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Evaluating Fire & Smoke Contamination in Indoor Air

IAQA 18th Annual Meeting

Acknowledgements

Katie Martin - Prism Analytical Technologies, Inc.

Dan Baxter - Environmental Analysis Associates

Fire & Smoke – What's the Concern?

Effect on:

- Appearance
- Health
- Odor

Residual contamination

- Before cleanup
- During cleanup
- After cleanup

Fire & Smoke – Challenges

- Complexity of particulate and chemical residues

- Existing particulate methods not effective in comprehensive evaluation
  - ASTM D1506 (Ash Content-Carbon Black)
  - IESO/RIA 6001 (Residue on HVAC Surfaces)

- No VOC methods specific to fire residues

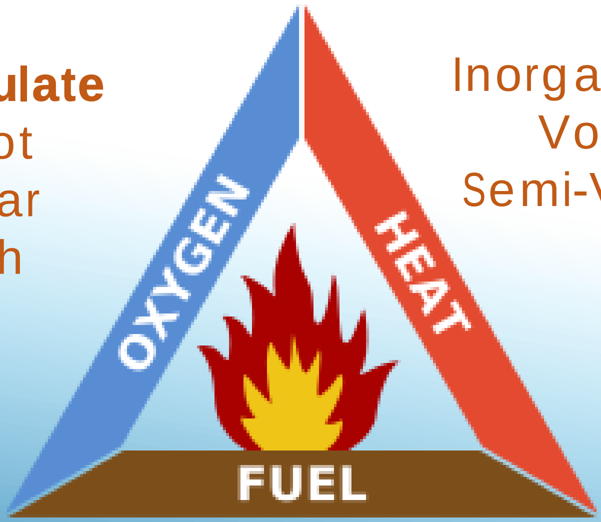
What is Fire?

Rapid oxidation process involving

fuel, heat, and oxygen

that releases heat, light, and various reaction products

Particulate
Soot
Char
Ash



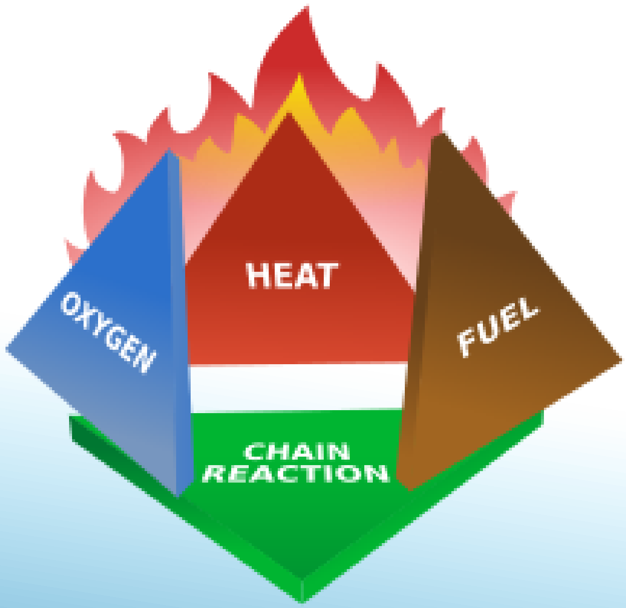
Gases
Inorganic Gases (CO, CO_2, etc.)
Volatile Organics (VOCs)
Semi-Volatile Organics (SVOCs)

NFPA, “All About Fire”

4th Component of Fire

Chain reaction necessary to sustain fire

Heat of fire releases energy, which further feeds the oxidation process



Fire will burn until one or more components are removed

NFPA, "All About Fire"

Anatomy of a Fire

Ignition

- Fuel, oxygen and heat join together in a sustained chemical reaction.

Growth

- With the initial flame as a heat source, additional fuel ignites. Convection and radiation ignite more surfaces. The size of the fire increases and the plume reaches the ceiling. Hot gases collecting at the ceiling transfer heat, allowing all fuels in a room to come closer to their ignition temperature at the same time.

Fully developed

- Fire has spread over much if not all the available fuel; temperatures reach their peak, resulting in heat damage. Oxygen is consumed rapidly.

Decay (Burnout)

- The fire consumes available fuel, temperatures decrease, fire gets less intense.

NFPA, "All About Fire"

Types of Combustion

- Complete
  - Fuel (Hydrocarbons) + O_2 + Heat → CO_2 + H_2O
  - Rare in most environmental fires

- Incomplete
  - Not enough O_2 to completely oxidize hydrocarbons
  - Produces a variety of chemical compounds in various stages of oxidation
    - furans, phenols, carbonyls, aldehydes, ketones, esters, acids, etc.
  - Common in most environmental fires

Indoor Fire

Fire as a result of burning of specific materials within structure or the structural components

- Electrical
- Food/Protein/Grease
- Fuels (Gasoline, Fuel Oil, Diesel)

- Building materials
  - Drywall, insulation, flooring, roofing, structural supports, coatings and paints, etc.
- Building contents
  - Clothing and other textiles, furniture, plastics, rubber, electrical components, appliances, etc.

Wildfire

Uncontrolled fire in an area of combustible vegetation that occurs in the countryside or wilderness area

Biomass

- Hard woods
- Soft woods
- Grasses

Reaction Products: Particulate Fire Residues

3 Common Types

- Soot: fine carbonaceous material produced during incomplete combustion; aciniform structure
- Char: larger, mostly carbonaceous irregular fragments of burned material
- Ash: larger, decarbonized (mostly inorganic) remaining residue of cellulose material; typically mineral salts, carbonates, and oxides or metal/non-combustible compounds and oxides

Methods

- Carbon black
- Microscopy

Measuring
Particulate Fire Residues

- Optical Microscopy
  - Polarized Light (PLM)
  - Combined TL/RLDF/PLM
  - Stereo RL low power

