
Ocena kemijske izpostavljenosti na delovnem mestu

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Prepoznavna kemijske izpostavljenosti

- Prepoznavna.
 - Podobne industrije.
 - Poznavanje procesa.
 - MSDS.
- Ocena tveganja.
- Kontrola.



Asbestos removal

Prepoznavna kemijske izpostavljenosti

- Prepoznavna.
- Ocena tveganja.
 - Kemijska oblika.
 - Način izpostave.
 - Št. izpostavljenih.
 - Stopnja izpostavljenosti.
 - Dovoljene mejne vrednosti
(Permissible exposure limit (PEL))
- Kontrola.



Lead abatement

Kemijske oblike (Agregatno stanje)

- Trdna onesnaževala.
 - dim.
 - megla.
 - Prah & vlakna.

- Plini in hlapi.



Trdna onesnaževala

- Dim.
 - Nastane s kondenzacijo izparjenih snovi v hladnem zraku.
 - Nastanejo pri varjenju, obločno rezanje, spajkanju, etc.
 - Ponavadi manj kot $1.0 \mu\text{m}$ premera.
 - V večini primerih reagirajo vroče pare z zrakom in nastanejo oksidi.



Trdna onesnaževala

- Megla.

- Suspendirane kapljice tekočine nastajajo zaradi:
 - » Kondenzacije tekočine iz hlapov *ali*
 - » Razprševanja tekočine v drobne kapljice.
- Term “mist” is applied to finely divided liquid suspended in atmosphere.



Trdna onesnaževala

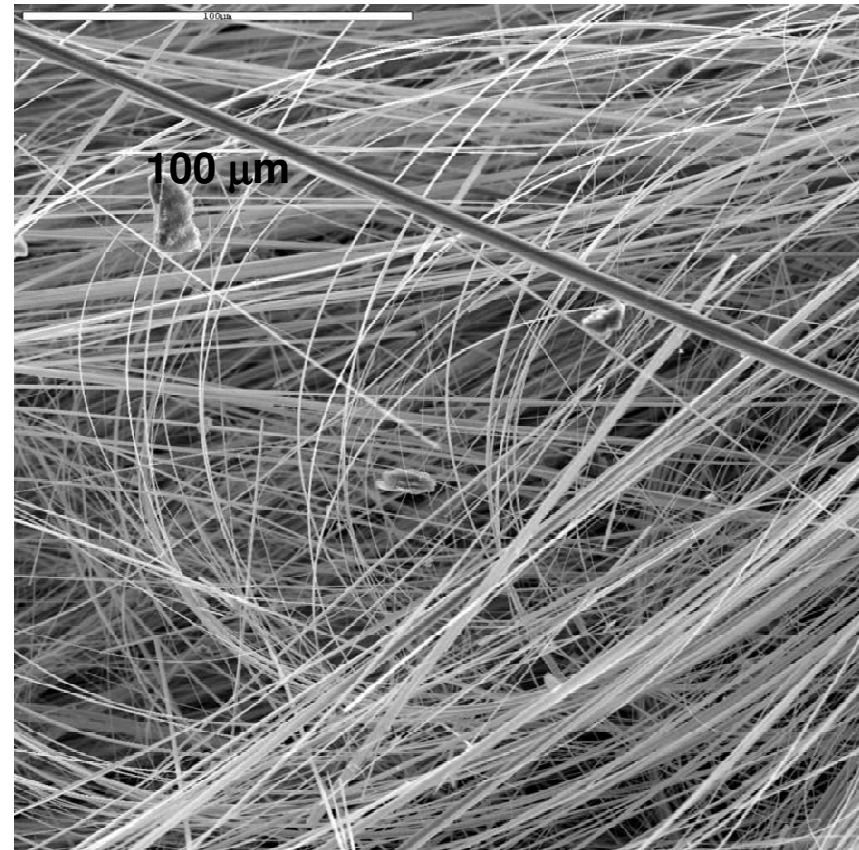
- Prah.

- Nastaja pri obdelavi, drobljenju, brušenju, razstreljevanju,...
- Označujemo prašne delce v zraku z velikostjo od 0.1 - 25 μm .

- Vlákna.

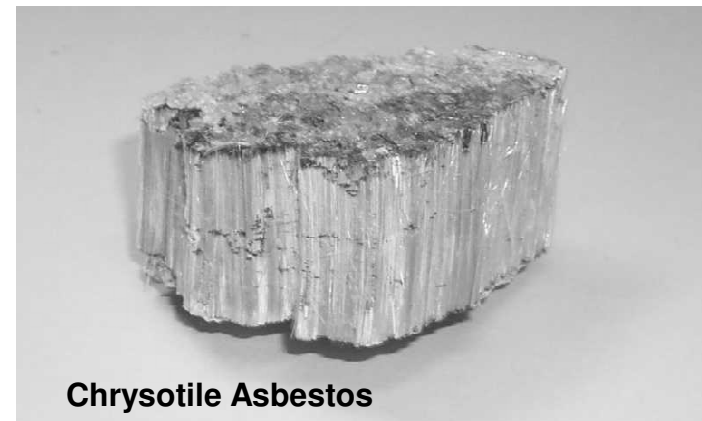
- Podobna velikost.
 - Bistveno večja dolžina od 6-12 mm.
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Nevarna trdna onesnaževala



Selected Hazardous Particulates

- Asbestos.^{20 μm}
 - Asbestosis, cancer.
- Beryllium.
 - Berylliosis, cancer.
- Bacteria.
 - Humidifier fever.
- Cotton dust.
 - Byssinosis.



