Online monitoring of particulate matter (PM2.5) using thermal desorption and GC–TOF MS

Markes & SepSolve: Part of the Schauenburg Analytics group

SCHAUENBURG Analytics

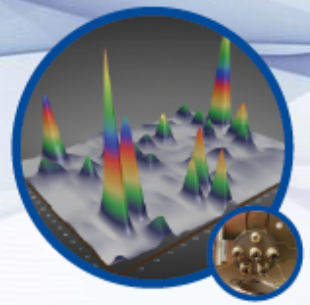
MARKES international

SepSolve Analytical

Sampling technologies

Thermal desorption

Sample enrichment



Separation technologies

Unique identification

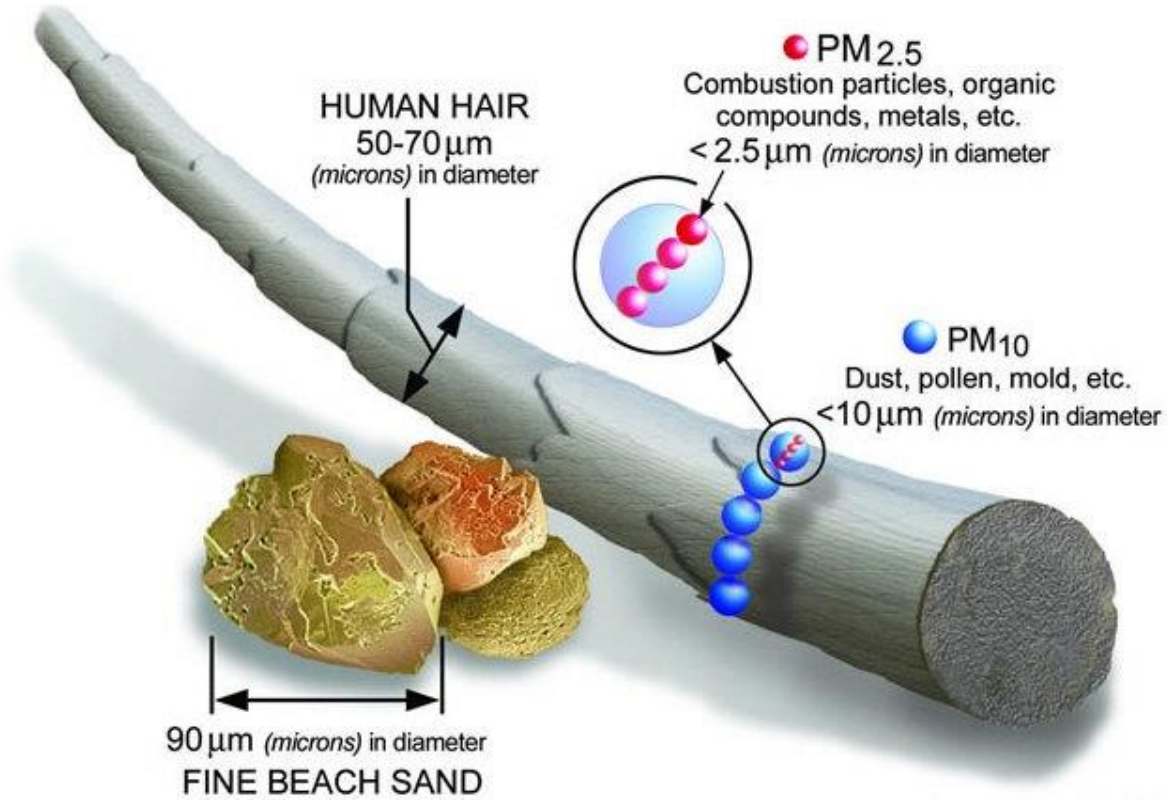
Data analysis

Particulate matter (PM) in air

- Airborne particulate matter is made up of a collection of solid and/or liquid materials of various sizes
  - PM2.5 (fine particles): d ≤ 2.5 µm
  - PM10 (coarse particles): d ≤ 10 µm

- PM pollution consists of materials (including dust, smoke, and soot) either:
  - Directly emitted into the air
  - Result from the transformation of gaseous pollutants

- *Secondary organic aerosol* relates to the (S)VOCs adsorbed onto PM particles



Source: www.epa.gov/pm-pollution/particulate-matter-pm-basics

Sources of particulate matter

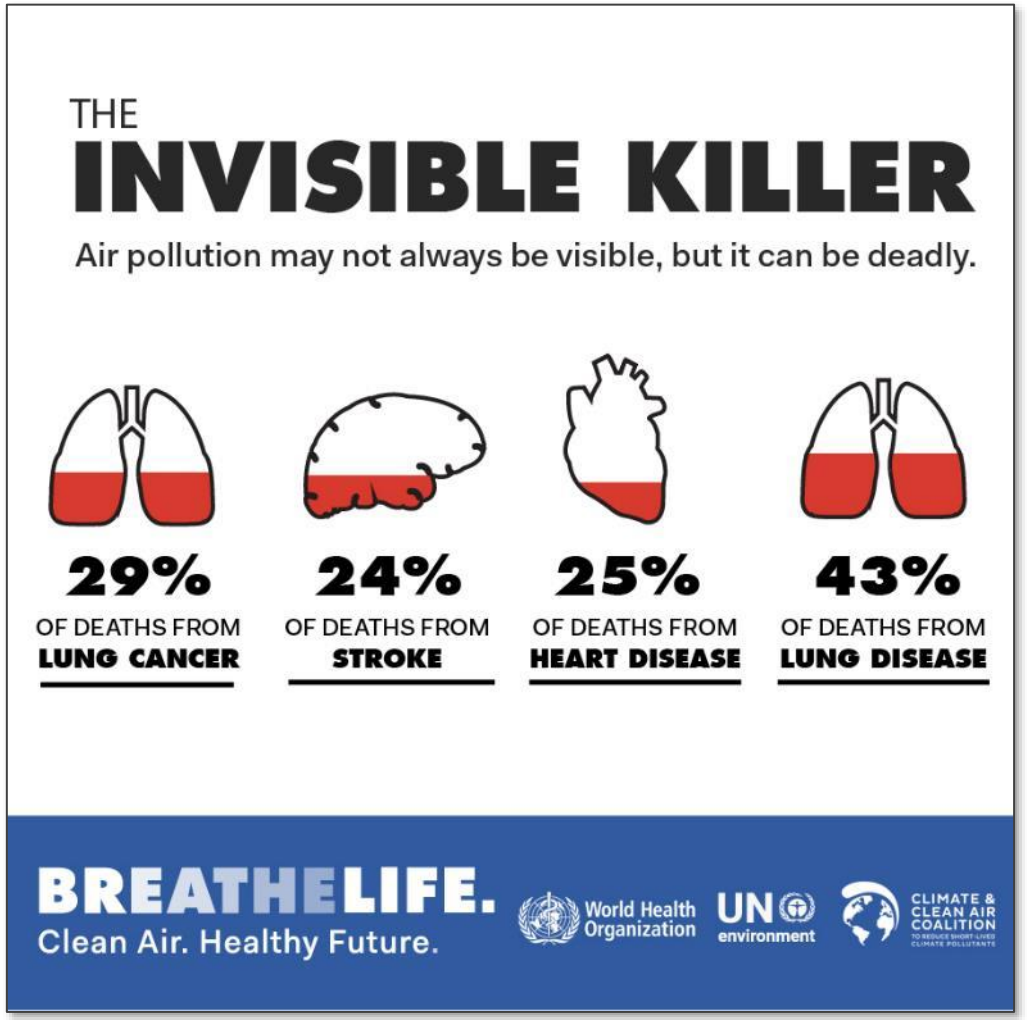
Industry
(power plants, factories…)

