

Analysis Methods and Requirements

for

Coal Tar Pitch Volatiles (CTPV) &
Polynuclear Aromatic Hydrocarbons (PAH)

Southern
African
Institute for
Occupational
Hygiene



Presented by
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r



Coal Tar Pitch Volatiles (CTPV) & Coke Oven Emissions (COE)

Definitions

- Coal Tar, Coal Tar Pitch & Creosote – NIOSH
- Pyrene, Phenanthrene, Acridine, Chrysene, Anthracene & Benzo(a)pyrene (48-65% PAH) – OHSA
- 90% PAH & lesser % Phenols – European Commission
- Mainly PAH – HSE
- Mixture of Phenols, PAH & Heterocyclic Compounds (around 200) – Wikipedia

Coal Tar Pitch Volatiles (CTPV) & Coke Oven Emissions (COE)

Sources

- Coking Operations
- Tar Distillation, Heating of Coal Tar & Pitch
- Downstream uses of Tar & Pitch e.g.
 - Aluminium Smelting
 - Roofing
 - Road Paving
 - Wood Preserving

Available Methods & History

CTPV

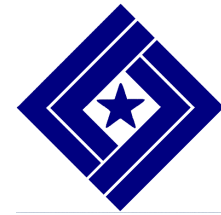
- OSHA Method 58 (1986)
- NIOSH Method 5042 (1998)
- MDHS Method 68 (1990 withdrawn)

PAH / PACs

- OSHA Method 58 (1986)
- NIOSH Method 5506 (1998)
- NIOSH Method 5515 (1994)
- NIOSH Method 5800 (1998)



OHSA Method 58



for

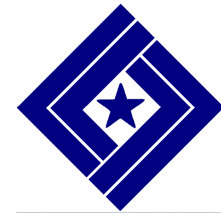
Coal Tar Pitch Volatiles (CTPV)

Coke Oven Emissions (COE)

Selected Polynuclear Aromatic Hydrocarbons



OHSA Method 58

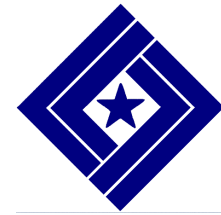


Procedure

- Air is drawn through cassettes containing Glass Fibre Filters (GFF)
- Samples are transferred to container
- Filters are extracted with Benzene
- Gravimetric determination of benzene-soluble fraction (BSF)
- Optional instrumental analysis of selected PAH compounds

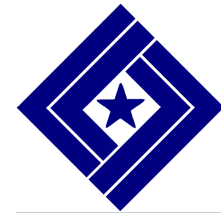


OHSA Method 58





OHSA Method 58



Special Requirements

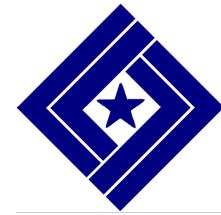
- Transfer sample to container in the field by Industrial Hygienist
- Protect sample from light (UV)

Reliable Quantitation Limits

- 0.033mg / sample for BSF
- 0.06 to 1 μ g/sample for selected PAH



OHSA Method 58



Advantages

- Sampling procedure is relatively simple

Disadvantages

- Sample transferred in field by Industrial Hygienist
- Expensive equipment needed for a gravimetric analysis (6 Decimal Balance etc.)
- Working with a confirmed carcinogen (Benzene)
- Method non-specific for CTPV compounds
- Quantitation limit = 20% of OEL



NIOSH Method 5042



for

Benzene-Soluble Fraction (BSF)

Total Particulate

Asphalt Fume



NIOSH Method 5042



Procedure

- Air is drawn through cassettes containing Teflon filters (PTFE)
- Gravimetric determination of total particulate fraction
- Filters are extracted with Benzene
- Gravimetric determination of benzene-soluble fraction (BSF)



NIOSH Method 5042



Special Requirements

- None

Reliable Quantitation Limits

- 0.13mg / sample for Particulates
- 0.14mg / sample for BSF



NIOSH Method 5042



Advantages

- Sampling procedure is relatively simple

Disadvantages

- Expensive equipment needed for a gravimetric analysis (6 Decimal Balance etc.)
- Working with a confirmed carcinogen (Benzene)
- Method non-specific for CTPV compounds
- Quantitation limit = 100% of OEL



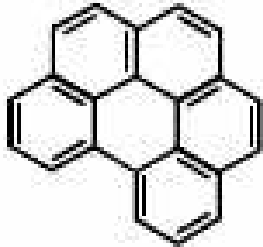
NIOSH Method 5506



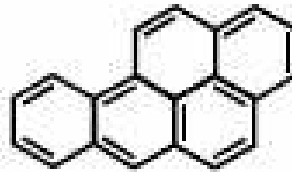
for

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benz(a)anthracene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(ghi)perylene
- Benzo(a) pyrene
- Chrysene
- Dibenz[a,h]anthracene
- Fluoranthene
- Fluorene
- Indeno[1,2,3-cd]pyrene
- Naphthalene
- Phenanthrene
- Pyrene