Selected Hazardous Particulates

- Diesel exhaust.
 - Lung cancer.
 - Lead & compounds.
 - CNS, PNS, blood.
 - Nickel.
 - Nasal cancer, allergic contact dermatitis.
 - Pesticides.
 - CNS, cancer.
 - Cadmium, chromium, cobalt, manganese.
 - Cancer, CNS, pneumoconiosis.
-



Lead ore

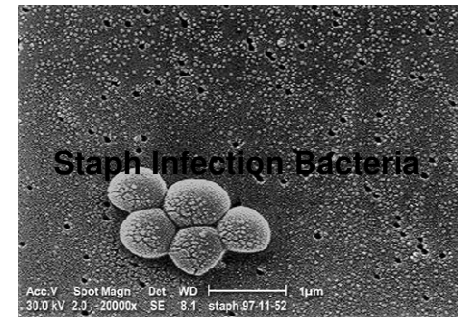
Gases and Vapors

- **Gas** is a fluid in the gaseous state having neither independent shape or volume.
- **Vapor** refers to a gas-phase material that that normally exists as a liquid or solid under a given set of conditions.



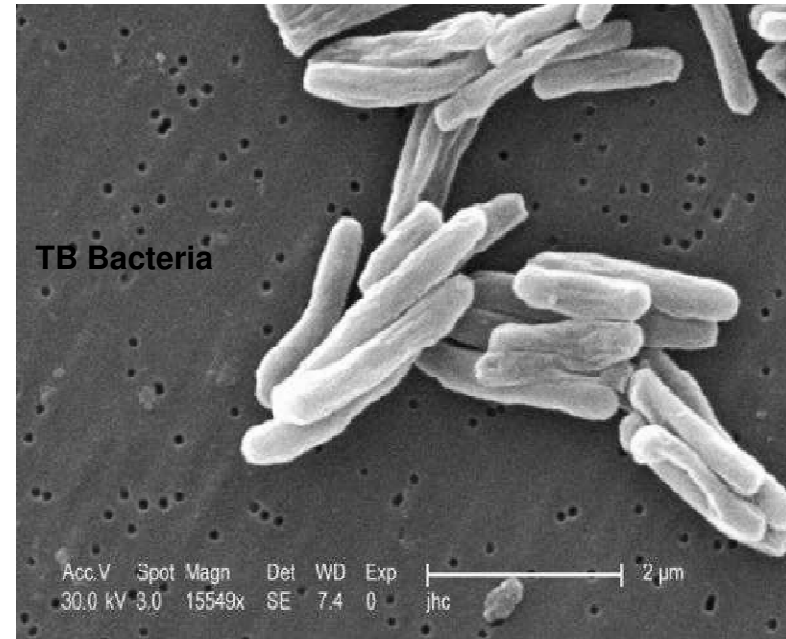
Critical Factors

- Determining exposure.
 - Chemical composition.
 - Crystalline, structural, & isotopic forms of particles.
 - Shape of particles.
 - Size of particles.
 - Dose: concentration vs. duration.
 - Pre-existing health or genetic status.
 - Concurrent exposure to other toxic agents.



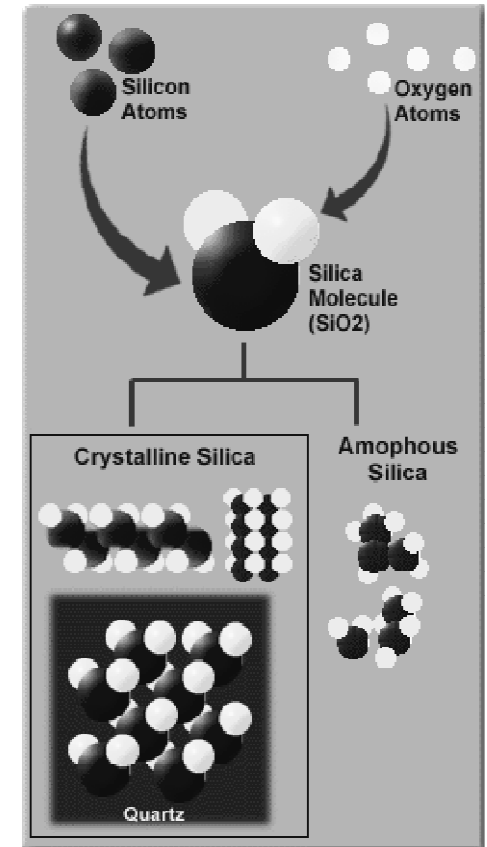
Chemical Composition

- Chemical composition can be primary concern.
 - Lead, cadmium, silica, smoke composition, radiological particles, etc.
- Biological organisms.
 - Type and numbers.



Crystalline, Structural, Isotopic Nature

- Silica dust.
 - “free crystalline silica”.
 - Diatomaceous earth.
 - Fumed silica.
 - Silica gel.
- Smokes, soots, organic origin.
- Radioisotopes.