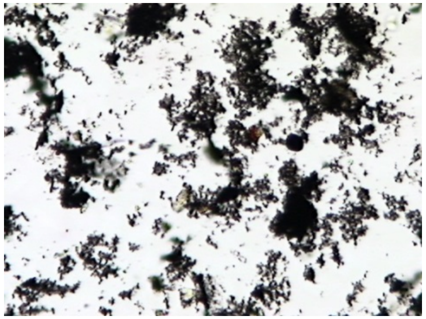
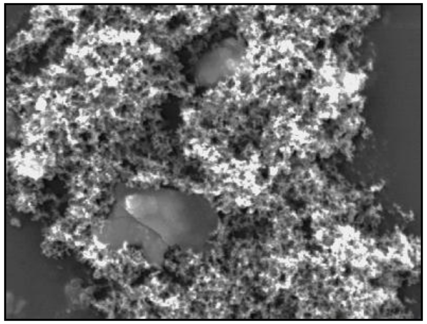
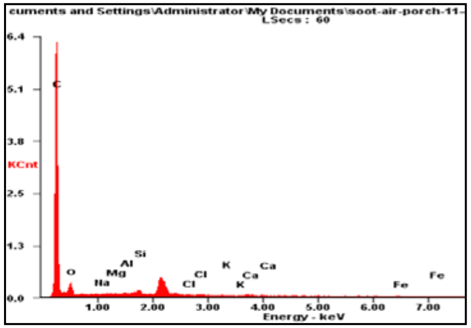
- Scanning Electron Microscopy & Dispersive X-Ray
  - Surface topography
  - Elemental composition

Data provided by Dan Baxter-Environmental Analysis Associates

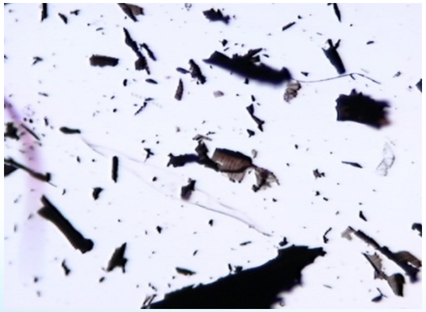
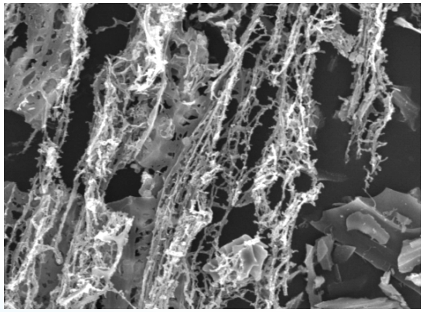
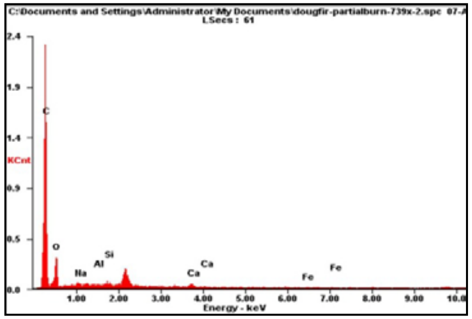
Morphology of Fire Residue Particles

Optical Microscopy | **SEM** | **Dispersive X-ray**

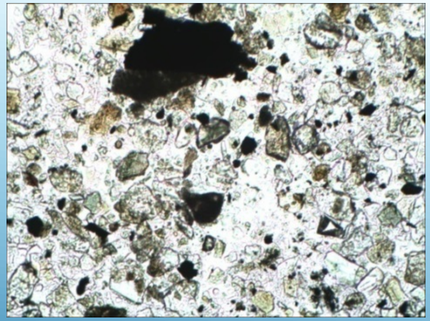
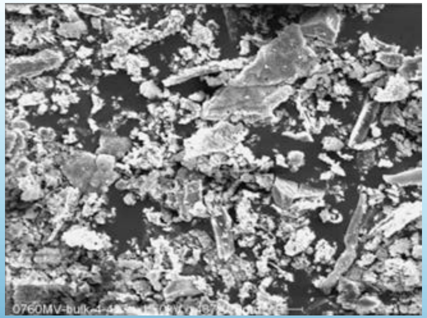
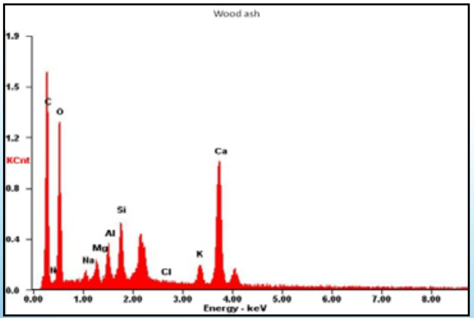
Soot

