Effects of fire conditions on the formation of polycyclic aromatic hydrocarbons (PAHs): Sampling and analysis of fire effluents

Presented by:

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University of Central Lancashire
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Overview

- Introduction
- Factors affecting fire
- Characterization of Polycyclic Aromatic Hydrocarbons (PAHs)
- PAH's generation and analysis
- Different methods of sampling
- Results
- Conclusions

Introduction

Since 1950s there have been increasing quantities of synthetic polymer materials derived from crude oil. These materials used for construction, transport, electrical and electronic equipment, furniture etc. These materials make life easier and more comfortable.



However, these materials are easier for ignition and flame spread, accompanied by significant release of toxic combustion products.

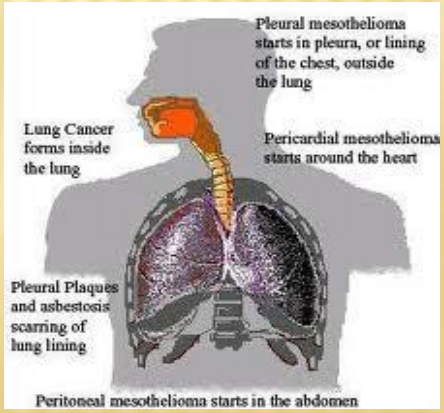


What is in fire?

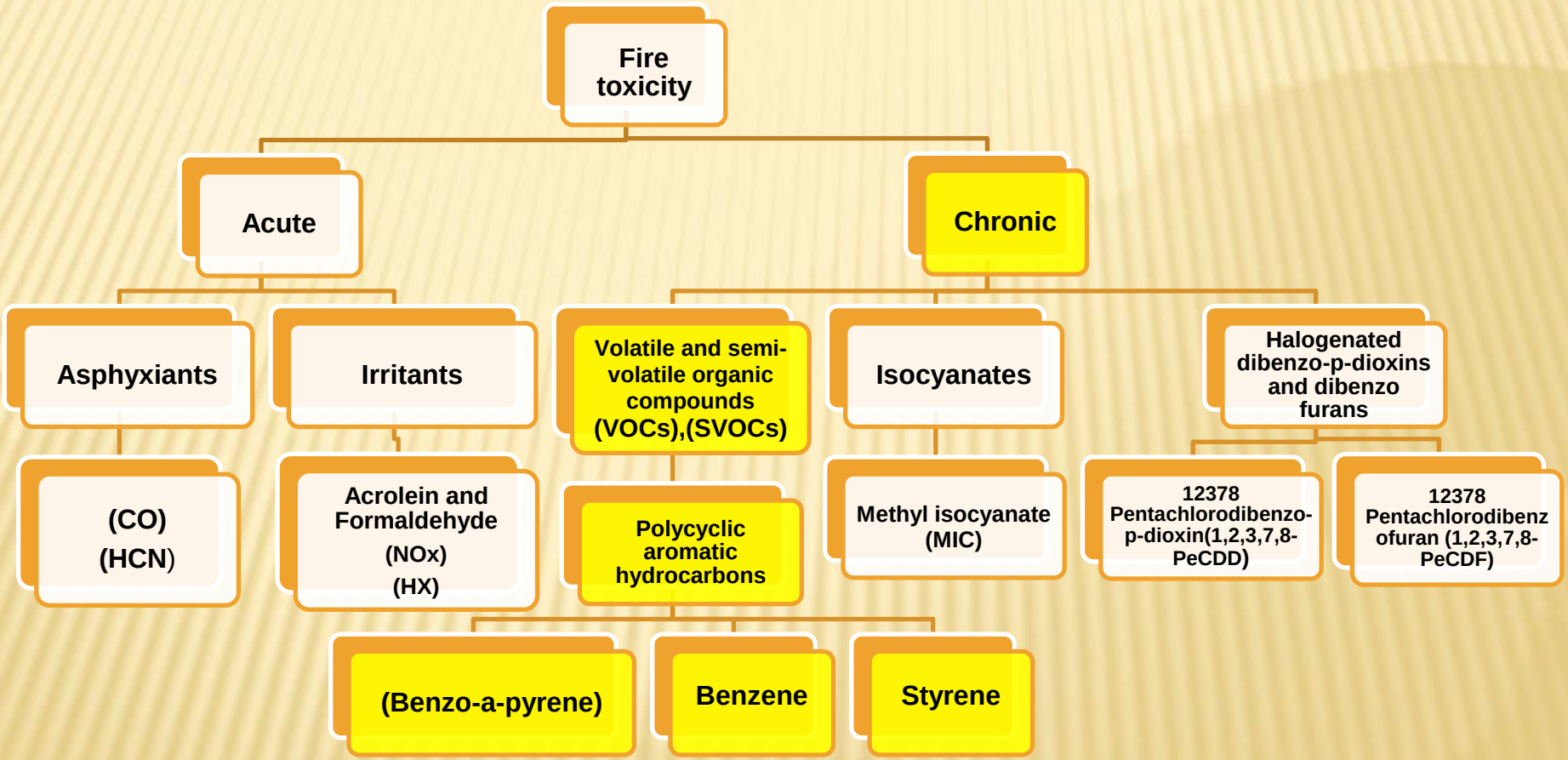
Majority of the toxic organic compounds such as volatile organic compounds (VOCs) or semi-volatile organic compounds (SOVCs) including polycyclic aromatic hydrocarbons (PAHs) are formed and released in fires, particularly as a result of incomplete combustion.