Particulate Size Determination

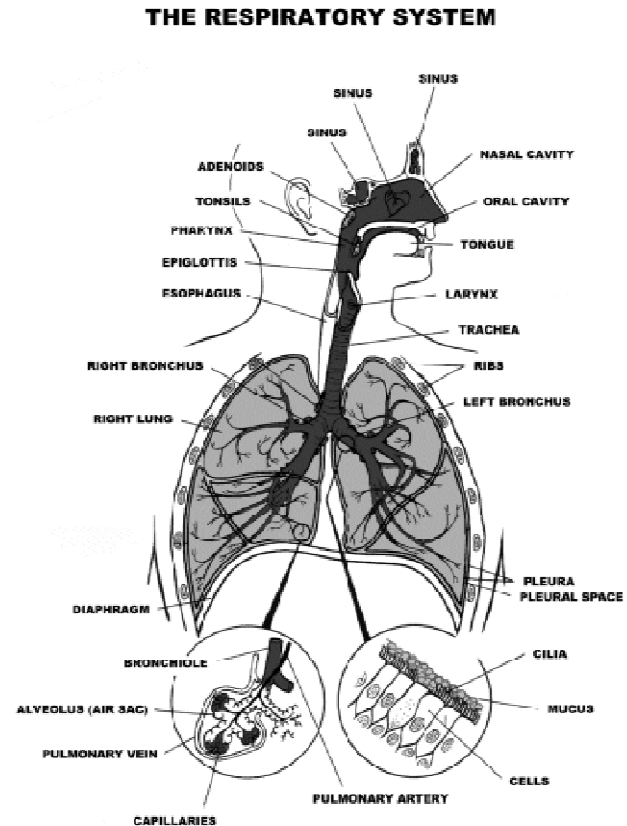
- Workers are not exposed to single particles but rather to large masses of particles suspended in air (particle clouds).
 - Particle clouds may be:
 - Monodisperse.
 - » Composed of airborne particulates with a single size or a small range of sizes.
 - » e.g. fog from boiling acid; welding fumes.
 - Polydisperse.
 - » Composed of airborne particulates of many different sizes.
 - » e.g. sand blasting; paint spraying.
-

Particle Size Terminology

- Micrometer (μm). A unit of length equal to one millionth of a meter. Also known as “micron.” Equal to 1/25, 400th of an inch.
 - Non-respirable. Particles $\geq 10 \mu\text{m}$ in diameter. Deposited in respiratory system before reach alveolar sacs in lungs.
 - Respirable. Particles $< 10 \mu\text{m}$ in diameter. Likely to reach alveolar sacs in great quantities.
-

Routes of Exposure

- Inhalation.
 - Through the lungs.
- Ingestion.
 - Swallowed.
- Absorption
 - Through the skin or eyes.
- Injection.
 - Needle stick.



Inhalation

- Chemicals in the air are inhaled into the body through the mouth or nose.
 - In the workplace, airborne chemicals may occur in different forms such as gases, vapors, dusts or mists.



Ingestion

- Ingestion can occur through eating or smoking with contaminated hands or in contaminated work areas.



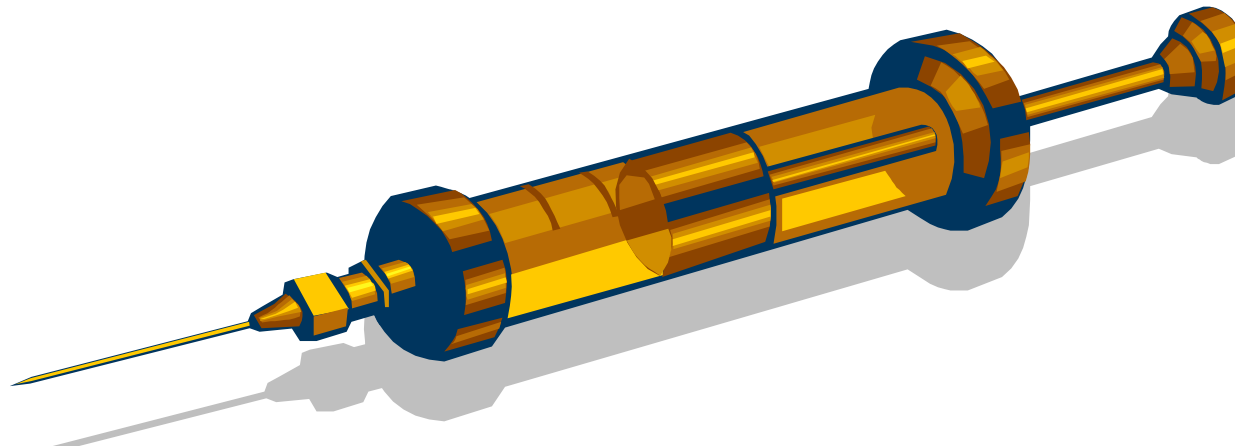
Absorption

- Skin contact with chemicals can result in irritation, allergic response, chemical burns, and allergic contact dermatitis.
- Physically damaged skin or skin damaged from chemical irritation or sensitization will generally absorb chemicals at a much greater rate than intact skin.



Injection

- Chemical substances can be injected into the body by accidentally puncturing the skin with a contaminated needle or other sharp device.



Exposure Terminology

- A **Permissible Exposure Limit (PEL)** is the maximum amount or concentration of a chemical that a worker may be exposed to under OSHA regulations.
 - **8-hour Time Weighted Averages (TWA)** are an average value of exposure over the course of an 8 hour work shift.
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Exposure Terminology

- **Threshold Limit Values (TLV)** are guidelines (**not** standards) prepared by the American Conference of Governmental Industrial Hygienists, Inc. (ACGIH) to assist industrial hygienists in making decisions regarding safe levels of exposure to various hazards found in the workplace.
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Exposure Terminology

- **Ceiling Values (C)** is an exposure limit for which at no time should it be exceeded.
 - **“Skin”** designation serves as a warning that cutaneous absorption should be prevented in order to avoid exceeding the absorbed dose received by inhalation at the permissible exposure level.
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Exposure Terminology

- **Short Term Exposure Limit (STEL)** is defined by ACGIH as the concentration to which workers can be exposed continuously for a **short** period of time without suffering from:
 - Irritation.
 - Chronic or irreversible tissue damage.
 - Narcosis of sufficient degree.
-

Exposure Terminology

- Acute.
 - Contact with a substance that occurs once or for only a short time.
 - Chronic.
 - Occurring over a long time.
 - Additive effect.
 - A biologic response to exposure to multiple substances that equals the sum of responses of all the individual substances added together.
-