Char

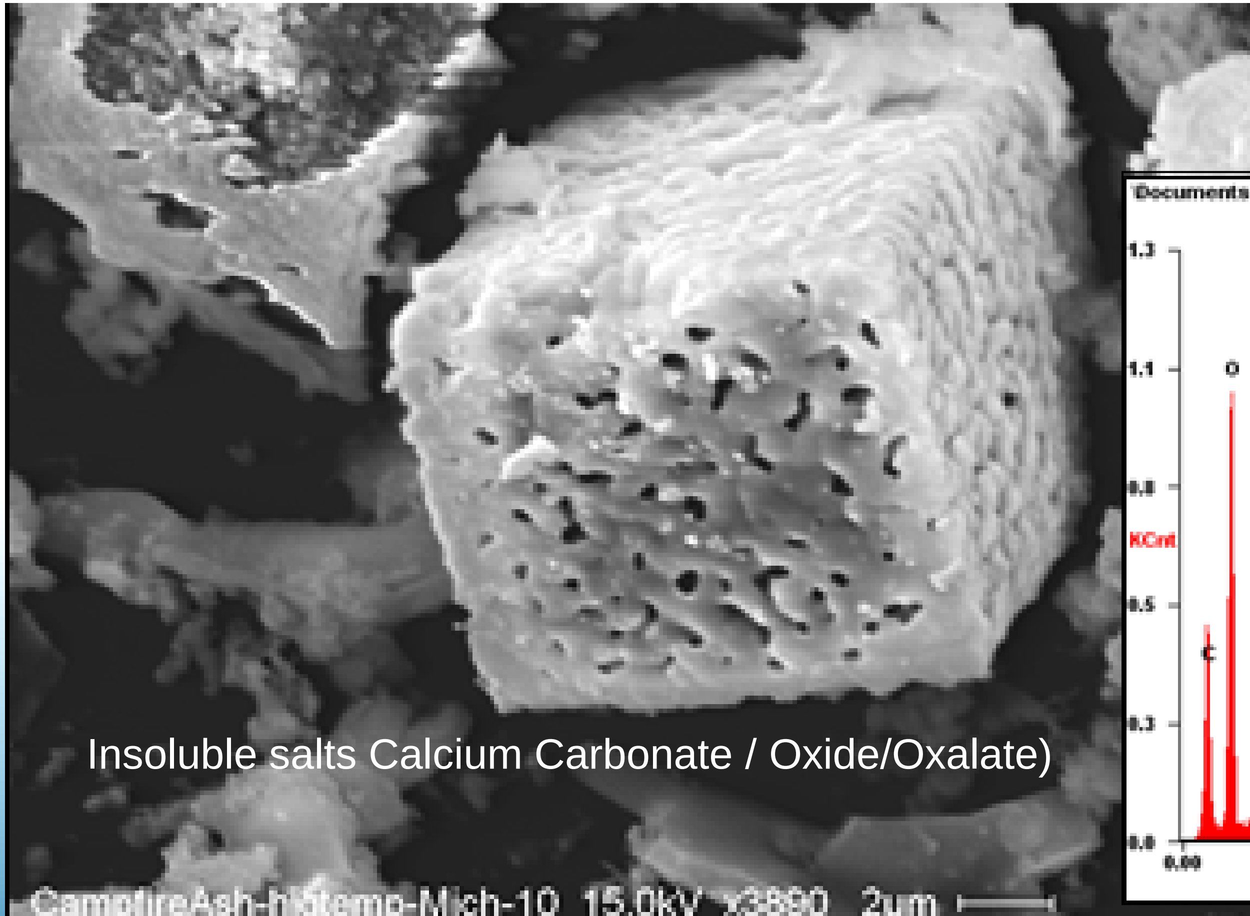




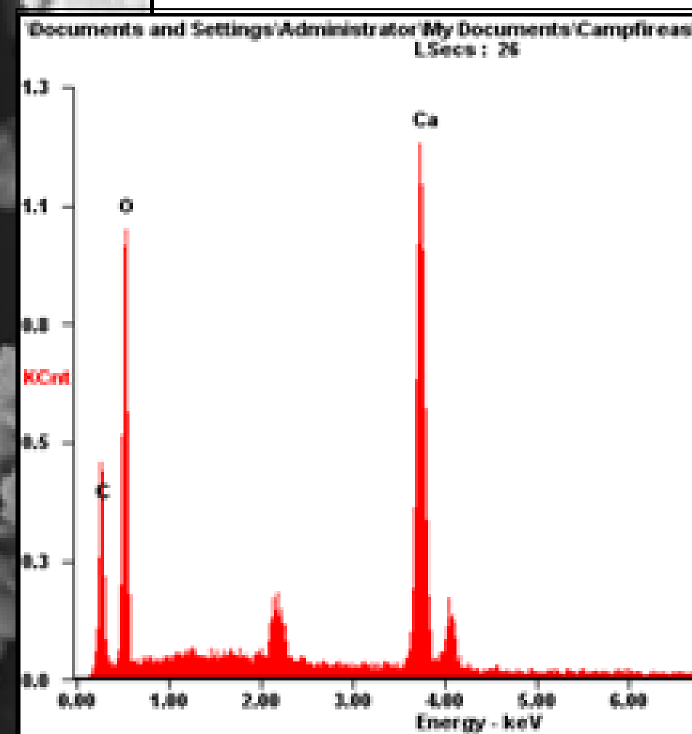
Ash

Data provided by Dan Baxter-Environmental Analysis Associates

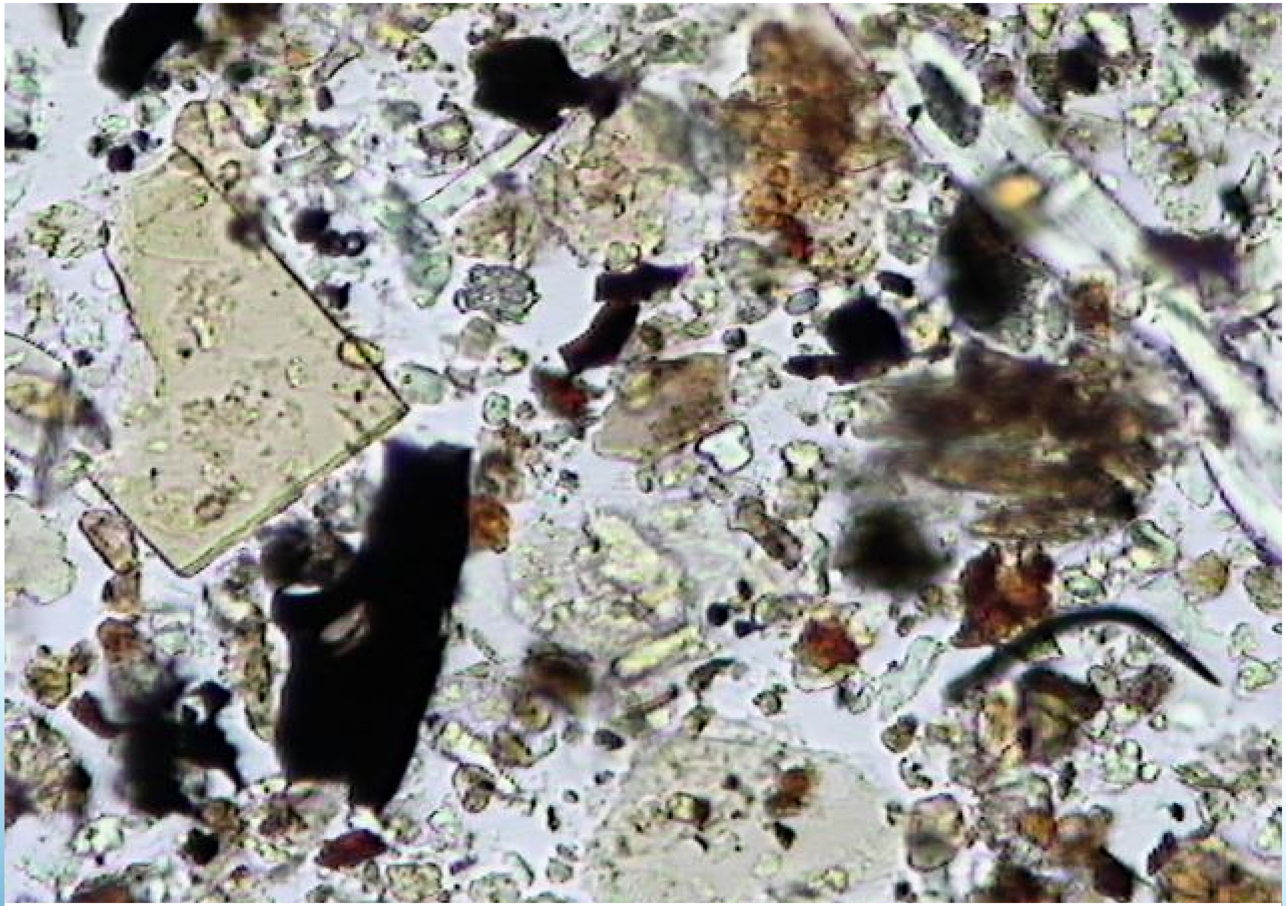
Ash Components





Data provided by Dan Baxter-Environmental Analysis Associates

"Firestorm" Air Sample 10/23/07 - Pacific Beach



Complex mixture of lofted soil and fire debris

Data provided by Dan Baxter-Environmental Analysis Associates

Particulate Contamination Guidance

Optical Microscopy: Total Soot/Char/Ash Debris

0.1% **1%** **5%** **10%** **50%**

Normal **Possible - Likely** **Present**

Surface fire residue particles cannot be used directly as measure of "damage"
Laboratory variability 1% ±3%

pH: Presence of Ash

6.0 **8.3** **9.0** **10** **12**

Normal **Possible - Likely** **Present**

Wildfire gaseous emissions primarily acidic (low pH)
Particulate settled wildfire "ash" is caustic (high pH)

Data provided by Dan Baxter-Environmental Analysis Associates

Reaction Products: Chemical Fire Residues

Hundreds of chemicals

- Many chemical classes
  - inorganics, hydrocarbons (alkanes, alkenes, cyclic), aromatics, aldehydes, furans, phenols, esters, acids, PAHs, etc.
- Large volatility range
  - Permanent gases → VOCs → SVOCs → solids

Must use unique indicators as surrogates to represent all chemicals

- Minimal secondary sources
- Analytically distinct

Determining Chemical Indictors: Literature Review

Schauer et al., EnvSciTech, 200
n-alkanes
branched alkanes
n-alkenes
branched alkenes
alkynes
diolefins