Exposure to some of these compounds may show both acute and chronic toxicity. The acute and chronic effects can occur immediately or over a couple of weeks. Painful sensory irritation occurs immediately in the upper respiratory tract, while lung inflammation and pulmonary oedema occur several days after exposure deeper in the lung

Subsequence to exposure of these compounds may result in different types of cancers as documented in fire fighters, who are subject to more frequent exposure.



Factors affecting fire

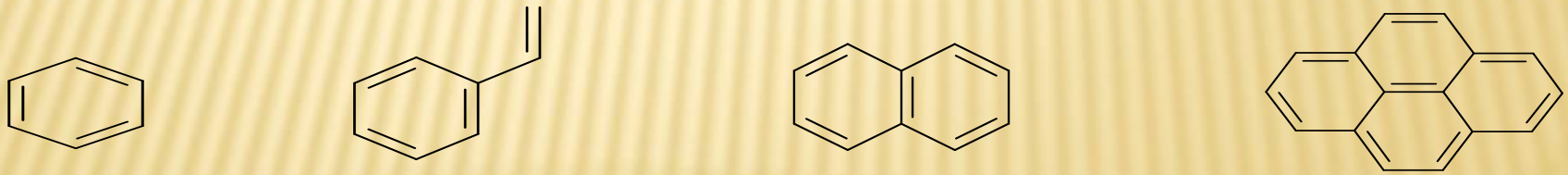


Characterization of Polyaromatic Hydrocarbons (PAHs)

PAHs are a large group of organic compounds that are consisted of two or more joined aromatic rings. It can be formed small unstable precursor compounds for PAHs by two paths;

From saturated hydrocarbons in vitiated combustion atmospheres. In this case, low molecular weight hydrocarbons act as precursors in the pyro-synthesis of PAH compounds that take place at temperatures above 500°C.

Thermal breakdown of heavier hydrocarbons. Several hundred of PAHs have been found. The best known is benzo[a]pyrene (BaP), metabolised to oxygenated forms acting as a carcinogen in the body.

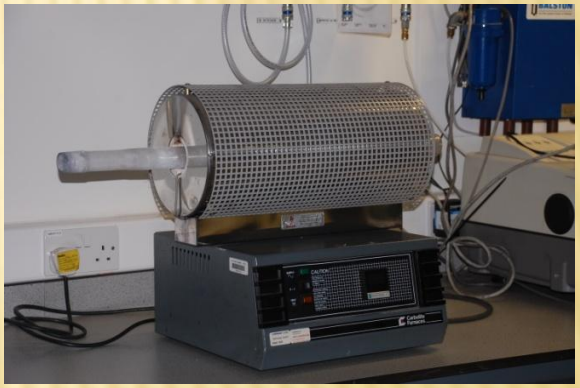


Individual PAHs can also cause a range of non-cancer effects (mutagenicity, teratogenicity).

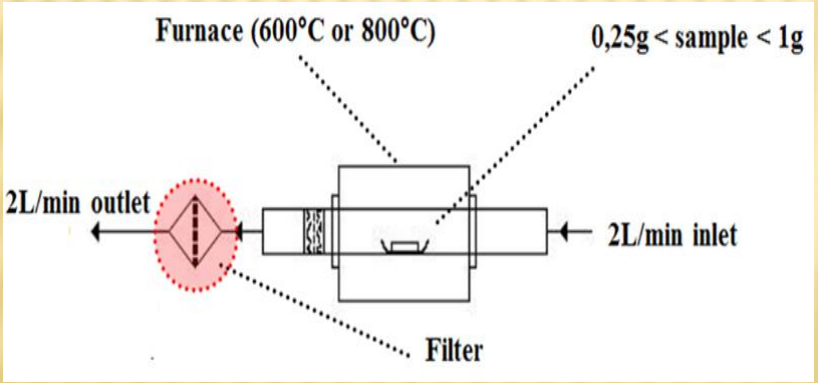
PAHs generation and analysis

Different sampling methods were used and compared (SPME, syringe, midget impingers, etc) for PAHs quantification. A range of different fire conditions was generated using NF X 70-100.

Fire conditions varied from non-flaming (oxidative pyrolysis) to well-ventilated and under-ventilated flaming by using different combinations of temperature and fuel/air ratios.



GC-MS was used to identify different components of mixtures in the effluent.