PELs Are Dosages (D C & t)

- **Concentration (C).**
 - ppm – parts per million.
 - mg/m³ – milligrams per cubic meter.
 - mppcf – million particles per cubic foot.
 - μg/m³ – micrograms per cubic meter.
 - f/cc – fibers per cubic centimeter.
 - **Time period (t).**
 - 8-hour time-weighted average.
 - 15-minute short term exposure limits.
 - 30-minute excursion limits (EL).
 - Instantaneous or ceiling values.
 - Skin designation.
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Pre-Existing or Genetic Status

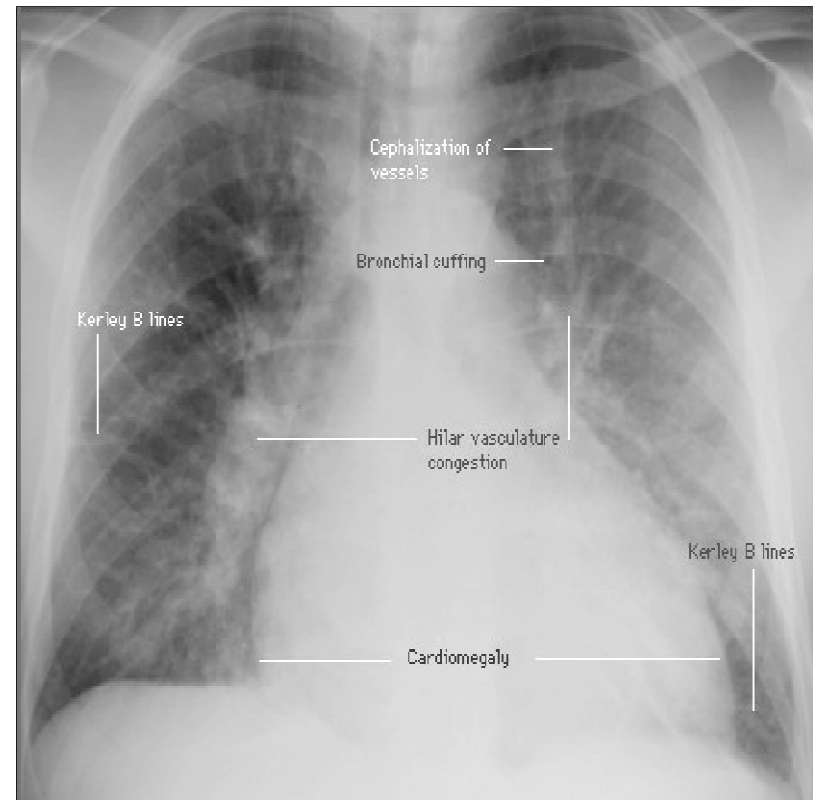
- Permissible exposure limits (PEL) and threshold limit values (TLV) are set for healthy workers.
 - Susceptibility of individuals is not taken into account when setting these levels.
 - Some medical evaluation is done as in pre-employment physicals and medical history.
-

Concurrent Exposures

- Exposures do not normally occur in isolation.
 - Some exposures follow the same route but have very different effects on body.
 - Some materials may also be additive, synergistic or potentiators.
 - Lead & thallium can be additive as they have similar toxic effects.
 - » When the exposures are measured together, the TWA fractions of the exposure limits are added, if total is >1.0 than overexposure has occurred.
 - Asbestos & smoking are synergistic (multiplier effect).
-

Biological Reactions

- Pulmonary irritants.
- Pulmonary edema.
- Acute or chronic bronchitis.
- Allergic sensitization.
- Fibrosis.
- Emphysema.
- Systemic toxicity.
- Lymphatic toxicity.
- Infection.
- Oncogenesis.
- Metal fume fever.



Meritve v delovnem okolju

- Meritve v delovnem okolju glede na mesto odvzema vzorcev delimo na:
 - meritve v širšem območju,
 - meritve osebne izpostavljenosti in
 - meritve vira onesnaženja.

Meritve v širšem območju

Meritve v širšem območju služijo za oceno imisijskih vrednosti merjenih spojin. Z meritvami želimo pokriti čim širše območje. Tak tip meritev ponavadi uporabljamo za meritve onesnaženja v okolju.

Če ni možno izvesti drugačnih meritev lahko takšne meritve uporabljamo tudi za oceno osebne izpostavljenosti v delovnem okolju (npr. meritve na večih mestih v proizvodnji hali lahko služi za oceno izpostavljenosti delavcev, ki se nahajajo v tem delovnem okolju).

Meritve osebne izpostavljenosti

- Če želimo, da so meritve osebne izpostavljenosti opravljene v skladu z OSHA standardi, moramo izvesti odvzem vzorca v dihalnem območju razen, če je to prepovedano zaradi specifik merilne tehnike ali delovnega okolja.
- Dihalno območje je definirano z namišljenim pravokotnikom, ki je omejen s širino ramen, sredino prsi in višino glave.