cycloalkanes
cycloalkenes
aromatic hydrocarbons
polycyclic aromatic hydrocarbon
phenol and substituted phenols
guaiacol and substituted guaiac
syringol and substituted syringols
aliphatic aldehydes
aliphatic ketones
olefinic aldehydes
aromatic carbonyls
dicarbonyls
n-alkenoic acids
resin acids
Sugars (e.g., levoglucosan)
PAH ketones
other compounds

Clark County, Exceptional Event Report, 2003
PM2.5
Organic carbon
Elemental carbon
Elemental Species
- Potassium
- Chloride

CO
CO2
Alkanes (C2-C10)
Alkenes (C2-C9)
Aromatics (BTEX)
Oxygenated VOCs
- Methanol
- Formic acid

Ward, et al., J AWMA 201
Phenol
2-methylphenol
4-methylphenol
2,4-dimethylphenol
Naphthalene
2-methylnaphthalene
Acenaphthylene
Acenaphthene
Dibenzofuran
Fluoreneb Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
thene
thene
hane
zene
zene
ne
e
enzene
enzene

Heitmann et al., Chemosphere 2009, 2011
Acetophenone
Benzyl alcohol
4-Ethyl-2-methoxyphenol
2-Hydroxybenzaldehyde
2-Hydroxy-5-methylbenzaldehyde
2-Methoxyphenol
2-Methoxy-4-methylphenol
2-Methylphenol
3-/4-Methylphenol
Naphthalene

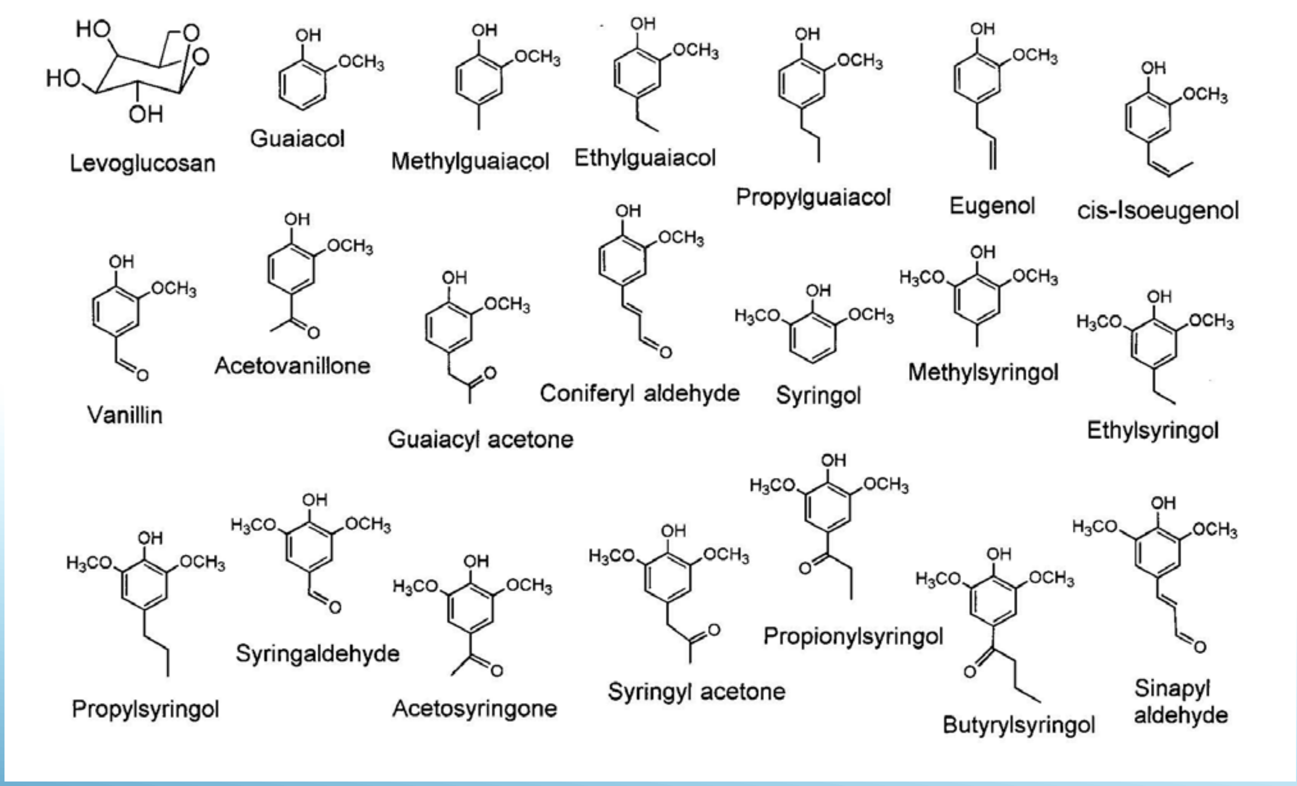
Larson et al., Ann F Health, 1994
Carbon monoxide
Methane
VOCs (Cz--CT)
Aldehydes
Formaldehyde
Acrolein
Propionaldehyde
Butryaldehyde
Acetaldehyde
Furfural
Substituted furans
Benzene
Alkyl benzenes
Toluene
Acetic acid
Formic acid
Nitrogen oxides (NO,N
Sulfur dioxide
Methyl chloride
Napthalene *Substitute napthalenes*
Oxygenated monoarc
Guaiacol (and deriva
Phenol (anc
Syringol (an
Catechol (a
Total partic
Particulate
Oxygenate
PAHs