NF X 70-100

GC-MS

Sampling methods

Typical extractive methods and examples of species analysed in each case include:

midget impingers

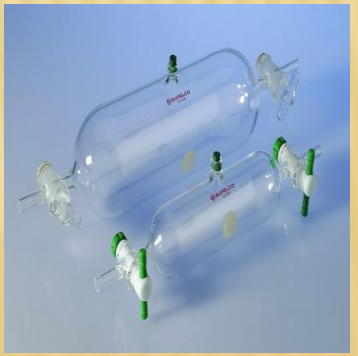
SPME

Tedlar bag

sorption tube

Syringe

Gas sampling bulb



Analytical methods

- EPA TO-15 and TO-17
- EPA 8270
- EPA 8275
- Supleco bulletin 922

Different methods of sampling

Sample	Condition	Methods									
Polymer	**Air flow/ temperature**	**Bubbler by solvent (EPA 8270)**			**Bubbler by solvent (EPA 8275)**			**SPME (direct) (Supleco bulletin 922)**	**SPME (glass 250 ml) (Supleco bulletin 922)**	**SPME (tedlar bag) (Supleco bulletin 922)**	**Syringe (direct) (Supleco bulletin 922)**	**Syringe (glass 250 ml) (Supleco bulletin 922)**	**Syringe (tedlar bag) (Supleco bulletin 922)**	**Sorption tube (EPA TO-15 and TO-17)**
LDPE (NFX)	2L/ 800C°	duplicate tests			duplicate tests			duplicate test	duplicate tests	Data analysis on-going	duplicate tests	duplicate tests	Data analysis on-going	Data analysis on-going
		Toluene	**Acetonitrile**	**Deionised water**	**Toluene**	**Acetonitrile**	**Deionised water**							
LDPE (NFX)	2L/ 600C°	**x**			**x**			duplicate tests	duplicate tests	x	duplicate tests	duplicate tests	x	Data analysis on-going
		Toluene	**Acetonitrile**	**Deionised water**	**Toluene**	**Acetonitrile**	**Deionised water**							

Sampling methods at 800C°

1-midget impingers at 800 C

Solvent	Time sampling
Toluene	Ignition time : 35 Sec
	Extinction time : 2.45 min
	Experiment time : 0.00-4.30 min
	Sampling time: from 0.35 to 3.30 min
	Flow rate (l/min):1

Solvent	Time sampling
Acetonitrile	Ignition time : 36 Sec
	Extinction time : 2.48 min
	Experiment time : 0.00-4.30 min
	Sampling time: from 0.35 to 3.30 min
	Flow rate (l/min):1

Solvent	Time sampling
Deionised water	Ignition time : 38 Sec
	Extinction time : 2.50 min
	Experiment time : 0.00-4.30 min
	Sampling time: from 0.35 to 3.30 min
	Flow rate (l/min):1

2-Solid Phase Micro Extraction (SPME) at 800 C

Method	Time sampling
SPME direct	Ignition time : 37 Sec
	Extinction time : 2.43 min
	Experiment time : 0.00-4.30 min
	Sampling time: (1:20 -1:30) = 10 Sec
	Flow rate (l/min):1

Method	Time sampling
(SPME) Tedler bag	Ignition time : 38 Sec
	Extinction time : 2.45 min
	Experiment time : 0.00-4.30 min
	Sampling time: after experiment for 10 Sec
	Flow rate (l/min):1

Method	Time sampling
SPME Glass 250 ml	Ignition time : 38 Sec
	Extinction time : 2.45 min
	Experiment time : 0.00-4.30 min
	Sampling time: after experiment for 5 min
	Flow rate (l/min): 1