Meritve v vira onesnaženja

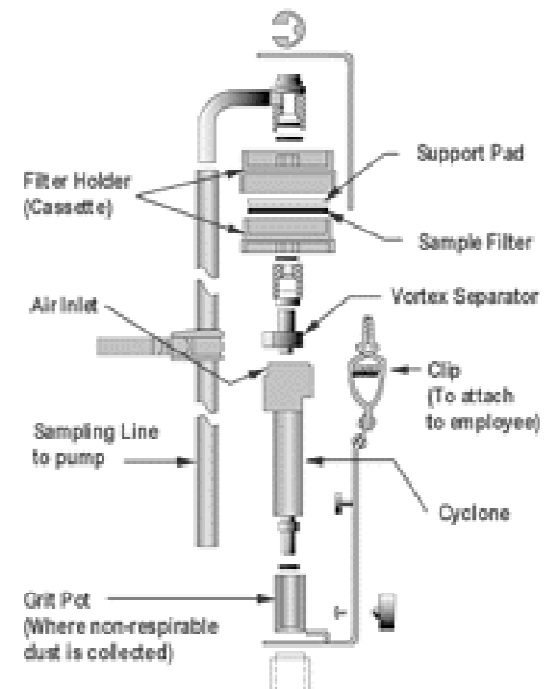
- Z meritvami vira onesnaženja določamo emisijske vrednosti merjenih spojin.
- V delovnem okolju s takimi meritvami predvsem kontroliramo znane vire onesnaženja delovnega procesa.
- Služijo lahko tudi za procesno kontrolo proizvodnje (npr. ob zaznavanju povišanih emisij strupenih spojin se lahko proizvodnja omeji/modificira ali celo ustavi).

Air Sampling & Analysis

- Area sampling.
 - Area where workers are located.
 - » Sampling pump and cassette placed in area.
 - » New instantaneous instruments to measure total, **PM10 and PM2.5**.
 - Microbiological sampling is generally area sampling using plates or impingers.
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Air Sampling

- Size selective particle sampling on filters for either gravimetric or microscope counting of fibers.
 - Respirable dust is collected on a filter (37mm) using a cyclone set up.
 - » Gravimetric analysis.
- Asbestos is collected on smaller filter.
 - 25 mm.



Cyclone filter

Gases and Vapors



Why Am I Making the Measurements?

- Personal protection.
 - Personal compliance monitoring.
 - TWA.
 - STEL or ceiling.
 - Area monitoring.
 - Confined space entry.
 - Hazardous spill.
 - May influence choice of range, battery life, etc. . . .
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What Gases/Vapors Do I Want to Measure?

- Gases or vapors measured limit the sensing technology used.
- Range will also limit sensing technology used.

**Magellan ammonia pipeline rupture in
Kingman Co., Kansas on Oct. 27, 2004.**



Integrirne tehnike

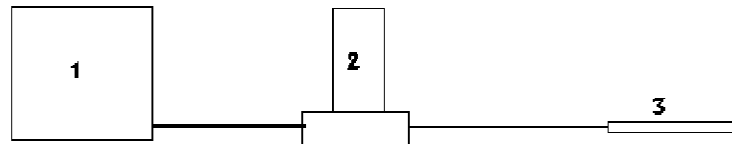
- Odvzem vzorca in meritev sta krajevno ločena (analiza poteka v laboratoriju).
- Meritve so enostavnejše (za izvedbo ne potrebujemo visoko usposobljenega osebja).
- Dobimo informacijo o povprečnih koncentracijah. Z njimi ponavadi ne zaznamo kratkotrajnih ekstremov.
- Integrirne tehnike so lahko aktivne ali pasivne.

Čas izpostavljenosti (jemanja vzorcev)

- Lahko sovpada s časom podanim v predpisu za omejevanje mejnih vrednosti (8 urna izpostavljenost).
- Čas jemanja vzorcev lahko skrajšamo, da dobimo informacijo o gibanju koncentracij tekom delovnega procesa (možna je zaznava tudi ekstremov).
- S krajšim časom jemanja vzorcev se v primeru kratkotrajnega izpada izognemo popolni izgubi informacije.

Aktivne tehnike

- Za aktivne tehnike je značilna uporaba energije (črpalke). Za določitev koncentracije merjene spojine potrebujemo poznati volumen prečrpanega zraka.



1 - črpalka
2 - masni regulator pretoka
3 - absorpcijska cevka

Med aktivne tehnike spadajo:

- črpanje na absorpcijske cevke,
- črpanje preko filtrov,
- izpiralke (impinger),
- črpanje v vreče ali cilindre itd.

Pasivne tehnike

● Pri pasivnih tehnikah ne potrebujemo vira energije. Za določitev koncentracije merjene spojine potrebujemo poznati čas izpostavljenosti vzorčevalnikov.

Med pasivne tehnike spadajo:

- difuzijske absorpcijske cevke,
- “badge” vzorčevalniki
- cilindri iz nerjavnega jekla itd.

Kot vidimo lahko določene tehnike uporabimo v aktivnem kot tudi v pasivnem načinu jemanja vzorcev.

Območje delovanja

- Odvzem vzorca mora biti prilagojen uporabljeni metodi končne določitve množine/mase merjene spojine ter specifikam vzorčevalnika.
- Sposobni moramo biti določiti merjeno spojino v območju od 0.1 do 2 MV.
- Glede na te omejitve moramo poznati minimalno in maksimalno količino prečrpanega zraka oz. časa izpostavljenosti.