Pechan, Developing NEI-Commercial Cooking: Tech. Memorandum, 2003
VOC
CO
PM
10 PM
2.5 PM
NAPHTHALENE
BENZO[A]PYRENE
ACENAPHTHYLENE
FLUORENE
PHENANTHRENE
FLUORANTHENE
PYRENE
BENZ[A]ANTHRACENE
INDENO[1,2,3-C,D]PYRENE
ACENAPHTHENE
ANTHRACENE
BENZO[G,H,I,]PERYLENE
PAH, TOTAL
BIPHENYL
BENZENE
TOLUENE
ETHYL BENZENE
XYLENES
STYRENE
FORMALDEHYDE
ACETALDEHYDE
DE

Dhammapala et al., Atm Env, 2007
PAHs
Methoxyphenols
Levoglucosan
Elemental Carbon
Organic Carbon

Determining Chemical Indictors: Literature Review

Wood Combustion - Fireplace



Schauer et al., Env Sci Tech, 2001

Measuring Chemical Fire Residues

- Chemically specific
  - Differentiate closely related chemical compounds
- Sensitive
  - Low detection limits
- Variety of sample collection media
  - Air, bulk, dust, wipe, etc.

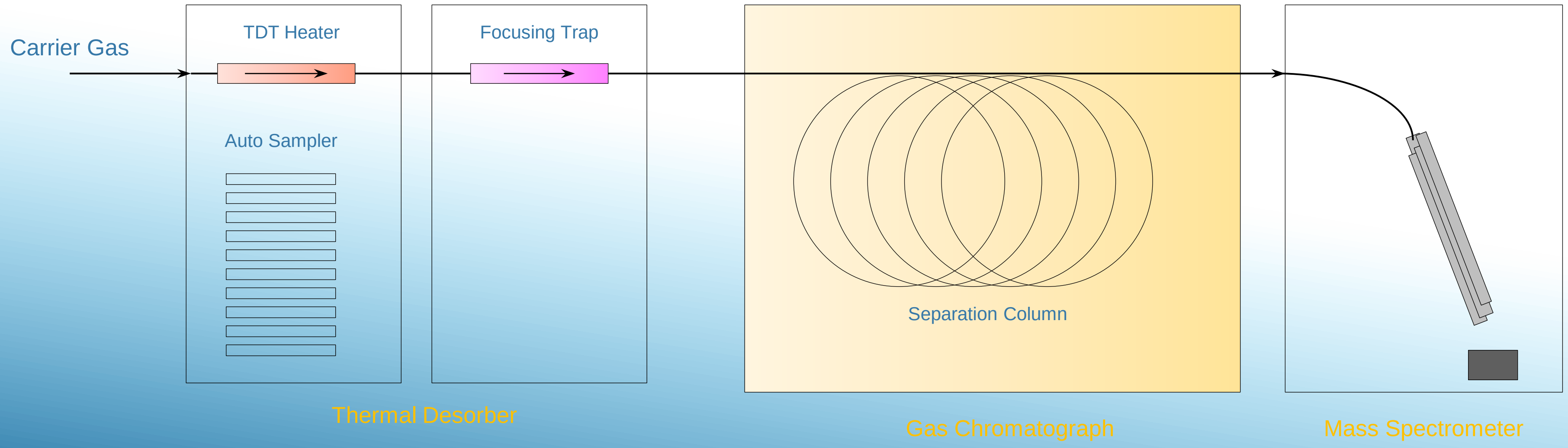
Gas Chromatography-Mass Spectrometry (GC-MS)

- Thermal desorption (TD) – wide range of volatilities and sampling environments

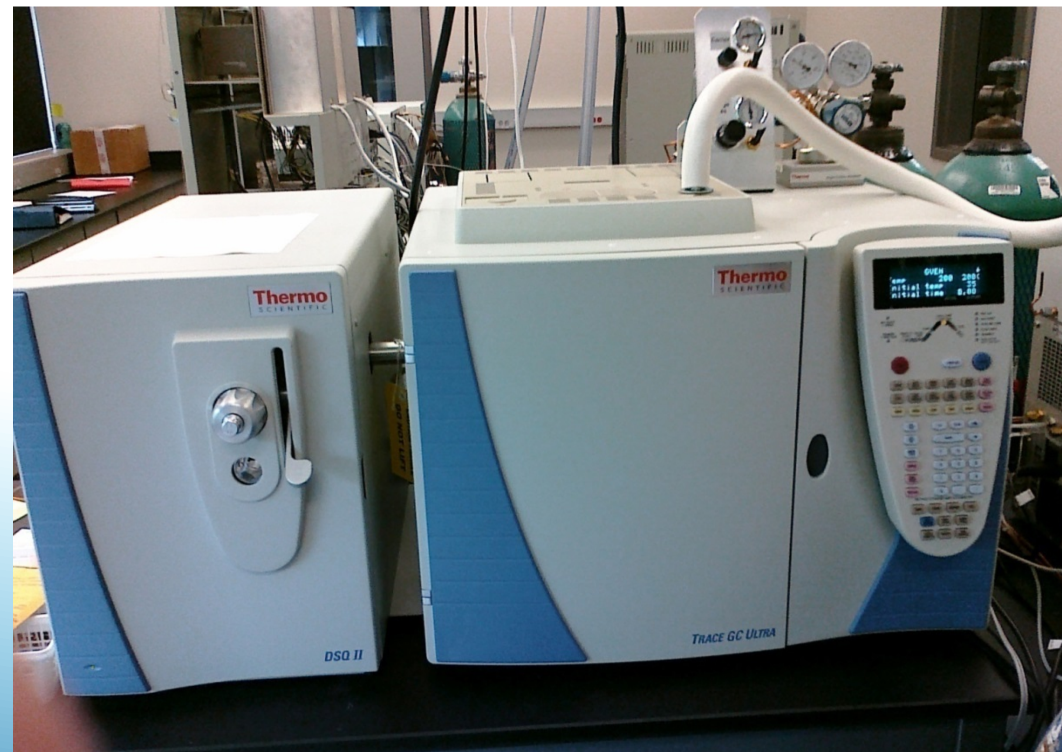
Measuring Chemical Fire Residues

Thermal Desorption Gas Chromatography-Mass Spectrometry (TD GC-MS)