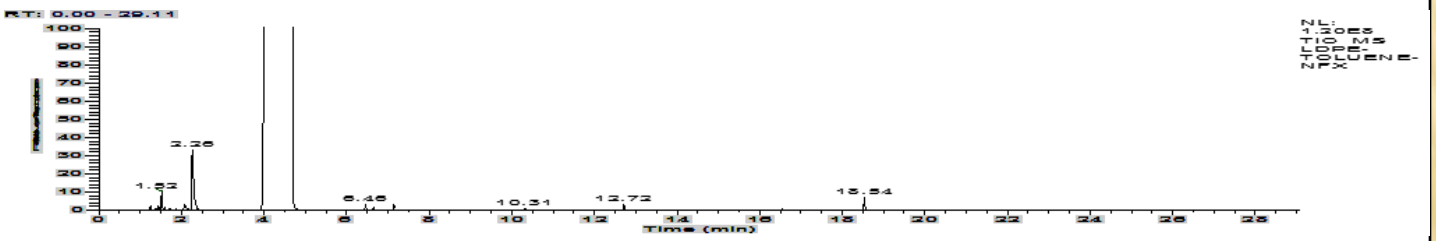
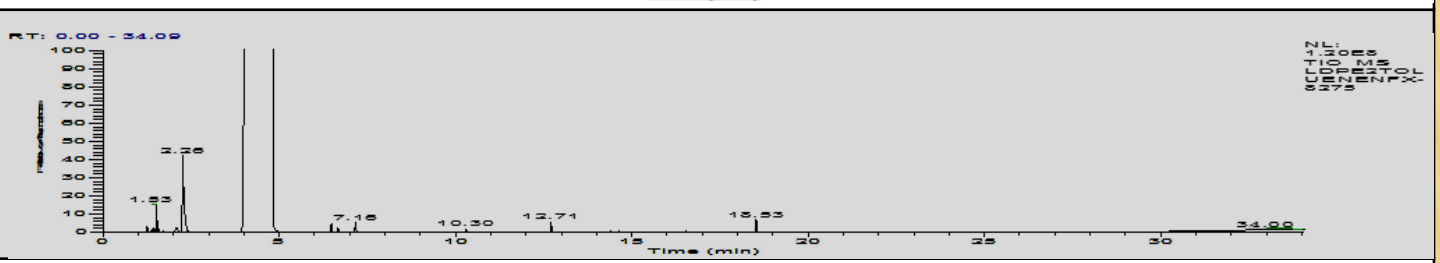
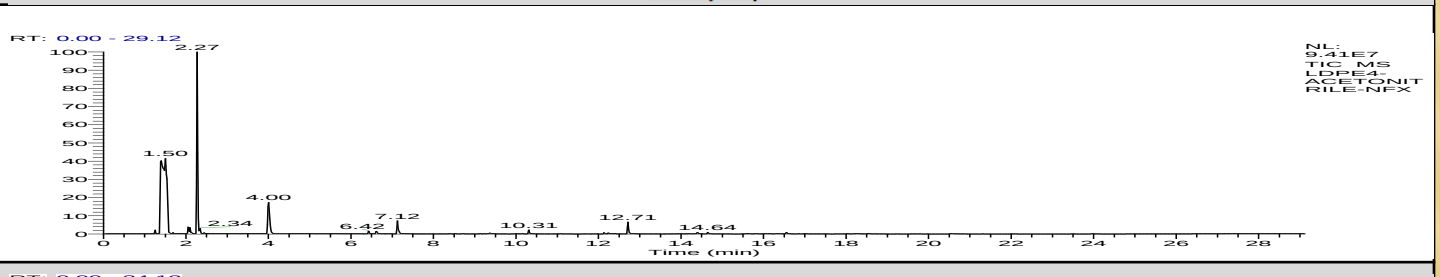
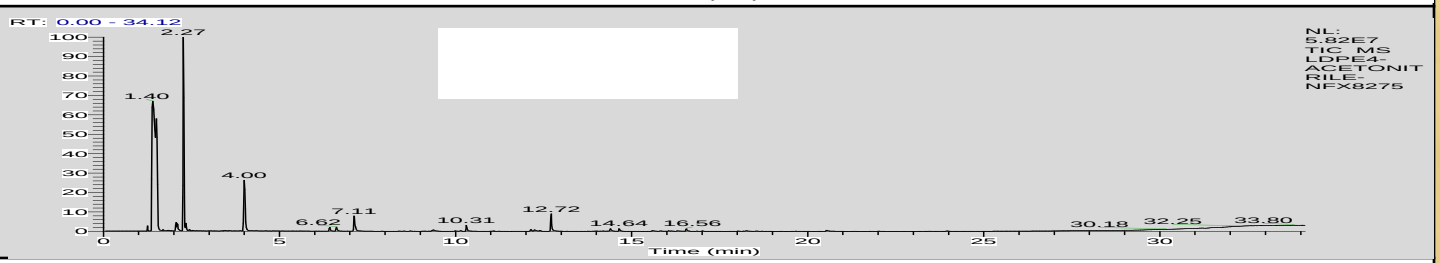
3-Syringe at 800 C

Method	Time sampling
Syringe direct	Ignition time : 34 Sec
	Extinction time : 2.42 min
	Experiment time : 0.00-4.30 min
	Sampling time: (1:20 -1:24) = 4 Sec
	Volume: 200µl
	Flow rate (l/min):1