Območje delovanja 2 (aktivno vzorčevanje)

- Minimalno količino prečrpanega zraka (MinPZ) določa meja detekcije instrumentalne metode. Izračunamo jo iz spodnje meje merilnega območja.

$$MinPZ(l) = \frac{MD(\mu g)}{0.1 * MV(\mu g / l)}$$

Maksimalno količino prečrpanega zraka (MaxPZ) določa kapaciteta absorbentov (KA). Izračunamo jo iz zgornje meje merilnega območja.

$$MaxPZ(l) = \frac{KA(\mu g)}{2 * MV(\mu g / l)}$$

Območje delovanja 3 (pasivni vzorčevalniki)

- Minimalen čas izpostave (t_{\min}) določa meja detekcije instrumentalne metode. Izračunamo jo iz spodnje meje merilnega območja in hitrosti vzorčevanja (hV), ki podaja hitrost nalaganja merjene spojine na vzorčevalnik.

$$t_{\min} (\text{min}) = \frac{MD(\mu\text{g})}{0.1 * hV (l / \text{min}) * MV(\mu\text{g} / l)}$$

Maksimalni čas izpostave (t_{\max}) določa kapaciteta absorbentov (KA) in hitrost vzorčevanja. Izračunamo jo iz zgornje meje merilnega območja.

$$t_{\min} (\text{max}) = \frac{KA(\mu\text{g})}{2 * hV (l / \text{min}) * MV(\mu\text{g} / l)}$$

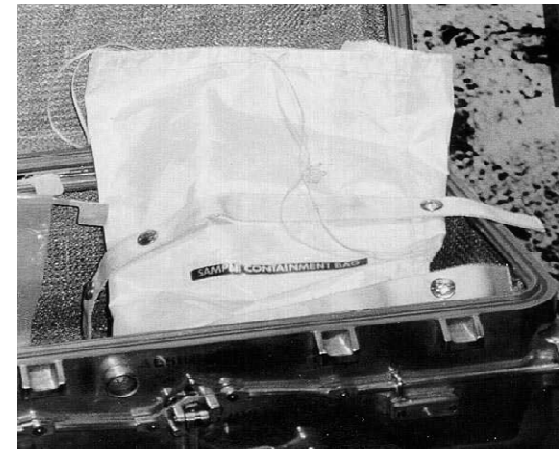
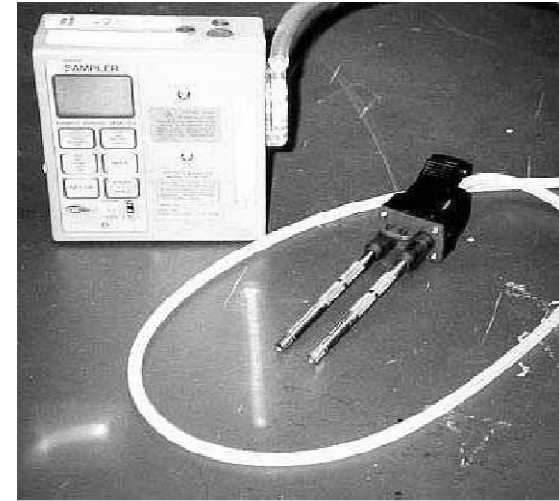
Gases and Vapors: Sampling Methods

- **Grab sampling.**
 - **Detector tubes.**
 - **Gas bags.**
- **Passive dosimetry.**
 - “Film badges”.
- **Active sampling.**
 - Sorbent tubes & personal sampling pump.
- **Direct reading instruments.**

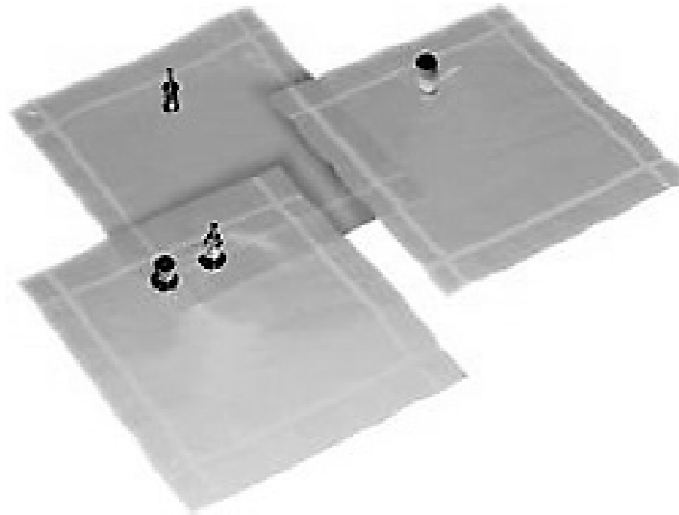


Gas Bags (Grab bags)

- Theory – samples are collected via a slow-flow sample pump and stored in a plastic or foil bag.
- A wide variety of gases can be measured.
- Advantages – Easy sample storage. A variety of bag materials adds to the unit's versatility.

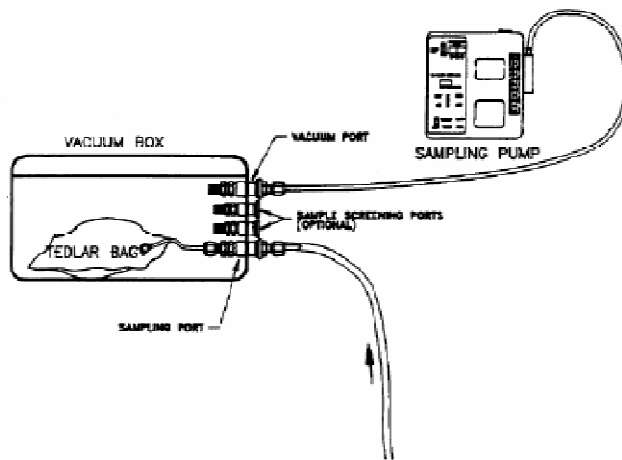


Jemanje vzorcev v vreče ali kanistre



V primeru uporabe Tedlerjevih vreč uporabimo poseben način odvzema vzorca. Tedlerjevo vrečo priključimo na posebno vakuumsko komoro, ki omogoči napolnitev vreče z zunanjim zrakom brez kontaminacije.

Volumen odvzetega zraka je omejen z volumnom vreče. Kupimo jih lahko različnih dimenzij.