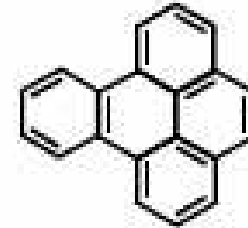
Structures of some PAH



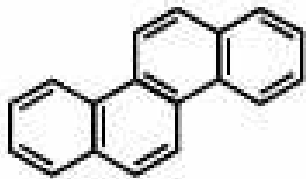
BENZO[ghi]PERYLENE



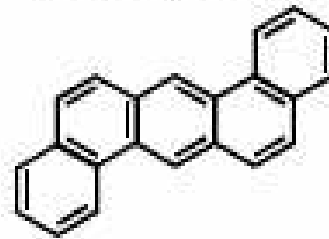
BENZO[a]PYRENE



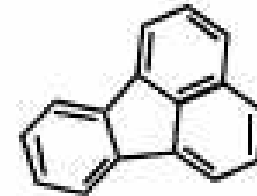
BENZO[e]PYRENE



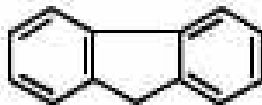
CHRYSENE



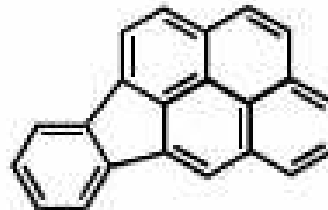
DIBENZ[a,h]ANTHRACENE



FLUORANTHENE



FLUORENE



INDENO[1,2,3-cd]PYRENE



NAPHTHALENE



NIOSH Method 5506



Procedure

- Air is drawn through a cassette containing a Teflon filter (PTFE) and a XAD-2 sorbent tube
- Filter is extracted with Acetonitrile
- Sorbent is extracted with Acetonitrile
- High performance liquid chromatography (HPLC) analysis of PAH compounds



NIOSH Method 5506





NIOSH Method 5506



Special Requirements

- Protect samples from UV light, heat, ozone and nitrogen dioxide

Reliable Quantitation Limits

- 0.005 to 0.5 μ g/sample for selected PAH



NIOSH Method 5506



Advantages

- Sampling procedure is selective for PAH
- Analysis is highly sensitive (<1% of OEL)
- Fast analysis times compared to CTPV analysis

Disadvantages

- Expensive equipment needed for analysis
- Samples need to be cooled and protected to prevent losses of PAH
- Highly trained technicians needed for analysis



NIOSH Method 5515



for

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benz(a)anthracene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(ghi)perylene
- Benzo(a) pyrene
- Chrysene
- Dibenz[a,h]anthracene
- Fluoranthene
- Fluorene
- Indeno[1,2,3-cd]pyrene
- Naphthalene
- Phenanthrene
- Pyrene



NIOSH Method 5515



Procedure

- Air is drawn through a cassette containing a Teflon filter (PTFE) and a XAD-2 sorbent tube
- Filter is extracted with Dichloromethane
- Sorbent is extracted with Dichloromethane
- Gas chromatography Mass spectroscopy (GC/MS) analysis of PAH compounds



NIOSH Method 5515



Special Requirements

- Protect samples from UV light, heat, ozone and nitrogen dioxide

Reliable Quantitation Limits

- 0.01 to 0.2 μ g/sample for selected PAH



NIOSH Method 5515



Advantages

- Sampling procedure is selective for PAH
- Analysis is highly sensitive (<0.5% of OEL)
- Fast analysis times compared to CTPV analysis

Disadvantages

- Expensive equipment needed (less than HPLC)
- Samples need to be cooled and protected to prevent losses of PAH
- Highly trained technicians needed for analysis



NIOSH Method 5515



Analysis Methods and Requirements for

Crystalline Silica (Respirable)

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Institute for
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Hygiene



Presented by
W.D.Wepene
r



Crystalline Silica (Quartz)

Types and forms

- Quartz is just one of 11 crystalline and 2 non-crystalline polymorphs of the compound Silica (SiO_2)
- 12 of these polymorphs are found in nature and 11 of them on earth

Quartz Rock Crystal



SiO₂ Polymorphs

Silica Polymorphs (Network polymorphs)