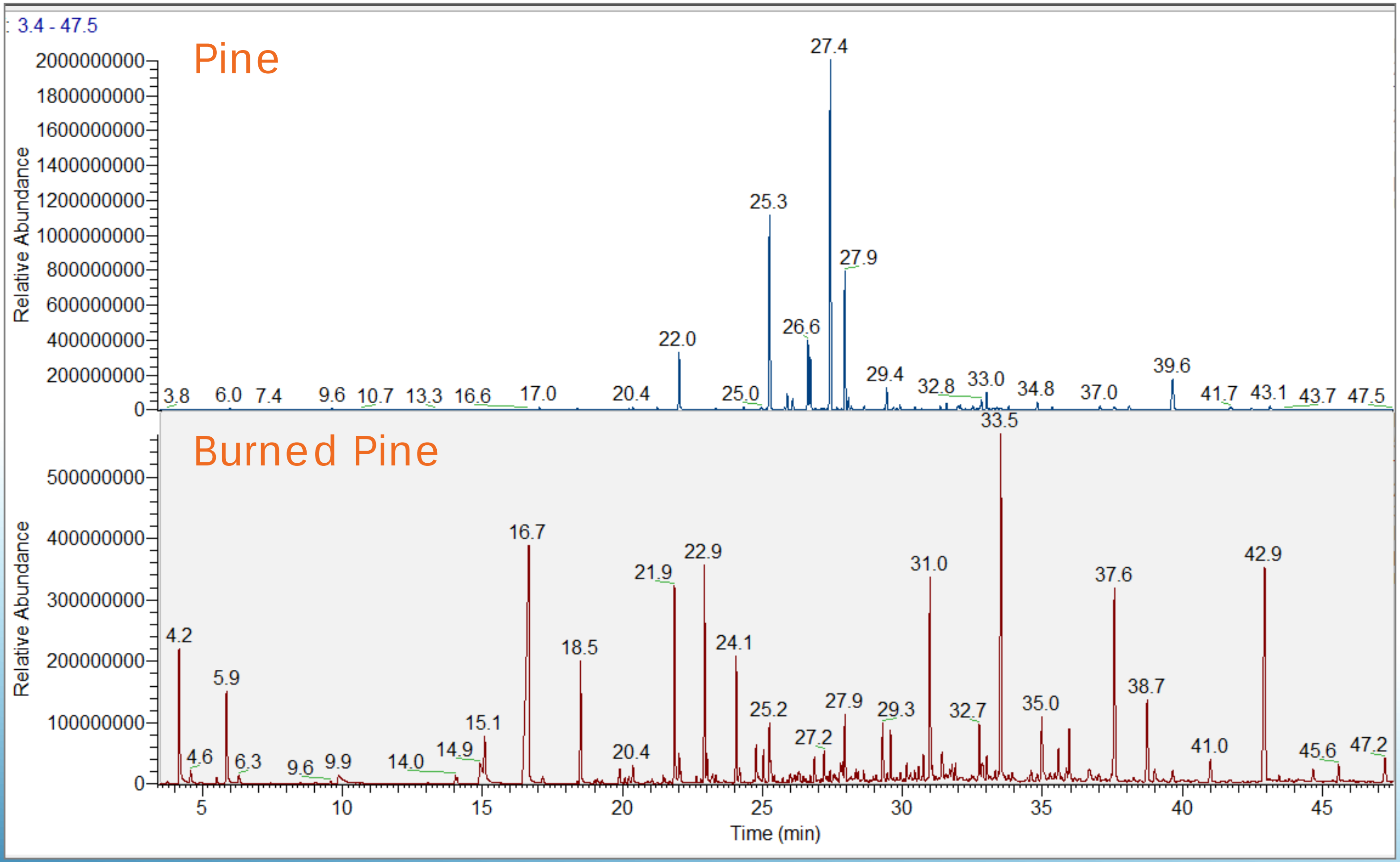
- Sample tube heated to drive off captured VOCs
- GC separates VOCs by volatility and chemical class
- MS identifies individual VOCs by fragmenting molecules into characteristic pieces