Jemanje vzorcev v vreče ali kanistre

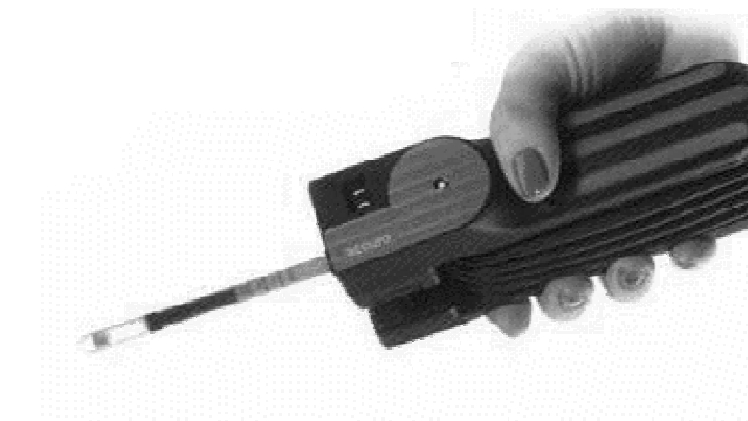
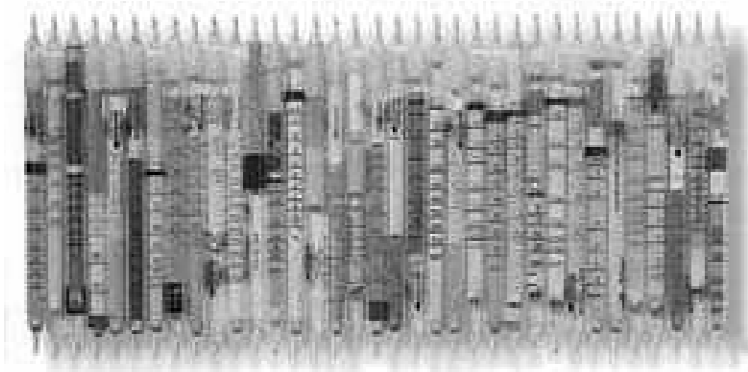


Kanistre pred vzorčevanjem evakuiramo in očistimo. Na terenu jih nato le odpremo in počakamo, da se tlak izenači z zunanjim tlakom.

Uporabljamo jih lahko za jemanje trenutnega vzorca ali kot integrirno tehniko.

Detector Tubes

- Theory - glass tubes filled with reagent that changes color in reaction to certain chemicals.
- Gases measured - Wide variety of gases can be measured.
- Advantages - Can measure many gases that cannot be measured by direct-reading instruments.



Detector Tubes

- Disadvantages –
 - Accuracy of $\pm 25\%$ under ideal conditions.
 - Must use hand pump (or electronic pump - RAE) and wait for reaction to take place.
 - Can't do continuous monitoring or sampling.
 - Temperature – pressure - time (TPT) dependence.
 - Examples of Tube Vendors: Dräger Safety, Kitegawa (Matheson), Sensidyne.
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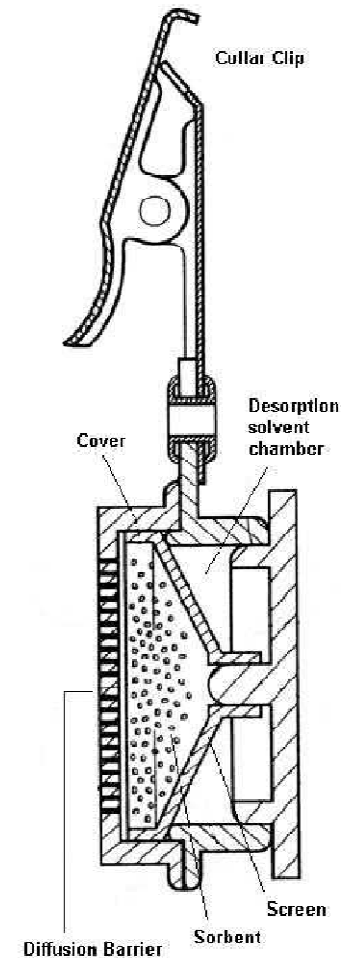
Gases and Vapors: Sampling Methods

- Grab sampling.
 - Detector tubes.
 - Gas bags.
- **Passive Dosimetry.**
 - “**Film badges**”.
- Active sampling.
 - Sorbent tubes & personal
- Direct reading instrument



Passive Sampling

- **Definition:** the collection of airborne gases and vapors at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane without the active movement of air through an air sampler.
- Diffusion of contaminated molecules from an area of high concentration to an area of low concentration on the sampler



Passive Dosimeters

- Partial list of substances for which badges are available:
 - Mercury (Hg).
 - Nitrous oxide (N_2O).
 - Ethylene oxide ($\text{C}_2\text{H}_4\text{O}$).
 - Formaldehyde (CH_2O).
 - Other organic substances.



Passive Dosimeters

- Advantages.
 - Easy to use.
 - Requires minimal training.
 - Economical — no costly pumps or sampling equipment is required.
 - Less burdensome to worker — only a lightweight badge or tube is worn.
 - Samplers are available that can be used for both short- and long-term sampling.
-

Passive Dosimeters

- Disadvantages.
 - No means to measure the air flow.
 - Theoretical uptake rate may not be valid for conditions of use.
 - Few analytical methods published by governmental agencies.
 - No indication of breakthrough or reverse diffusion.
 - Affected by wind velocity, temperature and humidity.
 - Sampling is either not accurate enough or not approved for compliance sampling.
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Gases and Vapors: Sampling Methods

- Grab sampling
 - Detector tubes
 - Gas bags
- Passive Dosimetry
 - “Film badges”
- **Active sampling.**
 - **Sorbent tubes & personal sampling pump.**
- Direct reading instruments



Active Sampling

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



Sorbent Tubes

- Common sorbent materials are:
 - Activated charcoal.
 - Silica gel.
 - Tenax.
 - XAD-2.
 - Chromosorbs.
- Sorbent used to collect specific chemicals will be specified in the sampling method.