Vehicle emissions

Natural Sources
(forest fires, volcanoes…)

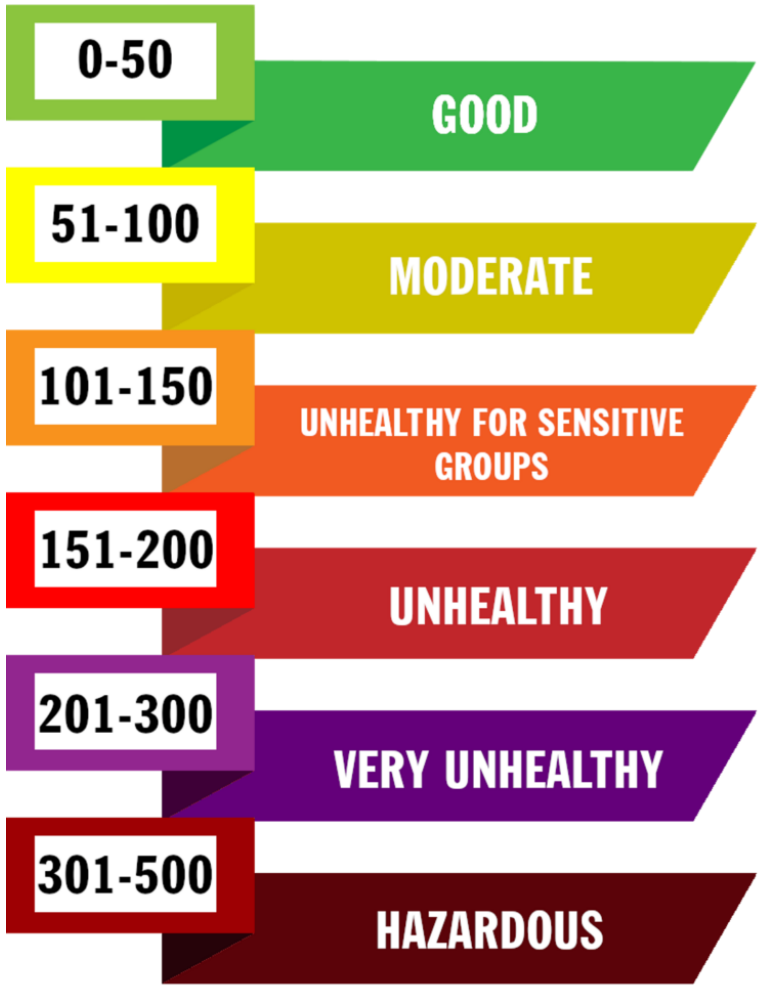
Particulate matter and health risks

- People are exposed to particle pollution when they breathe
- Can cause severe health effects
  - **4.2 million** deaths every year as a result of exposure to ambient (outdoor) air pollution
- **91%** of the world's population lives in places where air quality exceeds WHO guideline limits
- ***What does the SOA release within our body?***



Source: www.who.int/airpollution/en/

The Air Quality Index (AQI)



- A unit-less scale of 0 to 500 representing how good or bad the air quality is
- The higher the AQI the worse the air quality

Source: https://www.lrapa.org/aqi101/

World’s most polluted cities (2022)

Meets WHO guideline | Exceeds by 1 to 2 times | Exceeds by 2 to 3 times | Exceeds by 3 to 5 times | Exceeds by 5 to 7 times | Exceeds by 7 to 10 times | Exceeds by over 10 times

Rank	City	2022	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	2021	2020	2019	2018	2017
1	Lahore, Pakistan	97.4	133	102.5	85.6	69.3	60.9	52.1	47.8	46.2	64.2	123.2	190.5	192.9	86.5	79.2	89.5	114.9	133.2
2	Hotan, China	94.3	61.7	91.6	132.7	106.2	120.5	69.5	172.5	75	65.1	75	50.3	120	101.5	110.2	110.1	116	91.9
3	Bhiwadi, India	92.7	110.6	98	116.2	149.5	123.8	102.8	38.8	36.5	59.9	85.4	111.4	86.9	106.2	95.5	83.4	125.4	-
4	Delhi (NCT), India	92.6	141	100.9	91	98	73.2	56.2	34.3	31.1	38.3	99.7	176.8	171.9	96.4	84.1	98.6	113.5	108.2
5	Peshawar, Pakistan	91.8	110.2	103.5	78.3	68.5	53.5	56.3	51.8	57.8	79	100	132	212.1	89.6	-	63.9	-	-
6	Darbhanga, India	90.3	127	77.9	83.1	64.9	46.3	39.1	21	25.4	32.1	86.8	179.9	248	175.9	-	-	-	-
7	Asopur, India	90.2	110.3	89	104.6	124.4	73.4	52.3	44.1	34.9	37.1	74.1	139.7	201.2	-	-	-	-	-
8	N'Djamena, Chad	89.7	162.3	163.7	245.6	103.7	74.2	36.6	21.2	21.8	22.1	49.7	59.9	132.4	77.6	-	-	-	-
9	New Delhi, India	89.1	133.7	95.2	86.4	93.7	72.5	54.9	33.6	30.5	37.7	94.9	170.1	166.8	-	-	-	-	-
10	Patna, India	88.9	128	99.8	105.1	98.1	58	53.8	37.5	35.8	37.5	65.3	141.9	209.2	78.2	68.4	82.1	119.7	118.5