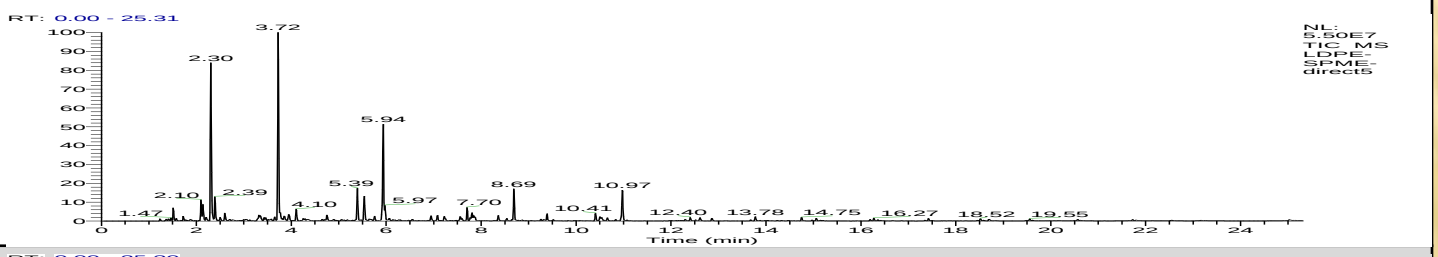
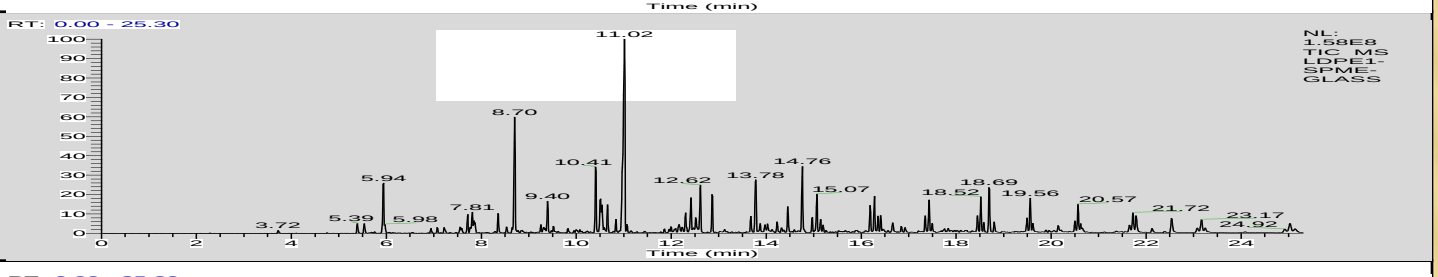
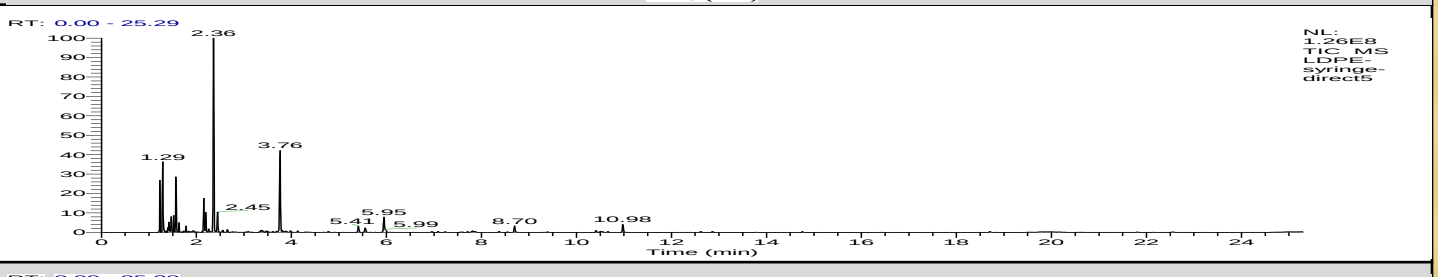
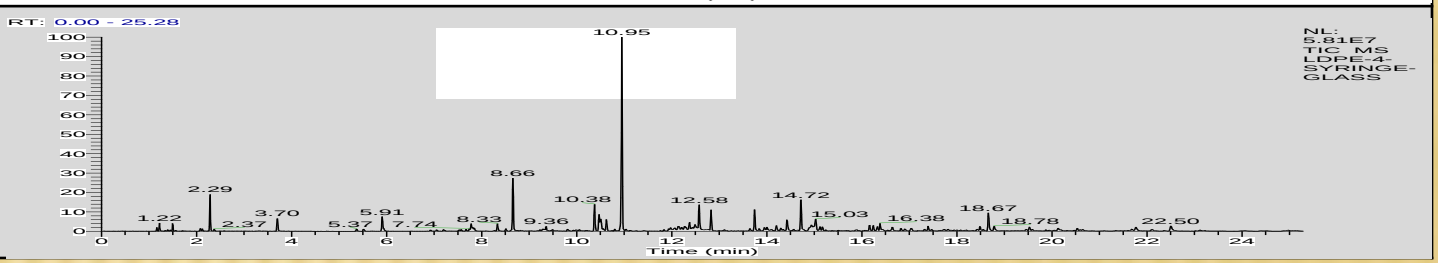
Method	Time sampling
Syringe tedler bag	Ignition time : 38 Sec
	Extinction time : 2.45 min
	Experiment time : 0.00-4.30 min
	Sampling time: after experiment
	Volume: 200µl
	Flow rate (l/min):1

method	Time sampling
Syringe glass 250 ml	Ignition time : 36 Sec
	Extinction time : 2.48 min
	Experiment time : 0.00-4.30 min
	Sampling time: after experiment
	Volume: 200µl
	Flow rate (l/min): 1