Quartz, Low-Quartz, α -Quartz, Alpha-Quartz

High Quartz, β -Quartz, Beta-Quartz

α -Tridymite, Low-Tridymite

β -Tridymite, High-Tridymite

α -Cristobalite, Low-Cristobalite

β -Cristobalite, High-Cristobalite

Moganite, Lutcite, Lutecine

Coesite

Keatite

Non-Silica Polymorphs

Stishovite

Seifertite

SiO₂ Polymorphs

Stability and Temperature

- Quartz is only stable polymorph @ STP
- All other forms will transform to Quartz in time

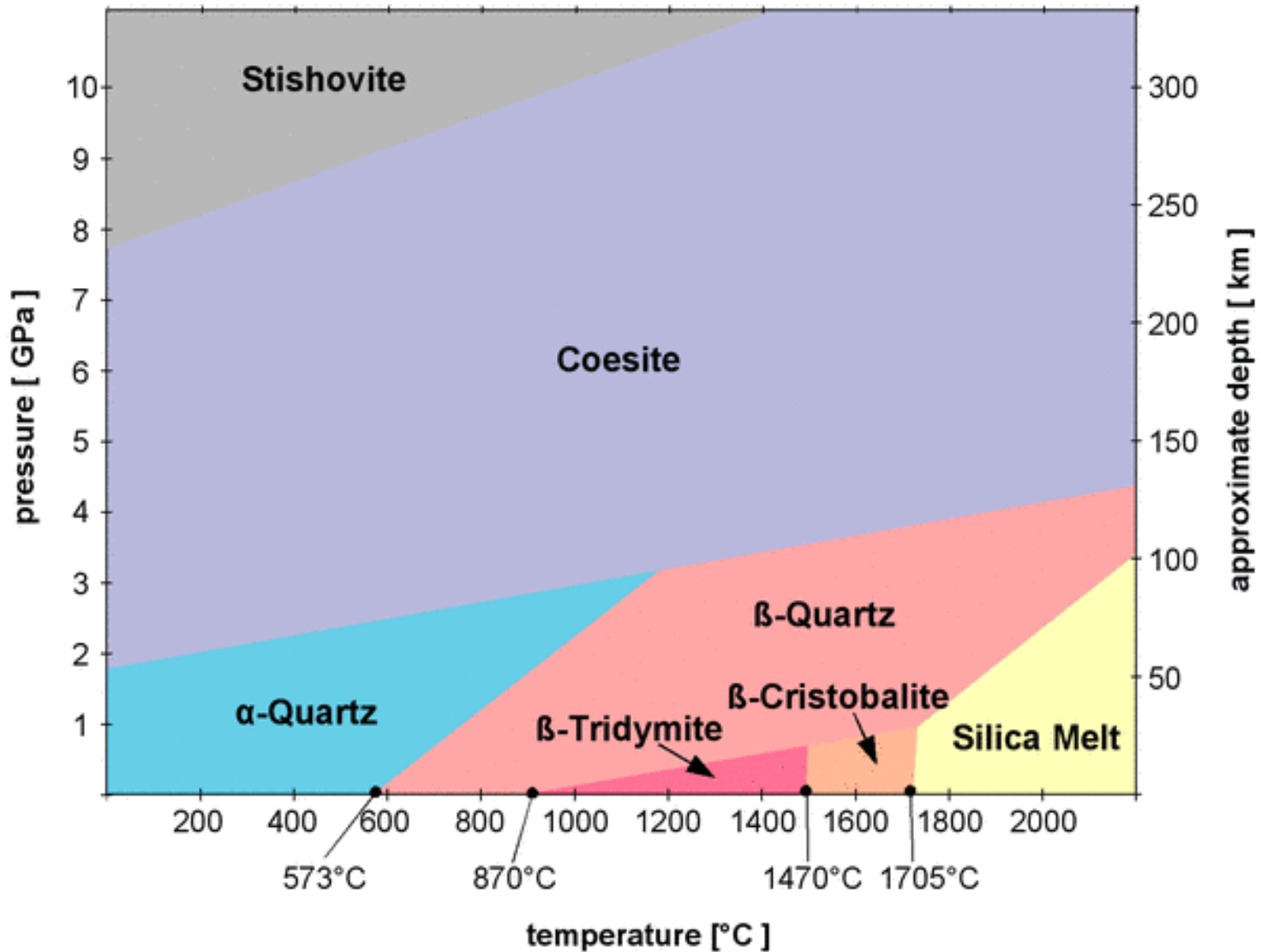
Transformations

- α -Quartz to β -Quartz @ 573°C
- β -Quartz to β -Tridymite @ 870°C
- β -Tridymite to β -Cristobalite @ 1470°C
- @ 1705°C β -Cristobalite Melts

SiO₂ Polymorphs



Phase Diagram of SiO₂



Available Methods & History

Crystalline Silica (Quartz)