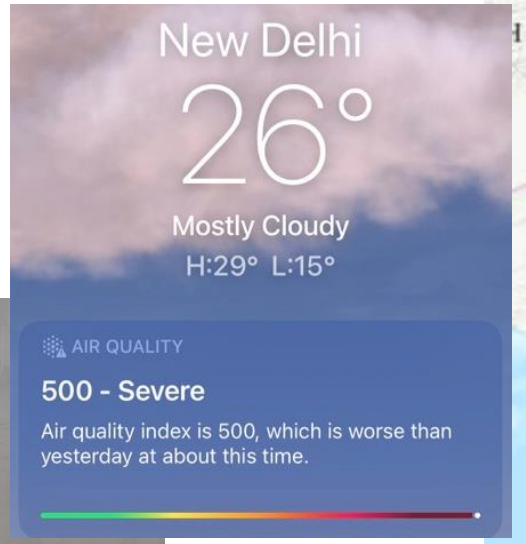
SepSolve Analytical

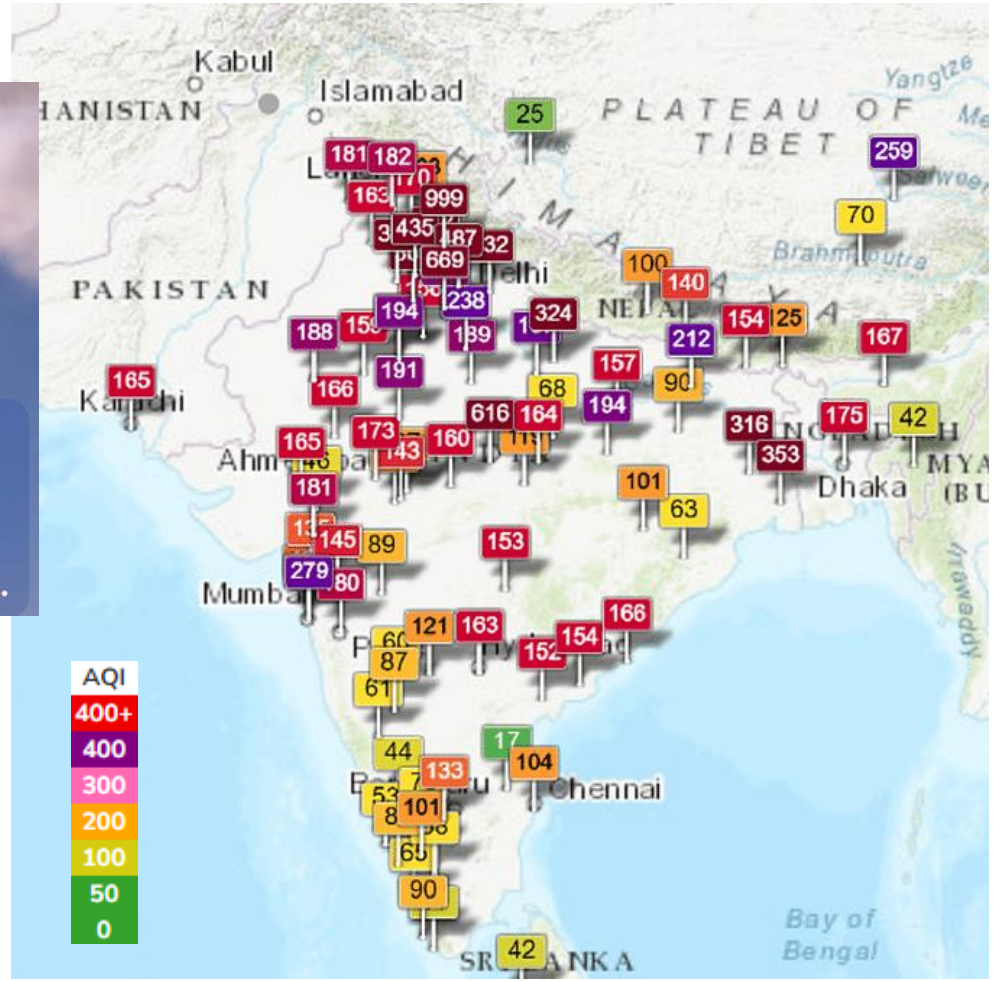
Source: IQAir, World's Most Polluted Cities in 2022, https://www.iqair.com/world-most-polluted-cities

Air quality in India

And the importance of real-time pollution source identification

- Sources of pollution may change on an hourly basis
- Accurate identification of the SOA help to trace the source





Source: https://www.nationalheraldindia.com/environment/saturday-air-quality-index-faridabad-ghaziabad-delhi-still-hazardous
https://indianexpress.com/article/cities/delhi/delhi-cm-kejriwal-supersite-real-time-data-air-pollution-8412449/

Analysis of secondary organic aerosol (SOA)

The Challenges

- Existing methods to monitor SOA are typically offline
  - Time-consuming and costly solvent extraction of filters
- Online methods tend to use a single filter
  - Carryover can be a concern
- Direct analysis is limited in terms of compound speciation
- Sample complexity may require advanced separation

Online analysis of SOA from PM2.5

Development of a TD–GC–TOF MS approach

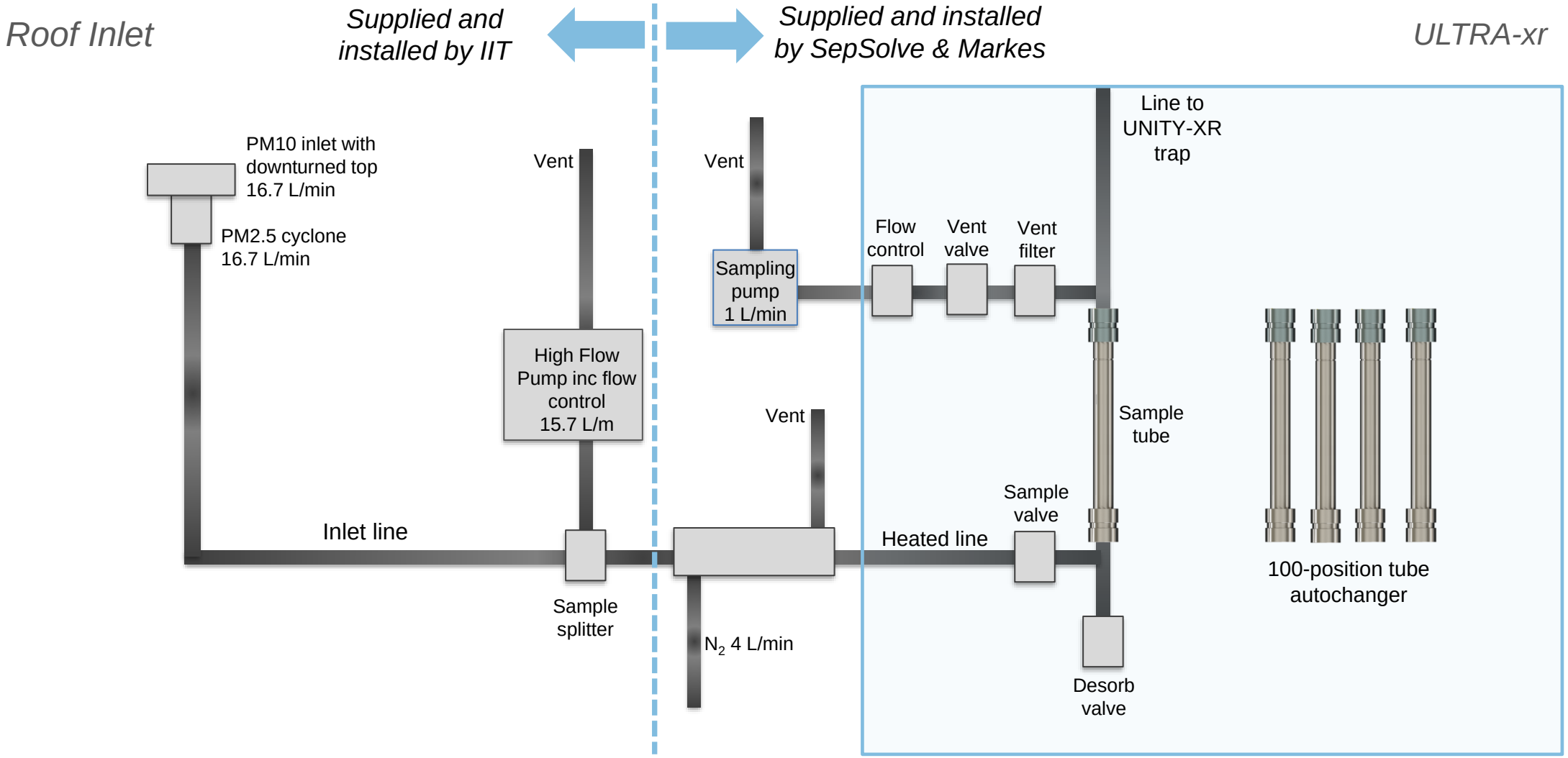
Rooftop sampling of PM2.5

Automated sampling onto thermal desorption (TD) tubes containing PM2.5 filters instead of sorbent

Separation and confident identification by gas chromatography and BenchTOF2 mass spectrometry (GC–TOF MS)