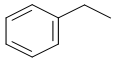
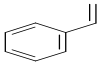
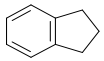
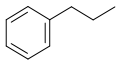
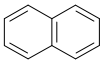
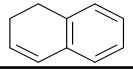
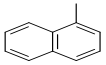
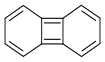
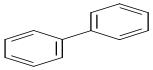
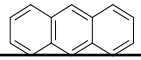
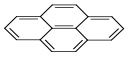
Results of experiments at 800C°

Method	Sampling Method	Chromatogram
midget impingers	Toluene EPA 8270	
midget impingers	Toluene EPA 82705	
midget impingers	Acetonitrile 8270	
midget impingers	Acetonitrile 8275	
midget impingers	Deionised water 8270	No species found
midget impingers	Deionised water 8275	No species found

Results of experiments at 800C°

Method	Sampling Method	Chromatogram
SPME	direct	
SPME	glass	
Syringe	direct	
Syringe	glass	

Summary of experiment results at 800C°

Method Volatile / Name	MW	Structure	Method EPA 8270 (toluene)	Method EPA 8275 (toluene)	Method EPA 8270 (acetonitrile)	Method EPA8275 (acetonitrile)	Method EPA 8270 (deionised water)	Method EPA 8275 (deionised water)	SPME direct	SPME glass	Syringe direct	Syringe glass
1,4-cyclohexadiene	80		√	√	√	√	X	X	√	X	√	X
Benzene	78		√	√	√	√	X	X	√	X	√	X
Toluene	92		X	X	√	√	X	X	√	√	√	√
Ethyl benzene	106		√	√	√	√	X	X	√	√	√	√
Styrene	104		√	√	√	√	√	X	√	√	√	√
Indane	118		X	X	√	√	X	X	X	√	√	√
Benzene, propyl	120		X	X	X	X	X	X	√	√	X	√
Indene	116		X	X	√	√	X	X	√	√	√	√
Naphthalene	128		√	√	√	√	X	X	√	√	√	√
Naphthalene, 1,2dihydro	130		X	X	X	X	X	X	√	√	√	√
Naphthalene, 1-methyl-	142		√	√	√	√	X	X	√	√	√	√
Biphenylene	152		√	√	√	√	X	X	√	√	√	√
Biphenyl	154		X	X	X	X	X	X	X	√	X	√
Anthracene	178		√	√	√	√	X	X	√	√	√	√
pyrene	202		√	√	X	X	X	X	√	√	√	√

Sampling methods at 600C°

5-SPME at 600 C°

method	Time sampling
SPME direct	Ignition time : 88 Sec
	Extinction time : 3.45 min
	Experiment time : 0.00-5.00 min
	Sampling time: (2:50 -3:00) = 10 Sec
	Flow rate (l/min): 1

