



SAIOH Mpumalanga Information Session

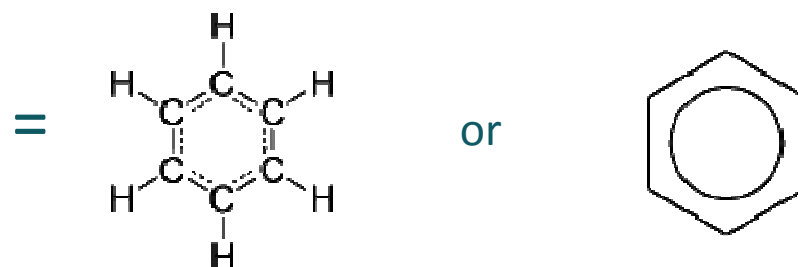
Poly-Aromatic Hydrocarbons and Coal Tar Pitch Volatiles

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Poly-Aromatic Hydrocarbons (PAHs)

- Poly = Plenty
- Aromatic = Ring structure organic compound (e.g. Benzene)



- Thus Poly-Aromatic Hydrocarbon = plenty of the above bound together (e.g. Naphthalene)



Coal Tar Pitch Volatiles (CTPVs)

- The name suggests that we are dealing with the volatile fraction (vapors/gas phase constituents) of Coal Tar or Pitch.
- But that is not the case – a true contradiction in terms
 - It actually refers to the fumes (airborne particulates) arising from the heating of Coal Tar/Pitch, or the Tar/Pitch fumes produced from the burning of Coal.
- Coal Tar is a by-product from the incomplete or anaerobic combustion of Coal

Poly-Aromatic Hydrocarbons (PAHs) – at least 19 known to be

Hazardous:

<u>Acenaphthene</u>	<u>Chrysene</u>
<u>Acenaphthylene</u>	<u>Coronene</u>
<u>Anthracene</u>	<u>Dibenz(a,h)anthracene</u>
<u>Benz[a]anthracene</u>	<u>Fluoranthene</u>
<u>Benzo[a]pyrene</u>	<u>Fluorene</u>
<u>Benzo[e]pyrene</u>	<u>Indeno(1,2,3-cd)pyrene</u>
<u>Benzo[b]fluoranthene</u>	<u>Naphtaline</u>
<u>Benzo[ghi]perylene</u>	<u>Phenanthrene</u>
<u>Benzo[j]fluoranthene</u>	<u>Pyrene</u>
<u>Benzo[k]fluoranthene</u>	

- Note that we are dealing with individual, identifiable substances
- PAHs occur in Oil, Coal, and Coal Tar deposits, and are produced as byproducts from incomplete combustion (whether fossil fuel or biomass).

Coal Tar Pitch Volatiles (CTPVs)

- Coal tars are complex and variable mixtures of Phenols, Poly-Aromatic Hydrocarbons and (PAHs), and hetero-cyclic hydrocarbons; about 200 substances in all.
- But, in Occupational Hygiene the standards are only concerned with those Constituents present in an airborne state as particulates/fume and which are also soluble in Benzene and/or Cyclohexane.

Coal Tar Pitch Volatiles (CTPVs)

- PAHs in an airborne particulate state (as a fume or adsorbed to a solid airborne particulate/soot) produced from the incomplete combustion of Coal

Poly-Aromatic Hydrocarbons (PAHs)

- PAHs in any airborne state (particulate or gas phase), produced from the incomplete combustion of any organic material.

CTPVs and PAHs - Chemistry

- From the above one realizes that in terms of chemistry/chemical composition, there is very little distinction between PAHs and CTPVs, to the point that they are almost synonymous.

- *Not to be confused with Asphalt/Bitumen*

CTPVs and PAHs - Confusion

- Where Coal Tar/Pitch is present, at conditions where CTPVs (fume/particulates) are liberated, the same compounds (that make up the fume) will also be present in the gas/vapor phase as well.
- Where incomplete combustion of organic material occurs, and gas phase PAHs are liberated, these same PAHs will also, always be present in the airborne particulate phase as well (that is what we call smoke/soot).

CTPVs and PAHs – Assessment

- Therefore, to only view Coal Tar processes as sources of exposure to CTPVs (fumes/particulates), one could be ignoring 50% or more of the hazard (the gas phase substances/PAHs).
- Similarly, if one only considers PAHs (gases/vapors) when assessing a process where combustion of organic material occurs, one could underestimate the risk by far.
- In any such situation, it thus make sense to rather consider exposure to PAHs; gas phase and airborne particulate
 - *Where there is smoke,there are PAHs - gas phase and particulates*

- **Cancer (particularly Lung and URT cancer) - CARCINOGENICITY DESIGNATION A1 - Confirmed Human Carcinogen.**
- **Probably also Liver tumors**
- **Phototoxic tar dermatitis** results from Coal Tar, in conjunction with sunlight exposure, which induces a sunburn reaction associated with severe burning sensation – also called erythema (severe sunburn) and heightened UV sensitivity, chronic tar dermatosis, tar or pitch warts, chronic melanosis, folliculitis, pitch acne and skin cancer (*remember the sad story of scrotum cancer*).

- High vapor or particulate concentrations can cause conjunctivitis sometimes combined with superficial keratitis (arc-eyes) – also photophobia.
- Coal tar is neurotoxic and can cause numbness or tingling in the hands or feet or in the area of directly exposed skin.
- This stuff really make you sick.

