", "A preventive maintenance programme should be implemented as soon as practicable", "Periodic reviews to determine if control measures need to be modified should occur at least once a year".*

Recommendations arising from regulatory requirements or similar guidelines should reference the relevant source document(s), eg *"The xxx Occupational Health and Safety (Noise) Regulations 1992 require that…", "xxx Standard 4114 Spray Painting Booths states that a minimum velocity of …".* "

Clearly the AIOH approach provides the reader with more information and options if control measures may be necessary. This approach is only one suggested example of report preparation and individual organizations will most probably have their own approach. What is fundamental in all cases is that the information collected and evaluated is communicated to all the stakeholders involved in the exercise in a manner and format that meets their needs or expectations. In almost all cases this will be different for each of the stakeholders.

11. REFERENCES

ACGIH (2007): Threshold limit values for chemical substances and physical agents and biological exposure indices. ACGIH, 2007

AIHA (1991): A strategy for occupational exposure assessment. AIHA, 1991

AIHA (1998): A strategy for assessing and managing occupational exposures 2nd Edn. AIHA, 1998

AIHA (2006): A strategy for assessing and managing occupational exposures 3rd Edn. AIHA, 2006

AIOH (2006): Guideline for writing occupational hygiene reports. Australian Institute of Occupational Hygienists 2006; www.aioh.org.au (accessed December 2006)

AIOH (2007): Principles of Occupational Health & Hygiene. AIOH, 2007

AS2290: Electrical equipment for coal mines – Maintenance and overhaul. Part 3: Maintenance of gas detecting and monitoring equipment. Australian Standard 2290.3, 1990

AS2985: Workplace atmospheres – Method for sampling and gravimetric determination of respirable dust. Australian Standard 2985, 2004

AS2986: Workplace atmospheres – Sampling and analysis of volatile organic compounds by solvent desorption gas chromatography. Part 1: Pumped sampling method, Part 2: Diffusive sampling method. Australian Standard 2986, 2003

AS3640: Workplace atmospheres – Method for sampling and gravimetric determination of inhalable dust. Australian Standard 3640, 2004

AS3853: Health and safety in welding and allied processes – Sampling of airborne particles and gases in the operator's breathing zone. Australian Standard 3853.1, 2006

AS/NZ4360: Risk management. Australian and New Zealand Standard 4360, 2004

BOHS (1993): Sampling strategies for airborne contaminants in the workplace. BOHS Technical Guide No.11, 1993

BSEN689 (1996): Workplace atmospheres – Guidance for the assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy. British and European standard 689, 1996

COSHH Regulations (2002): The control of substances hazardous to health regulations 2002 (as amended). Approved Code of Practice and Guidance L5 (5th Edn), HSE Books, 2005

Dost, A.A. (1996): Monitoring surface and airborne inorganic contamination in the workplace by a field portable x-ray fluorescence spectrometer. Ann. Occup. Hyg. J. 5, 589-610

Grantham, D. (2001): Simplified Monitoring Strategies. AIOH, November 2001

Hickey, J.L. & Reist, P.C., (1977): Application of occupational exposure limits to unusual work schedules. AIHA Journal 38(ii): 613-621, 1977

HSE (1992): Biological Monitoring for Chemical Exposures in the Workplace. Guidance Note EH56

ISO (1995): Air quality – Particle size fraction definitions for health related sampling. International Standards Organisation, 1995

MDHS 35/2: Hydrogen fluoride and fluorides in air. Methods for the determination of hazardous substances. HSE, April 1998

MDHS 82: The dust lamp. Methods for the determination of hazardous substances. HSE, March 1997.

MDHS 83/2: Resin acids in rosin (colophony) solder flux fume. Methods for the determination of hazardous substances. HSE, July 2006

NIOSH (1977): Occupational exposure sampling strategy manual. NIOSH January 1977

Oppl, R. Kalberlah, F, Evans, P.G. & Van Hemmem, J.J. (2003): A Toolkit for Dermal Risk Assessment and management: An Overview. Ann. Occup. Hyg. Vol.47, No.8, 629-640, 2003

Ottoboni, M.A., (1997): The dose makes the poison: A plain English guide to toxicology, 2nd Edition

Rappaport, S.M. and Selvin, S. (1987): A method for evaluating mean exposure from a lognormal distribution. Am. Ind. Hyg. Assoc. J. 48, 374-379

Rappaport, S.M., Selvin, S. and Roach, S.A. (1988): A strategy for assessing exposures with reference to multiple exposure limits. App. Ind. Hyg. J. 3, 310

SKC (2006): SKC Inc comprehensive catalog and sampling guide; www.skcinc.com (accessed December 2006)

Tranter, M. (1999): Occupational Hygiene and Risk Assessment

Tranter, M. (2004): Occupational Hygiene and Risk Management, 2nd Edn

Western Australia Department of Mines & Energy (1997): Adjustment of exposure standards for extended workshifts. Document No. ZME263AA, March 1999
http://ww.docep..gov.u/ResourcesSafety/Sectons/Mining_Safety/pdf_/MS%20GMP/Guidelines/MS_GMP_Guide_adjustmentexposurestandards.pdf
(accessed December 2006)

Wheeler, J.P. and Stancliffe, J.D. (1998): Comparison of methods for monitoring solid particulate surface contamination in the workplace. Ann. Occup. Hyg. J. 7, 477-488

WHO (1997): Determination of Airborne Fibre Number Concentrations: A recommended method by phase contrast optical microscopy (membrane filter method) published by the WHO (1997)