- Automated analysis with no time-consuming, offline sample preparation

PM2.5 sampling flow diagram for a modified TD instrument*



*Patent pending (Application no. GB2215214.4)

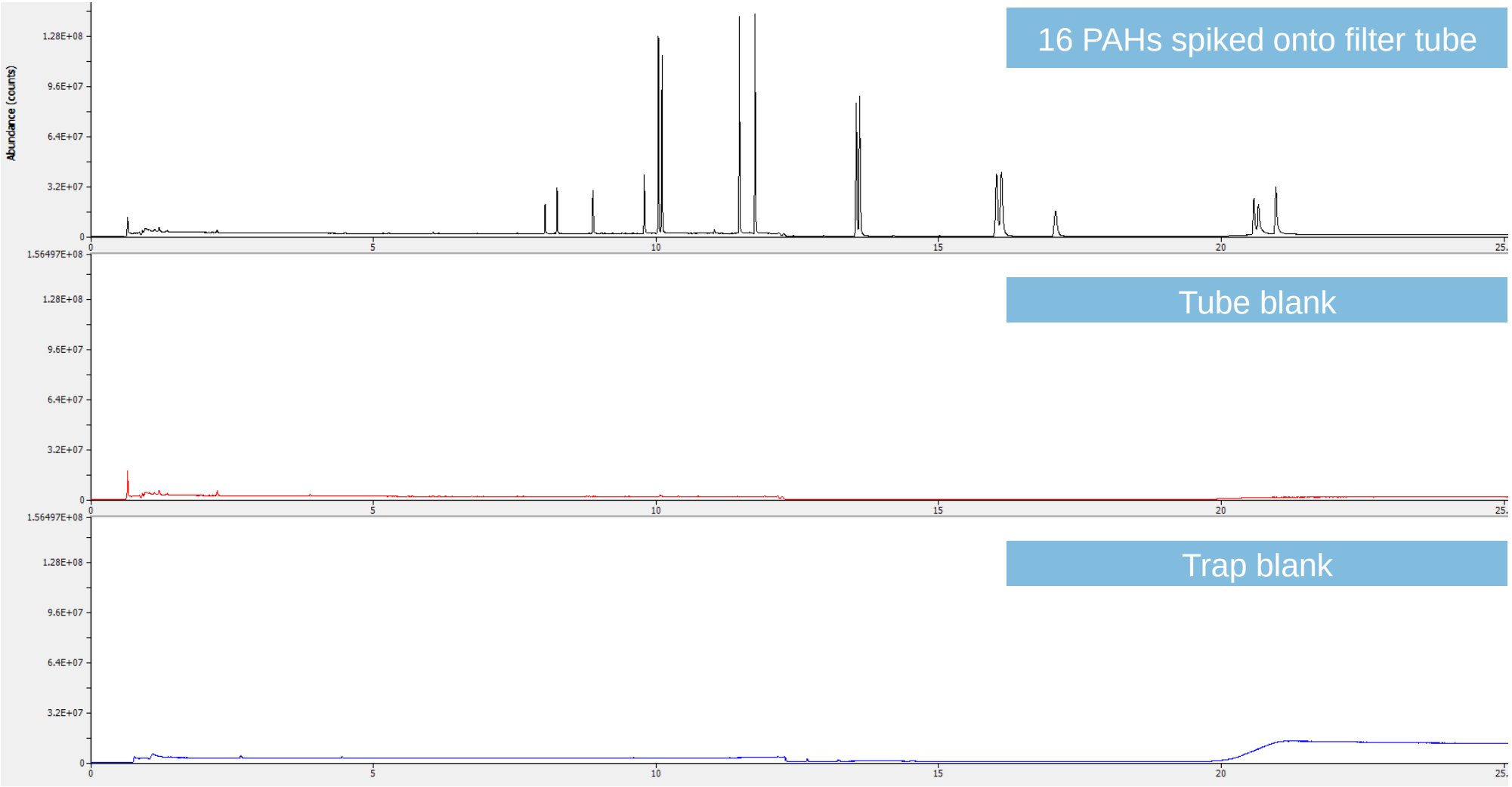
TD filter tubes for PM2.5 analysis*

- 2× 6mm quartz filters held between two protective gauzes and supported by two retaining springs
- Flow restriction measured prior to analysis
- Filters replaced and tubes conditioned prior to re-use