Measuring
Chemical Fire Residues



Determining Chemical Indictors: Data Review



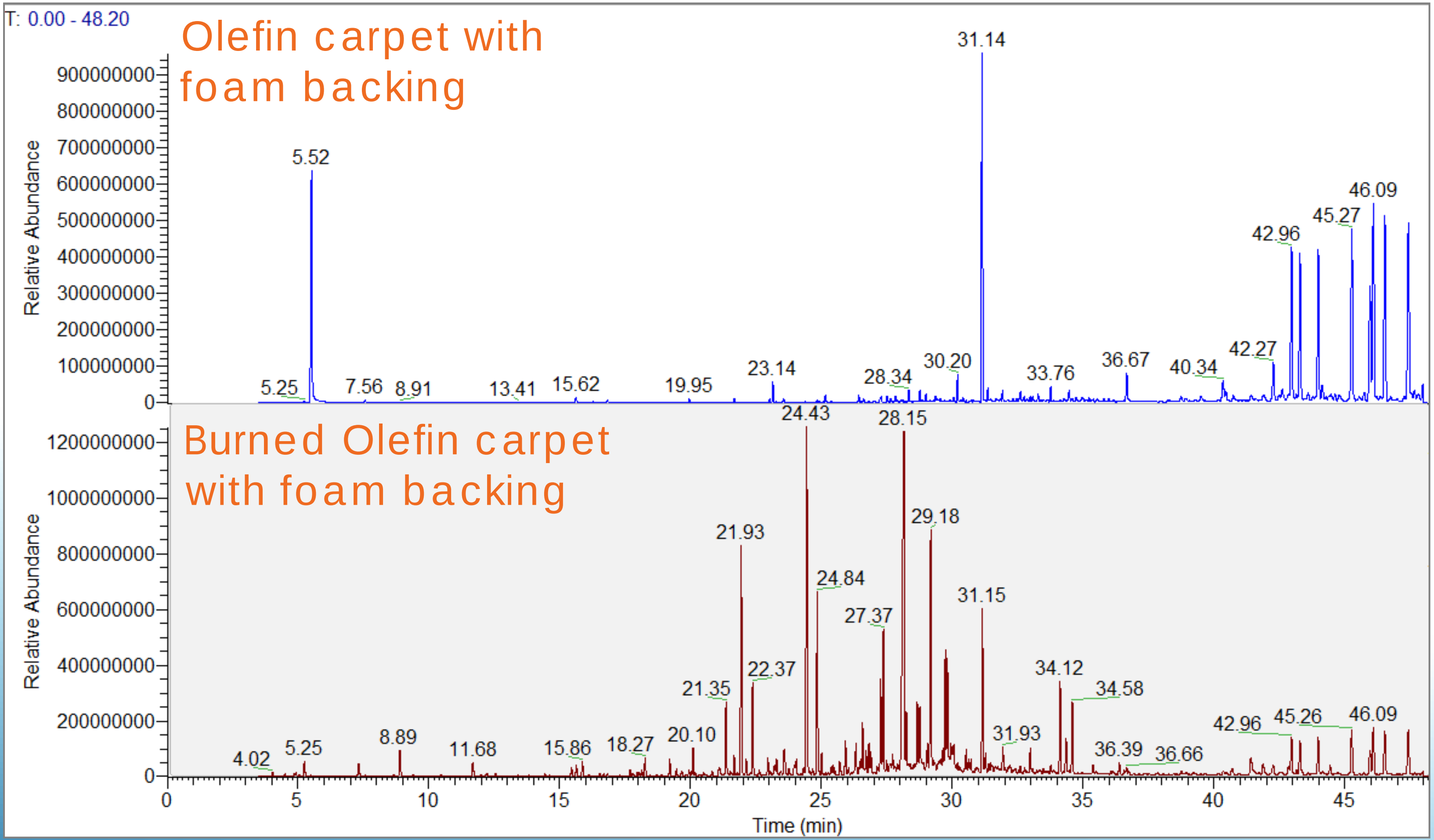
Emissions from Biomass

Lignin – complex polymer of aromatic alcohols

- Cell walls of plants; most commonly of woods

- Levoglucosan
  - Formed from pyrolysis of wood (lignin)
  - Atmospheric chemical tracer of biomass burning
- Softwoods
  - Guaicols (methoxyphenols)
- Hardwoods
  - Guaicols (methoxyphenols) and syringols (dimethoxyphenols)

Determining Chemical Indictors: Data Review



Emissions from All Materials

- Aliphatic
  - Branched alkanes/alkenes, cyclic alkanes/alkenes
- Aromatics
  - Benzene, toluene, xylenes, styrene
  - Polycyclic Aromatic Hydrocarbons (PAHs)
    - Naphthalene, acenaphthylene, phenanthrene
- Phenols
  - Methyl phenols (cresols)
  - Methoxy methyl phenols (creosols)
- Aldehydes
  - Formaldehyde, acetaldehyde, acrolein

Chemical Indictors

Indicators

Primary — Common to most fire residues and analytically distinct

Cresols, Creosol, Guaicol, 4-Ethylguaicol, 2-Furaldehyde, Acenaphthylene

Secondary — Common to some fire residues; may be analytically challenging

Acrolein, Acetonitrile, Salicaldehyde, 2,4-Dimethylphenol, Biphenyl, Naphthalene, 2-Methylnaphthalene

Ongoing development

New data will inform expansion and revision of indicators

Chemical Data Considerations

Sources
- Variety and crossover

Volatility
- High, Medium, Low – recent fire
- Low – older fire

Fuel Material
- Indoors – variability due to materials burned
- Wild fire – more homogeneous; based on type of biomass burned

Environmental Conditions
- High temperature & humidity – increased concentrations
- High ventilation rates – decreased concentrations

Chemical Data Considerations: Persistence

Decreasing Volatility / Increasing Size

Volatility	Compounds
Very Volatile (Permanent Gases)	CO, NOx, Cyanide, etc.
Light VOCs	Formaldehyde, Acrolein, Acetonitrile
Medium VOCs	Cresols, 2-Furaldehyde, Guaicol,
Heavy VOCs	Creosol, 4-Ethylguaicol, 2,4-Dimethylphenol
Light SVOCs	Naphthalene, 2-Methylnaphthalene, Biphenyl, Methylbiphenyl, Acenaphthylene, Levoglucosan*
Heavy SVOCs	Other PAHs

Sampling Strategy

- Type of fire
  - Indoor – large
  - Indoor – small
  - Outdoor or Wildfire
- Length of time since fire
  - Weeks, months, years
- Level of cleanup or remediation performed
  - None
  - Surface
  - Replacement

Chemical Sampling Media

Sample Type	Volatility	Time Frame (post fire)	Applicability
Air	High – Medium	Weeks – Months	Presence of odor; estimate of inhalation exposure
Bulk	Medium – Low	Weeks – Years	Persistence of chemical residue; re-emission of contaminants
Dust	Low	Months – Years	Persistence of chemical residue
Wipe	Low	Months – Years	Presence of surface residue