From here onwards, we shall consider PAHs and CTPVs as one and the same thing, but we will refer to it as PAHs, as PAHs can be present in the Particulate and gas/vapor phase.

- **Remember – where there is smoke....**
- **Any process dealing with the devolatilisation, or carbonization of Coal:**
 - Coal gasification/liquefaction (SASOL)
 - Production of Coke (Steel industries)
 - Production of Char (Steel industries)
 - Production of Electrode paste - Smelting
 - Production of Electrically Calcined Anthracite for the production of electrode Carbon/Graphite
 - Production of CO gas – Gas producers

- **Any process that uses the waste products and residue from the above processes (Tar/Pitch):**
 - Any viscous black waste product from SASOL (Tar, Pitch, Creosote, Furnace oil, etc.)
 - Wood preservation
 - Road surfacing
 - Roof sealants
 - Refractory mortars – and off-gassing during curing
 - Etc. SASOL produces a lot of it

- **Any process involving combustion of organic materials:**
 - Coal, wood (charcoal) and veld fires
 - Cigarette smoke
 - Toast
 - Braaivleis
 - Smoked meats
 - Dark beers
 - Etc. Wherever there is smoke.....

CTPV Sampling:

- NIOSH 5042: BENZENE-SOLUBLE FRACTION AND TOTAL PARTICULATE
 - TECHNIQUE: Gravimetric
 - OVERALL PRECISION (rT): not determined
 - ACCURACY: not determined

Yields a gravimetric value for particulate phase PAHs (only).

CTPV Sampling:

- **OSHA 58:** Airborne Particulate sampling and gravimetrically determining the Benzene-soluble fraction (BSF). If the BSF exceeds the appropriate PEL, then the sample is analyzed by high performance liquid chromatography (HPLC) with a fluorescence (μL) or ultraviolet (UV) detector to determine the presence of selected polynuclear aromatic hydrocarbons (PAHs) at “target” concentrations:
 - Phenanthrene
 - Anthracene
 - Pyrene
 - Chrysene
 - Benzo(α)pyrene
- *These selected PAHs are analyzed to confirm presence of CTPV only.*
- Overall Precision = 16.2%

NIOSH and OSHA Sampling Methods for CTPV:

- Both methods only consider the particulate phase PAHs.

PAH Sampling:

- **NIOSH Method 5506:** POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC (or GC I suppose) + acetonitrile extraction:
 - **SAMPLER:** FILTER + SORBENT TUBE (37-mm, 2- μ m, PTFE + washed XAD-2, 100mg/50 mg).
 - **OVERALL PRECISION (rT):** not determined
 - **ACCURACY:** not determined
- With this method, one can identify the presence of the specific PAHs present
- It has the great advantage that one can observe the amounts of PAHs in their different phases (particulates on the filter and gas phase on the tube) – why is this important?

PAH Sampling:

- **NIOSH Method 5506:** POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC (or GC, I suppose) + acetonitrile extraction:
- With this method one can Identify and quantify 17 PAHs (or more):
 - Acenaphthene, benzo[ghi]perylene, fluorene,
 - Acenaphthylene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene,
 - Anthracene, benzo[e]pyrene, naphthalene,
 - benz[a]anthracene, chrysene, phenanthrene,
 - benzo[b]fluoranthene, dibenz[a,h]anthracene, pyrene,
 - benzo[k]fluoranthene and fluoranthene.

International Exposure Limits for PAHs/CTPVs

- **OSHA GENERAL INDUSTRY PEL:** 0.2 mg/m³ TWA
- **OSHA CONSTRUCTION INDUSTRY PEL:** 0.2 mg/m³ TWA
- **ACGIH TLV:** 0.2 mg/m³ TWA; Appendix A1 (Confirmed Human Carcinogen)
- **NIOSH REL:** 0.1 mg/m³ TWA-Cyclohexane Extractable Fraction, Potential Carcinogen

Some of the institutions above (OHSA in particular) do not have separate OELs (PELs) for CTPVs and individual PAHs; meaning the same PEL apply regardless whether PAHs or CTPVs were sampled.

OHS Act Exposure Limits for PAHs/CTPVs

- Coal Tar pitch volatiles - as Cyclohexane solubles = 0.14 mg/m³ TWA
- Naphthalene = 50 mg/m³ TWA

Thus in this case we (in South Africa) only have an OEL for CTPVs (as total Cyclohexane soluble fraction of particulates) and one for one gas phase PAH (namely Naphthalene) – surely not enough, considering that at most processes, both particulate/fume phase CTPVs/PAHs as well as far more than just one gas phase PAH (Naphthalene) is liberated. Yet, exposure to both phases occurs simultaneously.

A possible solution

- Sample according to NIOSH Method 5506 (filter and tube in series) which will capture both, the particulate and gas phase PAHs
- HPLC (or GC) analyses will then Identify and quantify the individual PAHs, but separately for the particulate and gas phase PAHs. From this one can determine the focus of control interventions (controlling gas and particulate exposures require different strategies – at least now you know which one to follow)
- By adding all the PAH mass quantities together (from the filter and tube analyses) one can compute a total PAH/CTPV concentration, which one can compare to the OHS Act's OEL for Coal Tar pitch volatiles (0.14 mg/m³ TWA)
- *It is not perfect, but it is safe.*

- **General Discussion and Questions**

Thank You



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