*Patent pending

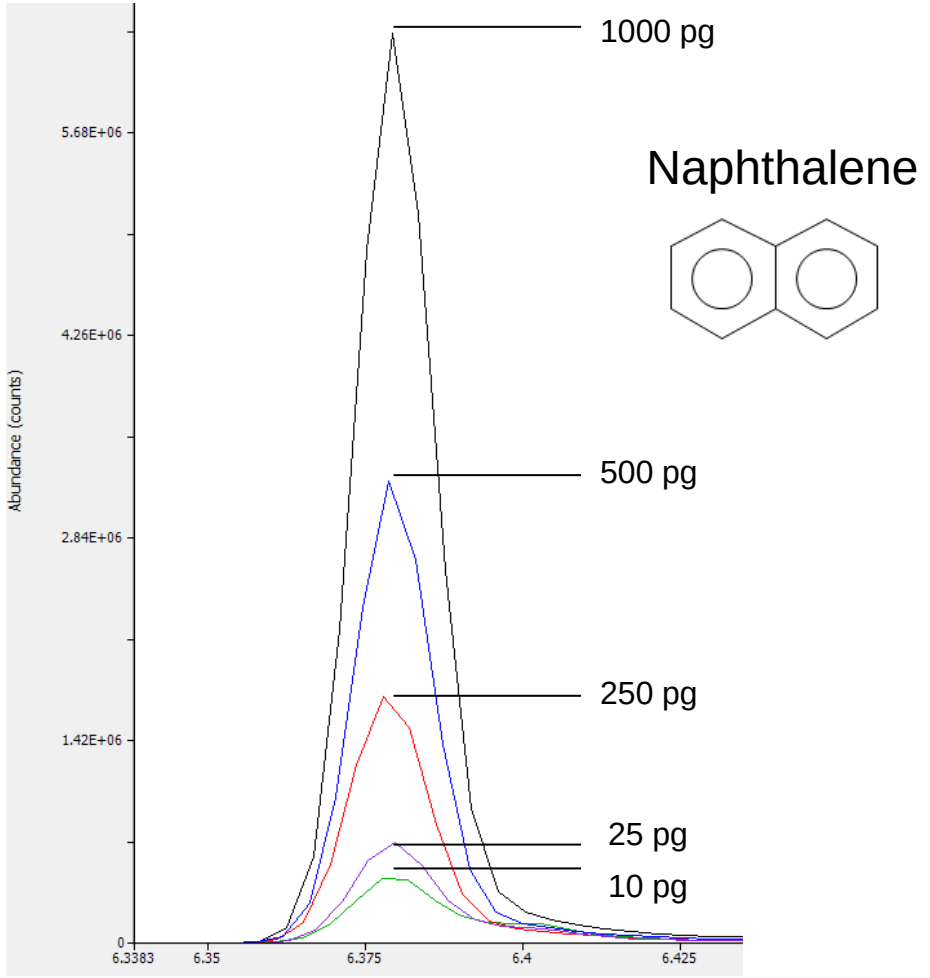
Validating the system

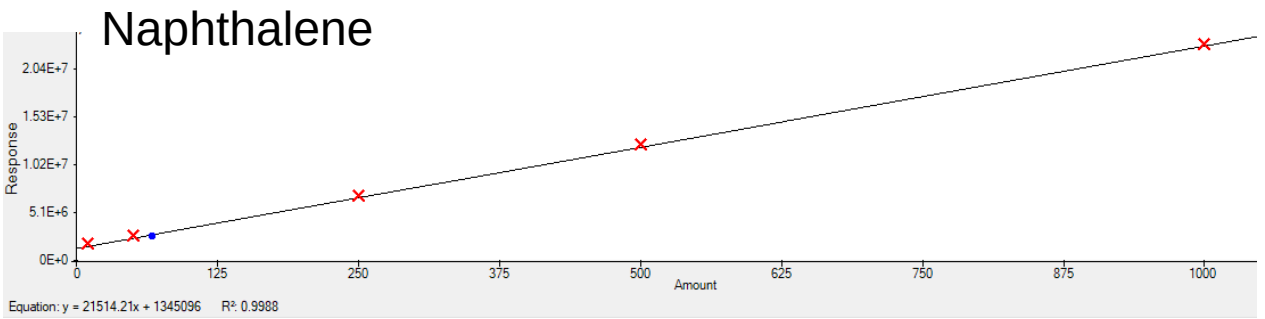
Monitoring carryover

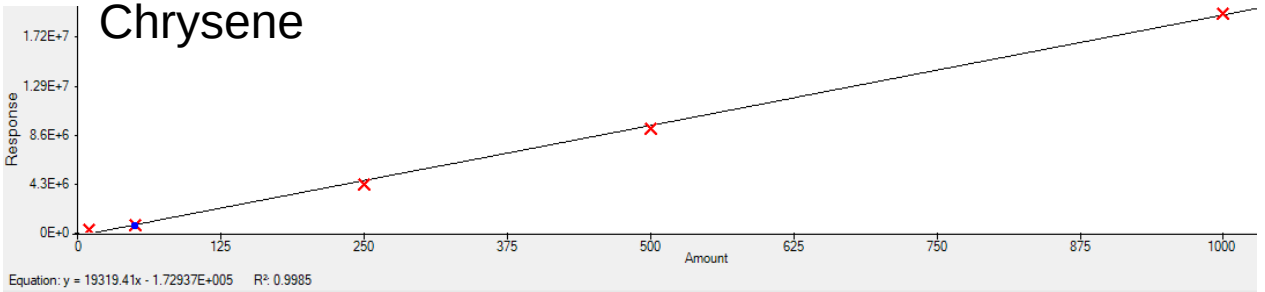


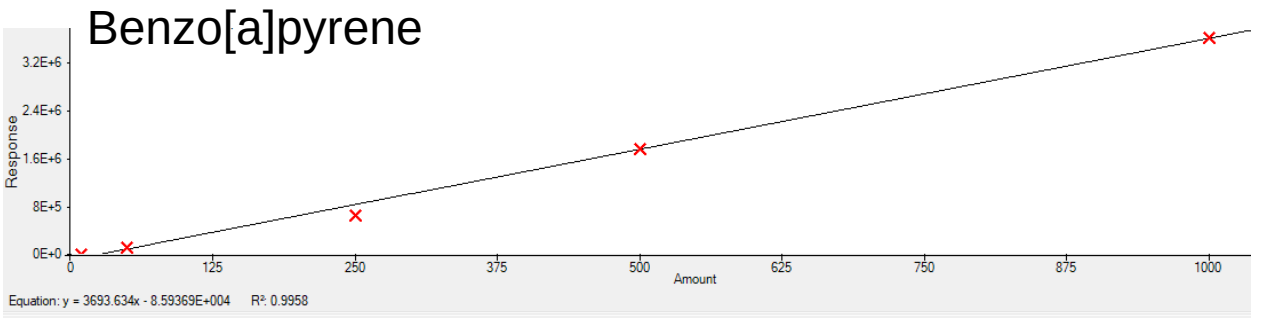
Validating the system

Calibration of 16 PAHs via spiked filter tubes

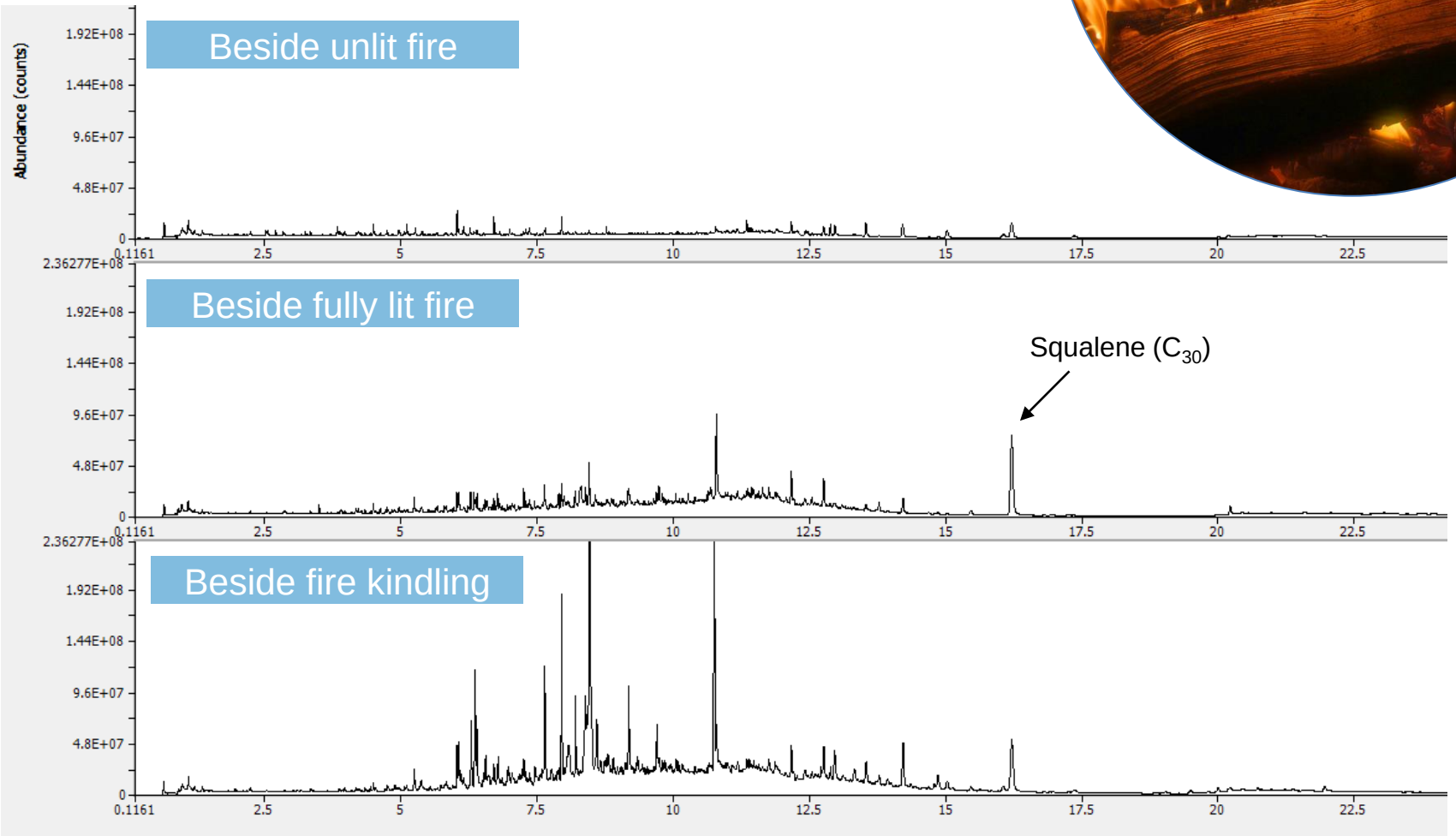






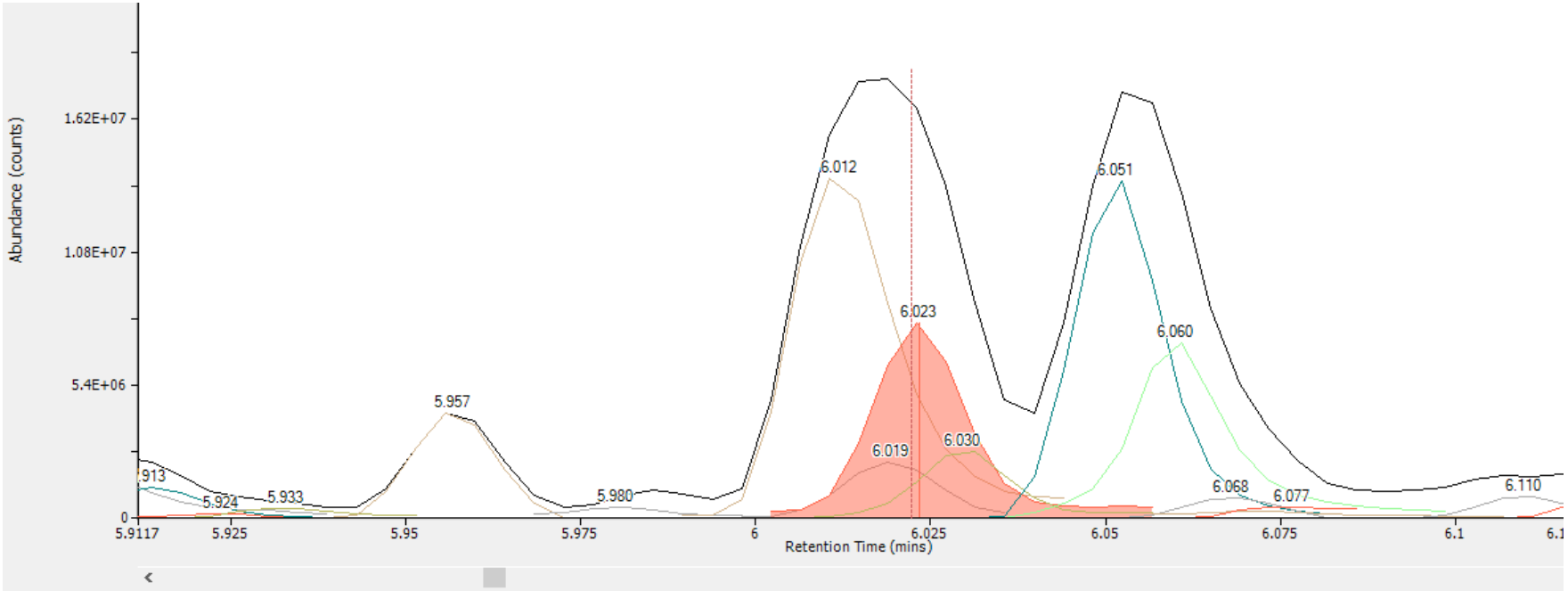


Validating the system…in the UK



Validating the system…in the UK

Sampling beside fully lit fire



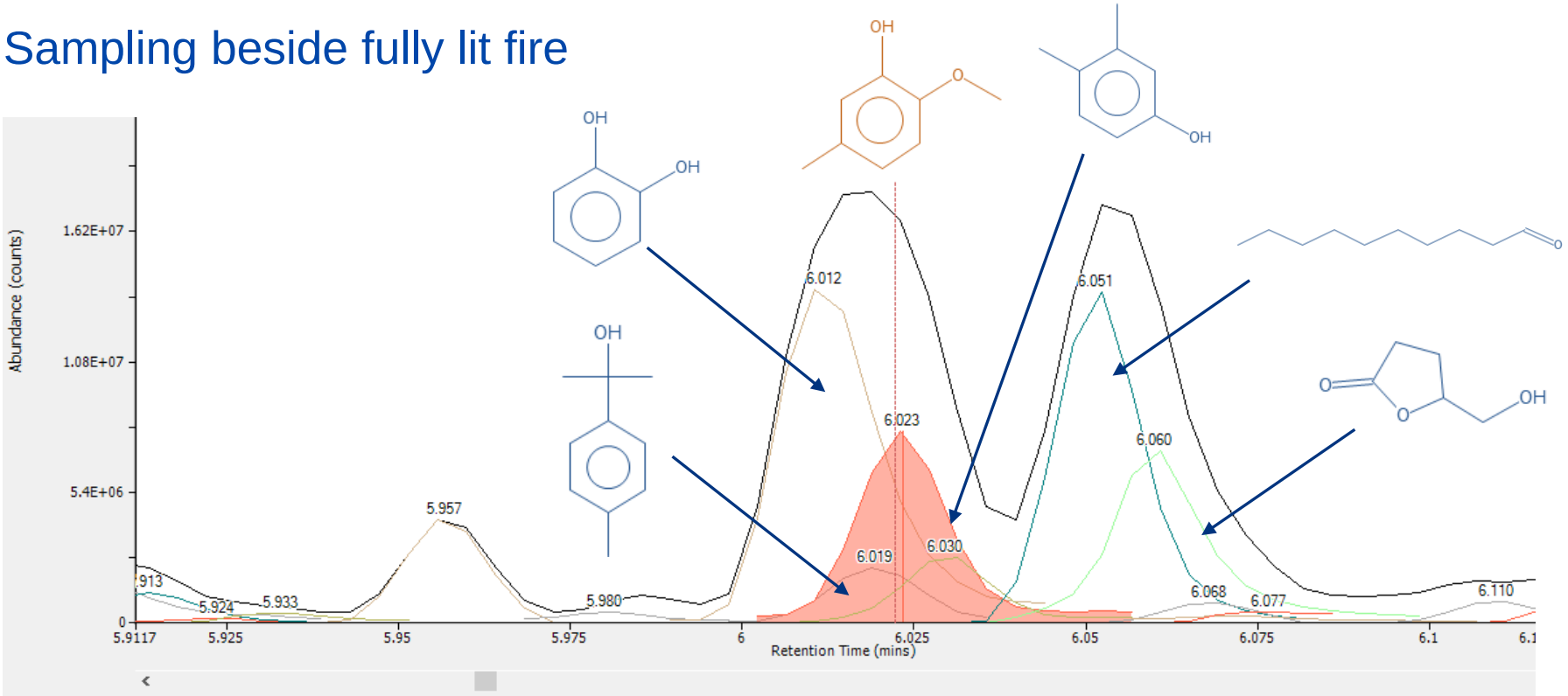
Area Percent | Num. Peaks: 998

Peak #	Source	RT	Compound	Synonyms	MF	Library RI	RMF	Probability	Area	Height	Area %	Status
258	TIC	6.012	Catechol	Catechol	884	1209	900	86.64	6.31447E+07	1.37851E+07	0.6	Unspecified
259	TIC	6.0193	Benzenemethanol, α,α,4-trimethyl-	Benzenem...	617	1183	681	34.53	9.10346E+06	2.27033E+06	0.09	Unspecified
260	TIC	6.0232	2-Methoxy-5-methylphenol	2-Methoxy-...	807	1193	824	35.64	3.21941E+07	7.90399E+06	0.31	Unspecified
261	TIC	6.0296	Phenol, 3,4-dimethyl-	Phenol, 3,4...	741	1193	764	19.55	1.09842E+07	2.67624E+06	0.11	Unspecified
262	TIC	6.0515	Decanal	Decanal	679	1206	704	20.18	5.12128E+07	1.36353E+07	0.49	Unspecified
263	TIC	6.06	5-(Hydroxymethyl)dihydrofuran-2(3H)-one	5-(Hydroxy...	661	1209	702	13.17	3.01275E+07	7.08187E+06	0.29	Unspecified