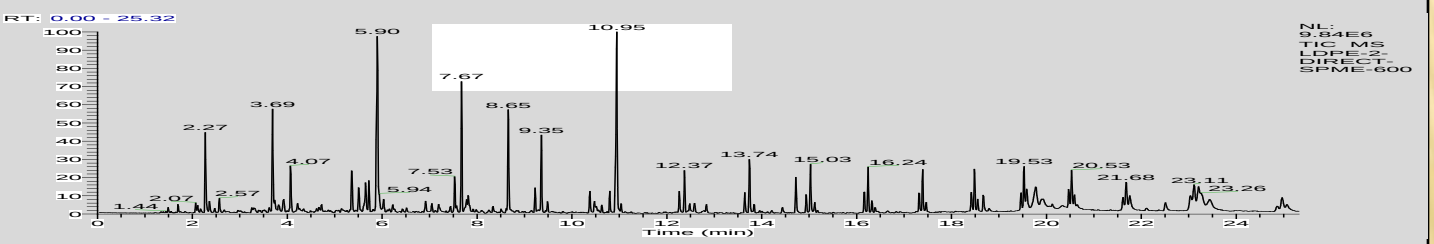
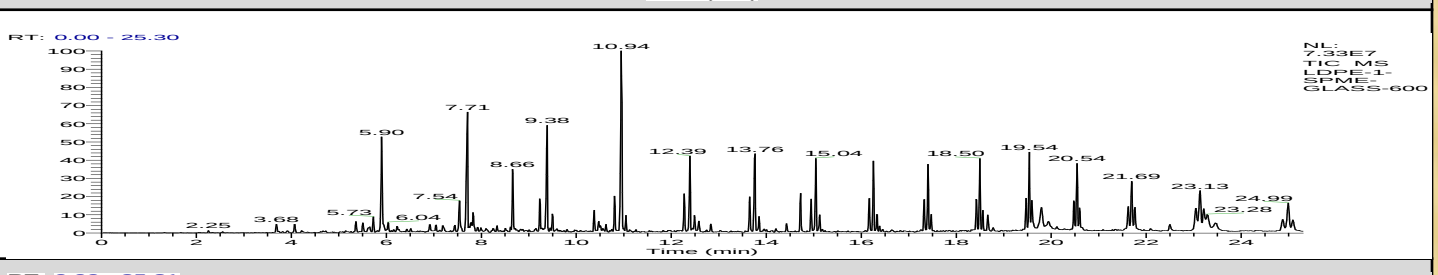
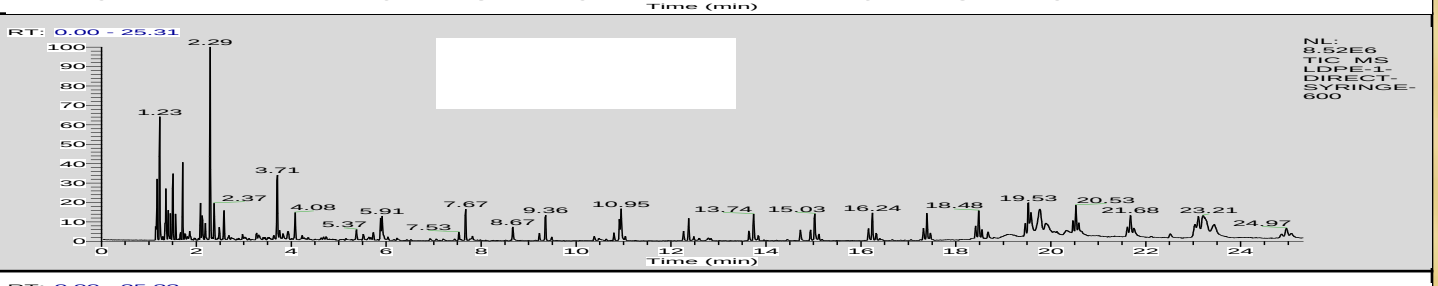
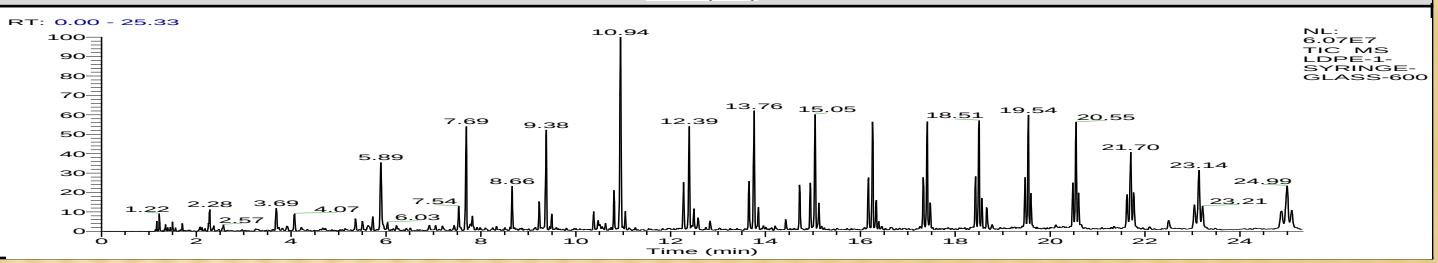
method	Time sampling
SPME glass 250 ml	Ignition time : 38 Sec
	Extinction time : 2.45 min
	Experiment time : 0.00-4.30 min
	Sampling time: after experiment for 5 min
	Flow rate (l/min): 1

4-Syringe at 600 C°

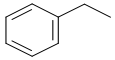
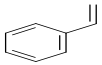
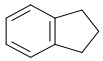
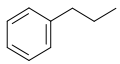
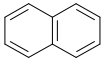
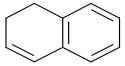
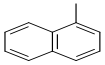
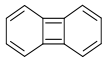
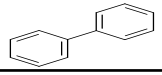
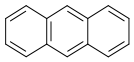
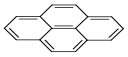
Method	Time sampling
Syringe direct	Ignition time : 85 Sec
	Extinction time : 3.42 min
	Experiment time : 0.00-5.00 min
	Sampling time: (2:40 -2:44) = 4 Sec
	Volume: 200µl
	Flow rate (l/min):1

Method	Time sampling
Syringe glass 250 ml	Ignition time : 88 Sec
	Extinction time : 3.47 min
	Experiment time : 0.00-5.00 min
	Sampling time: after experiment
	Volume: 200µl
	Flow rate (l/min):1

Results of experiments at 600C°

Method	Sampling Method	Chromatogram
SPME	direct	
SPME	glass	
Syringe	direct	
Syringe	glass	

Summary of experiment results at 600C°

Method / Volatile / Name	MW	Structure	SPME direct	SPME glass	Syringe direct	Syringe glass
1,4-cyclohexadiene	80		√	x	√	x
Benzene	78		√	x	√	x
Toluene	92		√	√	√	√
Ethyl benzene	106		√	√	√	√
Styrene	104		√	√	√	√
Indane	118		x	√	√	√
Benzene, propyl	120		√	√	x	√
Indene	116		√	√	√	√
Naphthalene	128		√	√	√	√
Naphthalene, 1,2dihydro	130		√	√	√	√
Naphthalene, 1-methyl-	142		√	√	√	√
Biphenylene	152		√	√	√	√
Biphenyl	154		x	√	x	√
Anthracene	178		√	√	√	√
pyrene	202		√	√	√	√

Conclusions

Different methods for PAHs sampling were used for different fire conditions.