Gases and Vapors: Sampling Methods

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-

Delitev merilnih tehnik glede na uporabljeno merilno opremo

- Meritve v realnem času
 - spektroskopske metode (enostavni spektrometri)
 - elektrokemijske metode (senzorji)

 - Integrirne merilne tehnike
 - uporaba absorpcijskih cevk
 - filtri (prah)
 - izpiralke
 - zbiranje celotnega vzorca v vreče ali cilindre
-

Meritve v realnem času

Take meritve so ponavadi povezane z višjimi stroški meritev.

Meritve so zahtevnejše z instrumentalnega stališča (problem izvedljivosti).

Odvzem vzorca in instrumentalna meritev poteka na istem prostoru.

Njihova prednost je predvsem podajanje rezultatov v realnem času v primeru alarmiranja in meritve v kratkih intervalih (možnost zaznavanja kratkih povišanih koncentracij merjenih spojin).

Flame Ionization Detector (FID)

- Examples of instruments:
 - Foxboro TVA 1000 Dual PID/FID.
 - Foxboro OVA 108 & 128 FIDs.
 - Fugitive Emissions LeakTracker Systems.
 - Heath DETECTO-PAK FID.
 - Photovac MicroFID.
 - Thermo Environmental 680.



Photo Ionization Detector

- Measures volatile organic compounds and other gases in concentrations from 1 parts per billion (ppb) to 10 000 parts per million (ppm).
- Efficient and inexpensive type of gas detector.
- capable of giving instantaneous readings and continuous monitoring.
- Widely used in military, industrial, and confined working facilities for safety.



Photo Ionization Detector

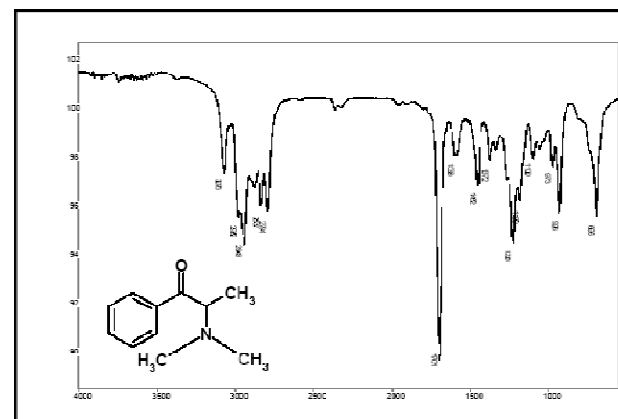
- Disadvantages.
 - Nonselective among organic vapors below ionization potential of lamp.
 - Affected by high humidity.
 - Higher potential lamps (11.7 eV) needed to measure CH_2Cl_2 have short life (~ 1 month).
 - UV lamps are expensive.
 - Examples of instruments: Photovac 2020, MSA Passport PID II, RAE Systems MiniRAE PLUS.
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Infrared Spectrophotometry

- An infrared spectrometer directs infrared radiation through a sample and records the relative amount of energy absorbed by the sample as a function of the wavelength or frequency of the infrared radiation.
 - the infrared radiation is selectively absorbed by the material to produce an absorption spectrum.
 - The spectrum produced is compared with correlation spectra from known substances.
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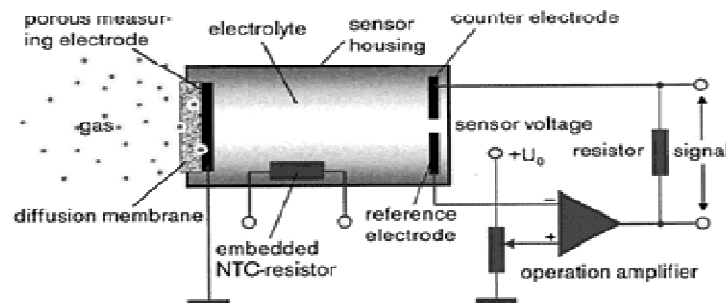
Infrared Spectrophotometry

- Advantages – can detect and measure some compounds that can't be measured by other methods.
- Disadvantages – expensive, complicated.
- Examples of instruments: Foxboro MIRAN SapphIRe.



Electrochemical Sensors

- Theory – Gas diffusing into sensor reacts at sensing electrode to cause current to flow.
- Gases measured - O_2 , CO , NO_2 , NO , H_2S , SO_2 , NH_3 , HCl , HCN , Cl_2 and organic vapors such as alcohols, aldehydes, or ketones.



Electrochemical sensor measuring principle

Electrochemical Sensors

- Disadvantages.
 - Not specific to single gas without use of filters or other methods.
 - HCl – zero drift due to bias voltage, zero drift at high temperatures, affected by rapid changes in %RH.
 - NH₃ – not entirely catalytic – electrolyte is used up, zero drift at high temperatures.
 - Examples of instruments: Dräger PAC III, Dräger Model 190, Quest SafeLog 100, Biosystems Toxi Ultra.
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Zaključek

- Izbira ustrezne merilne tehnike je odvisna od podatkov, ki jih želimo pridobiti za oceno tveganja.
 - Vse metode imajo svoje prednosti in slabosti, ki se jih upošteva pri izbiri optimalne merilne tehnike.
 - Sledi se pravilu, da se uporablja najenostavnejšo tehniko, ki še zagotavlja ustrezne rezultate.
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