Indoor Fire Scenario: Effect on Exposed Materials

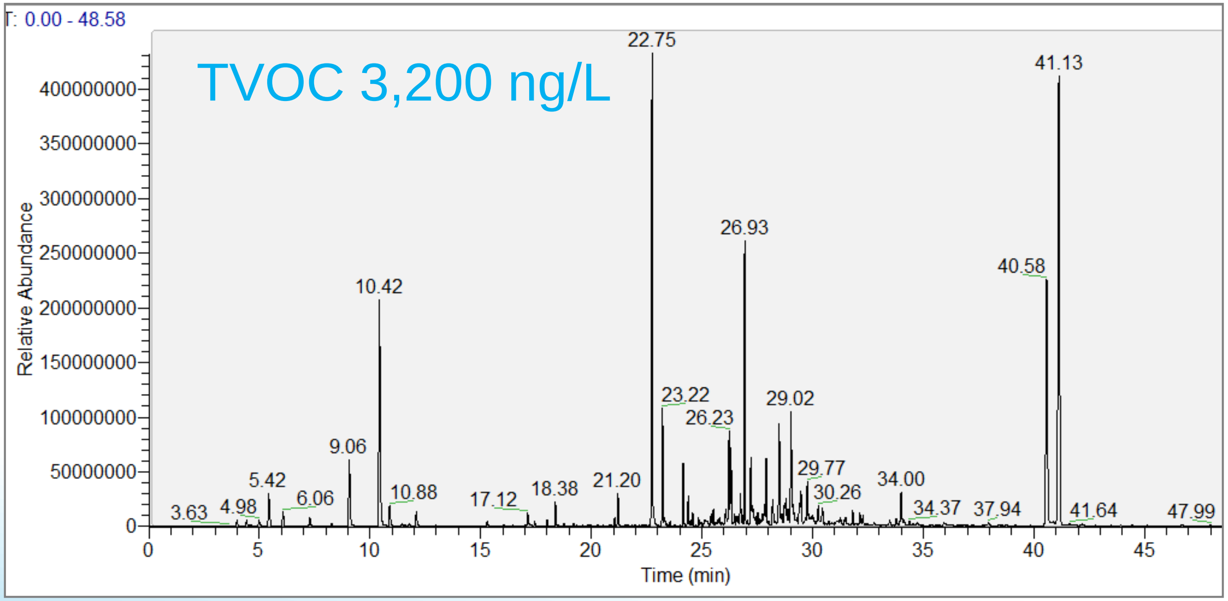
- Fire in clothing warehouse ~6 months prior to sample collection
- Bulk material off gas performed at 80 ºC (~175 ºF)

Compound	Affected #1	Affected #2	Unaffected #1	Unaffected #2
Average Concentrations (ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Acrolein	< 1	< 1	< 1	< 1
Acetonitrile	< 1	< 1	< 1	< 1
2-Furaldehyde	9	10	4	3
Salicylaldehyde	3	4	3	1
o-Cresol	2	6 *	1	1
2-Methoxyphenol	16	6	8	7
m,p-Cresol	5	5 *	1	1
2,4-Dimethylphenol	3	3	2	5
Naphthalene	180 *	20	25	33
Creosol	4	4	< 1	< 1
2-Methylnaphthalene	63	21	23 *	37 *
Biphenyl	23	44	2	9
Methylbiphenyl	52	21	22	68 *
Acenaphthylene	11	10	2	4

* One of more outliers increased the average concentration for this sample set.

Indoor Fire Scenario: Post Clean Up Air Sampling

Air Sample Results – Residence after clean up



Fire indicators

Acetonitrile – 0.8 ng/L

Guaicol – 1.3 ng/L

Cresols – 2.5 ng/L (total)

Creosol – 1.2 ng/L

4-Ethylguaicol – 0.6 ng/L

Data Reporting & Interpretation

Air Sample Results

Primary Fire Indicators

Compound	CAS	Concentration ng/L	Reporting Limit ng/L	RI	Additional Information
2-Furaldehyde	98-01-1	< 3	3.0	922	Furfural
o-Cresol	95-48-7	0.6	0.3	1180	
2-Methoxyphenol	90-05-1	3.2	0.3	1192	Guaicol
m,p-Cresol	108-39-4 & 106-44-5	1.3	0.5	1209	
Creosol	93-51-6	4.1	0.5	1301	
4-Ethyl-2-methoxyphenol	2785-89-9	2.4	0.5	1388	4-Ethylgı
Acenaphthylene	208-96-8	< 3	3.0	1657	

Secondary Fire Indicators

Compound	CAS	Concentration ng/L	Reporting Limit ng/L	RI	Additic
Acrolein	107-02-8	< 3	3.0	538	Reporte
Acetonitrile	75-05-8	< 0.3	0.3	574	
Salicylaldehyde	90-02-8	< 0.5	0.5	1148	
2,4-Dimethylphenol	105-67-9	0.5	0.3	1271	
Naphthalene	91-20-3	0.6	0.3	1295	
2-Methylnaphthalene	91-57-6	0.3	0.3	1408	
Biphenyl	92-52-4	< 3	3.0	1483	Reporte
Methylbiphenyl	N/A	< 3	3.0	1653	Cannot c Semiqua

Bulk Material Sample Results

Primary Fire Indicators

Compound	CAS	Concentration ng/g	Reporting Limit ng/g	RI	Additional Information
2-Furaldehyde	98-01-1	420	35	937	Furfural
o-Cresol	95-48-7	150	3.5	1197	
2-Methoxyphenol	90-05-1	80	3.5	1209	Guaicol
m,p-Cresol	108-39-4 & 106-44-5	160	7.0	1225	
Creosol	93-51-6	24	7.0	1316	
4-Ethyl-2-methoxyphenol	2785-89-9	20	7.0	1405	4-Ethylguaicol
Acenaphthylene	208-96-8	< 35	35	1662	

Secondary Fire Indicators

Compound	CAS	Concentration ng/g	Reporting Limit ng/g	RI	Additional Information
Acrolein	107-02-8	< 35	35	553	Reported Semiquantitatively
Acetonitrile	75-05-8	6.0	3.5	587	
Salicylaldehyde	90-02-8	25	7.0	1165	
2,4-Dimethylphenol	105-67-9	70	3.5	1288	
Naphthalene	91-20-3	84	3.5	1310	
2-Methylnaphthalene	91-57-6	8.7	3.5	1423	
Biphenyl	92-52-4	< 35	35	1500	Reported Semiquantiatively
Methylbiphenyl	N/A	< 35	35	1659	Cannot determine isomer; Reported Semiquantitatively

Conclusions

- Fire residues have significant effect on appearance, health, odor
  - Concern about residual contamination
  - Complexity of particulate and chemical residues
- Methods
  - Existing particulate methods do not provide comprehensive evaluation
  - No specific chemical (VOC) methods used for fire residues
- Use VOC indicators to represent hundreds of chemicals in fire and smoke
  - GC-MS provides chemical specificity and sensitivity
  - Categorize as primary and secondary

Conclusions Continued

- Planning and data interpretation must include consideration of:
  - Secondary sources, volatility, fuel material, and environmental conditions
- Sample collection must include consideration of:
  - Type of fire, time since fire, level of cleanup/remediation

Along with appropriate particulate data, VOC indicators can determine level of remaining fire and smoke residues for indoor air, materials and surfaces

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Questions?

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