- OSHA Method ID-142 (1981)
- NIOSH Method 7500 (1998)
- MDHS Method 101 (2005)
- NIOSH Method 7602 (1994)
- NIOSH Method 7603 (1994)



OHSA Method ID-142

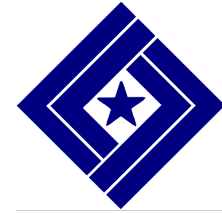


Procedure

- Air is drawn through cyclone and cassettes containing Polyvinyl Chloride filters (PVC)
- Samples are extracted with Tetrahydrofuran (THF) and sonicated to form a suspension
- Sample is redeposited on silver membrane filters
- Instrumental analysis by X-ray diffraction

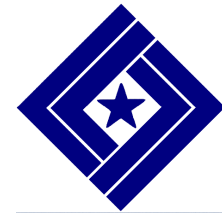


OHSA Method ID-142





OHSA Method ID-142

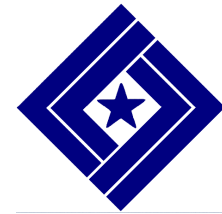


Reliable Quantitation Limits

- 0.01 mg / sample for Quarts
- 0.03 mg / sample for Cristobalite



OHSA Method ID-142



Advantages

- Can differentiate between Quarts and Cristobalite

Disadvantages

- Room for error introduction in sample preparation
- Expensive equipment needed for analysis (XRD)
- Highly trained technicians needed for analysis
- Quantitation limit = 10-30% of OEL



NIOSH Method 7500



Procedure

- Air is drawn through cyclone and cassettes containing Polyvinyl Chloride filters (PVC)
- Samples are ashed and suspended in 2-Propanol or extracted with Tetrahydrofuran (THF) and sonicated to form a suspension
- Sample is redeposited on silver membrane filters
- Instrumental analysis by X-ray diffraction



NIOSH Method 7500



Reliable Quantitation Limits

- 0.02 mg / sample for Quarts



NIOSH Method 7500



Advantages

- Can differentiate between Quarts, Tridymite and Cristobalite

Disadvantages

- Room for error introduction in sample preparation
- Expensive equipment needed for analysis (XRD)
- Highly trained technicians needed for analysis
- Quantitation limit = 20% of OEL



MDHS Method 101

Procedure

- Air is drawn through cyclone and cassettes containing Polyvinyl Chloride filters (PVC)
- Direct on Filter analysis by either Infrared Spectrometry (IR) or XRD



MDHS Method 101

Reliable Quantitation Limits

- 0.01 mg / sample for Quarts by IR
- 0.02 mg / sample for Quarts by XRD
- 0.04 mg / sample for Cristobalite by XRD



MDHS Method 101

Advantages

- Lower room for error (Minimal sample preparation)
- Can differentiate between Quarts forms
- Inexpensive equipment for analysis (IR)

Disadvantages

- Expensive equipment needed for analysis (XRD)
- Many interfering compounds with IR
- Highly trained technicians needed for analysis



NIOSH Method 7602



Procedure

- Air is drawn through cyclone and cassettes containing Polyvinyl Chloride filters (PVC)
- Samples are ashed, mixed with potassium bromide (KBr) and a wafer is pressed
- Instrumental analysis by IR



NIOSH Method 7602



Reliable Quantitation Limits

- 0.01 mg / sample for Quarts by IR



NIOSH Method 7602



Reliable Quantitation Limits

- 0.01 mg / sample for Quarts by IR



NIOSH Method 7602



Advantages

- Inexpensive equipment for analysis (IR)
- Quantitation limit = 10% of OEL

Disadvantages

- Lots of room for error in sample preparation
- Long and costly sample preparation times
- Many interfering compounds with IR
- Highly trained technicians needed for analysis



NIOSH Method 7603



Procedure

- Air is drawn through cyclone and cassettes containing Polyvinyl Chloride filters (PVC)
- Samples are ashed, suspended in 2-propanol and redeposited on DM-450 filter
- On filter Instrumental analysis by IR



NIOSH Method 7603



Reliable Quantitation Limits

- 0.03 mg / sample for Quarts



NIOSH Method 7603



Advantages

- Inexpensive equipment for analysis (IR)

Disadvantages

- Lots of room for error in sample preparation
- Long and costly sample preparation times
- Many interfering compounds with IR
- Highly trained technicians needed for analysis
- Quantitation limit = 30% of OEL

Sample Viability



References

- OSHA – US Department of Labour
- NIOSH – Centers for Disease Control and Prevention
- ATSDR – Agency for Toxic Substances & Disease Registry
- HSE – Health and Safety Executive
- EPA – Environmental Protection Agency
- EC – European Commission (Scientific Committees)
- Wikipedia
- The Quarts Page (<http://www.quartzpage.de>)