Deconvolution enables comprehensive chemical fingerprinting

Validating the system…in the UK

Sampling beside fully lit fire



Area Percent				Num. Peaks	998						
Peak #	Source	RT	Compound	Synonyms	MF	Library RI	RMF	Probability	Area	Height	Area %	Status
258	TIC	6.012	Catechol	Catechol	884	1209	900	86.64	6.31447E+07	1.37851E+07	0.6	Unspecified
259	TIC	6.0193	Benzenemethanol, α,α,4-trimethyl-	Benzenem...	617	1183	681	34.53	9.10346E+06	2.27033E+06	0.09	Unspecified
260	TIC	6.0232	2-Methoxy-5-methylphenol	2-Methoxy-...	807	1193	824	35.64	3.21941E+07	7.90399E+06	0.31	Unspecified
261	TIC	6.0296	Phenol, 3,4-dimethyl-	Phenol, 3,4...	741	1193	764	19.55	1.09842E+07	2.67624E+06	0.11	Unspecified
262	TIC	6.0515	Decanal	Decanal	679	1206	704	20.18	5.12128E+07	1.36353E+07	0.49	Unspecified
263	TIC	6.06	5-(Hydroxymethyl)dihydrofuran-2(3H)-one	5-(Hydroxy...	661	1209	702	13.17	3.01275E+07	7.08187E+06	0.29	Unspecified

Deconvolution enables comprehensive chemical fingerprinting

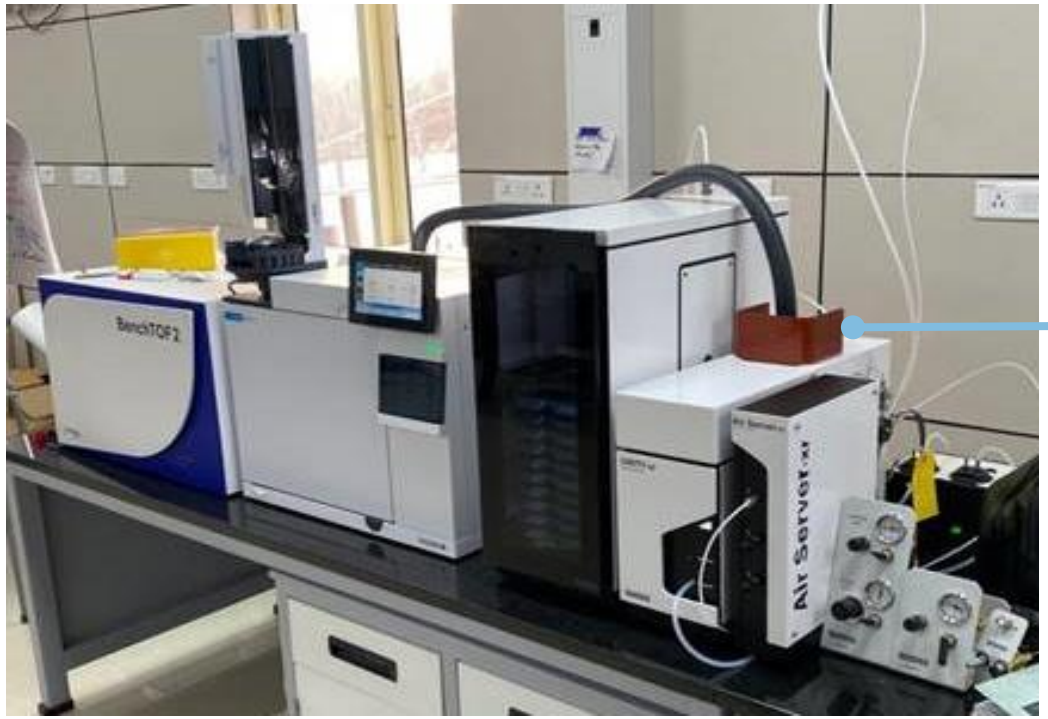
‘Supersite’ for real-time data monitoring

Indian Institute of Technology, New Delhi

PM2.5 cyclone

Rooftop

Laboratory



SOA

https://indianexpress.com/article/cities/delhi/delhi-cm-kejriwal-supersite-real-time-data-air-pollution-8412449

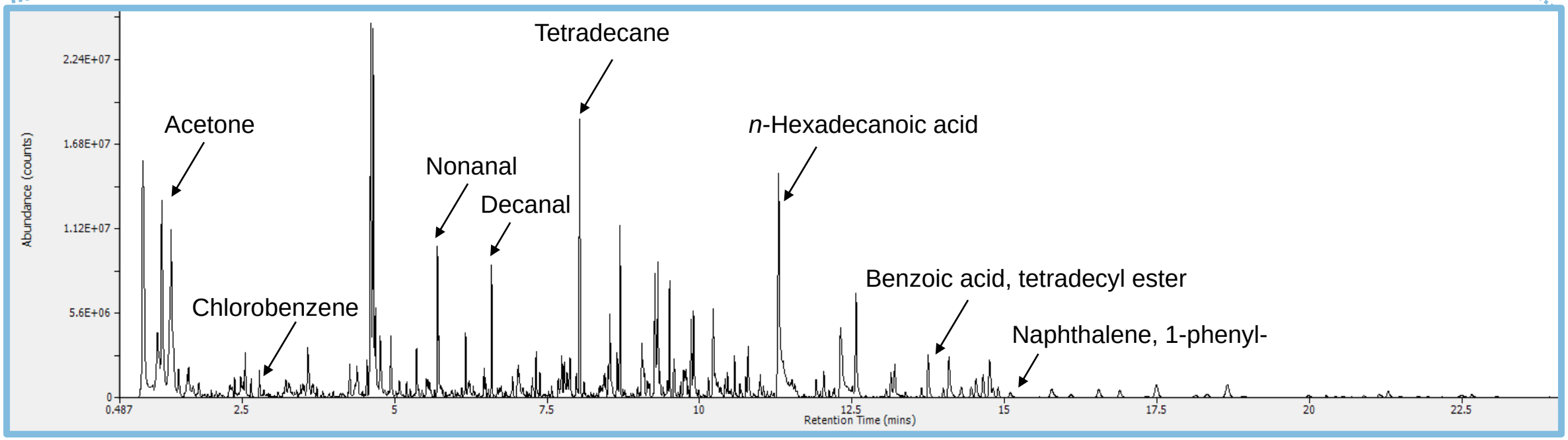
Online monitoring of SOA in New Delhi

Sampling
(0.5 L/min for 20 minutes)

Tube desorption

Analysis
(GC runtime = 25 minutes)