1-Midget impinger was used with acetonitrile, toluene and deionised water as solvents. The best results were obtained from acetonitrile.

2- SPME was used either by a direct injection or from the gas sampling vessel which was proven to have the best results.

3-Syringe was also used either by a direct injection or by gas sampling vessel. It was found that sampling by a gas sampling vessel has given better results compared to the direct sampling.

4-Many experiments were performed using Tedlar bag and sorption tubes, but results were much poorer compared to the other sampling techniques.

5- Benzene, a known carcinogen, was repeatedly identified as a volatile released from LDPE. Styrene and Naphthalene, two possibly carcinogenic compounds, were also identified amongst the PAHs products.

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Thank you for your attention

ANY QUESTIONS?

GC-MS and Py-GCMS Data analysis

University of Central Lancashire

Centre for Fire and Hazards Science

Method	EPA 8270	EPA 8275
Sample	LDPE	LDPE
Analytical instrument	GC-MS	GC-MS
Solvents	deionised water, toluene and acetonitrile	deionised water, toluene and acetonitrile
Instrument control method		
Instrument type:	Thermo Scientific Trace 1300	Thermo Scientific Trace 1300
Channel Parameters		
Run time:	29.00	34.00
Autosampler method		
Injection volume(µl)	1µL	1 µL
Column	Thermo TG-SQC 30 meter, 0.25mmID, 0.25umdf	Thermo TG-SQC 30 meter, 0.25mmID, 0.25umdf
Mass range	35-650 amu	35-650 amu
Scan time	0.94 sec/scan	0.95 sec/scan
Carriers Parameters		
Carrier control:	PFLow-He	PFLow-He
Carriers length:	30.0 m	30.0 m
Diameter:	250 µm	250 µm
Split Flow:	50mL/min	50mL/min
Flow rate:	1.00mL/min	1.00mL/min
Detector	MS	MS
HeatedZones		
Injector:	Split/ splitless	Split/ splitless
Initial Setpoint:	250 °C	250 °C
Oven Program		
Initial Temp.:	40°C	40°C
Initial Hold:	4 min	4 min
Ramp 1:	10.0°C /min to 270°C	10.0°C /min to 320°C
Final Temp.:	270 °C, hold until 2 min after benzo[g,h,i]perylene elutes	320 °C, hold until 2 min after benzo[g,h,i]perylene elutes
Total Run Time:	29.00min	34.00min

Method	SPME and syringe (Supleco bulletin 922)
Samples	LDPE,PS
Analytical instrument	GC-MS
Instrument control method	
Instrument type:	Thermo Scientific Trace 1300
Channel Parameters	
Run time:	25.30min
Manual sampling	
Sampling	10sec , headspace
SPME Fiber	100µm polydimethylsiloxane
Column	Thermo TG-SQC 30 meter, 0.25mmID, 0.25umdf
Mass range	41-650
Scan time	0.59 Sec
Carriers Parameters	
Carrier control:	PFLow-He
Carriers length:	30.0 m
Diameter:	250 µm
Split Flow:	50mL/min
Flow rate	1.00mL/min
Detector	MS
HeatedZones	
Injector:	Splitless (closed 1 min.)
Initial Setpoint:	250°C
Oven Program	
Initial Temp.:	38°C
Initial Hold:	2 min
Ramp 1:	10.0/min to 220°C
Final Temp.:	hold until 5 min to 30°C/min at 300°C
Total Run Time:	25.30min

Method	Sorption tube (EPA TO-15 and TO-17))
Samples	LDPE
Analytical instrument	Py-GCMS
Instrument control method	
Instrument type:	PE Autosystem GC with built-in Autosampler
Channel Parameters	
Delay time:	0.00 min
Run time:	30.00 min
Channel offset:	5.0 mV
Manual sampling	
Sampling	5 min
Type of sorption tube	Tanex AG
Column	Thermo TG-SQC 30 meter, 0.25mmID, 0.25umdf
Mass range	41-650
Scan time	0.59 Sec
Carriers Parameters	
Carrier control:	PFLow-He
Carriers length:	30.0 m
Diameter:	250 mL
Split Flow:	20mL/min
Flow rate	1.00mL/min
Detector	pyGC-MS
HeatedZones	
Injector:	PSSI
Initial Setpoint:	280oC
Oven Program	
Initial Temp.:	50oC
Initial Hold:	2 mins
Ramp 1:	10.0/min to 230oC
Final Temp.:	30.00 min
Total Run Time:	30.00 min