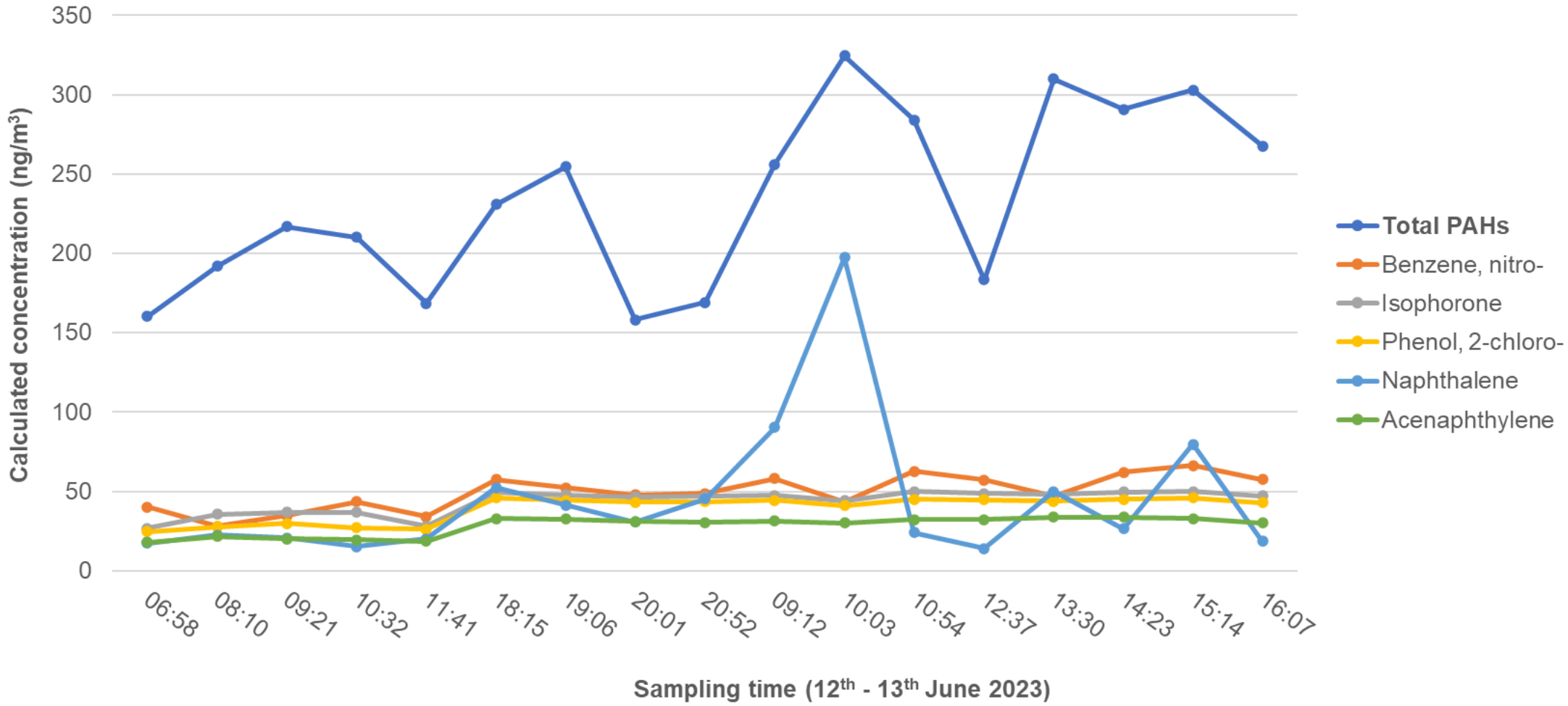
Oven cooldown



SepSolve Analytical

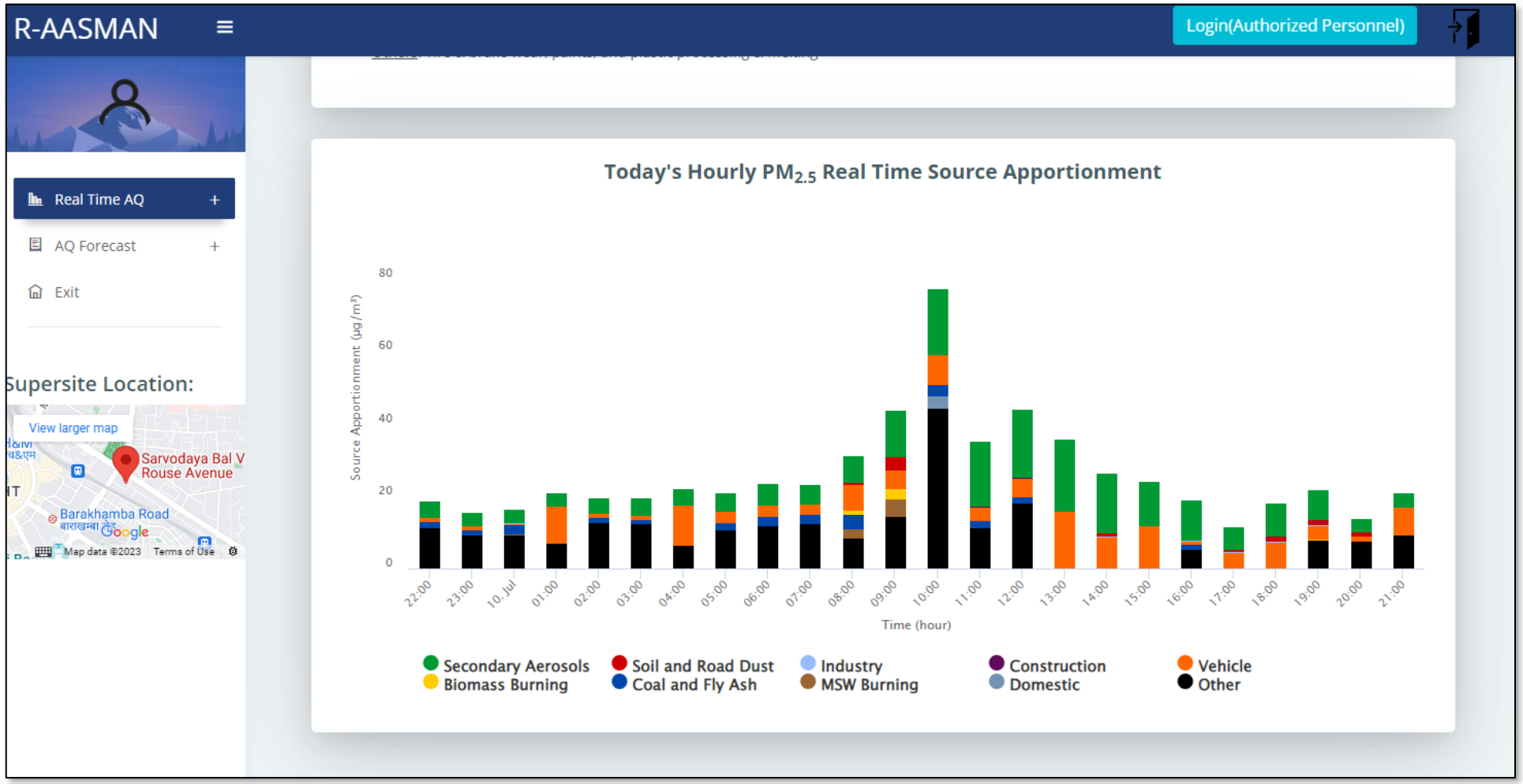
Online chemical fingerprinting of SOA in PM2.5

Hourly monitoring in New Delhi (June 2023)



What's next for the IIT supersite?

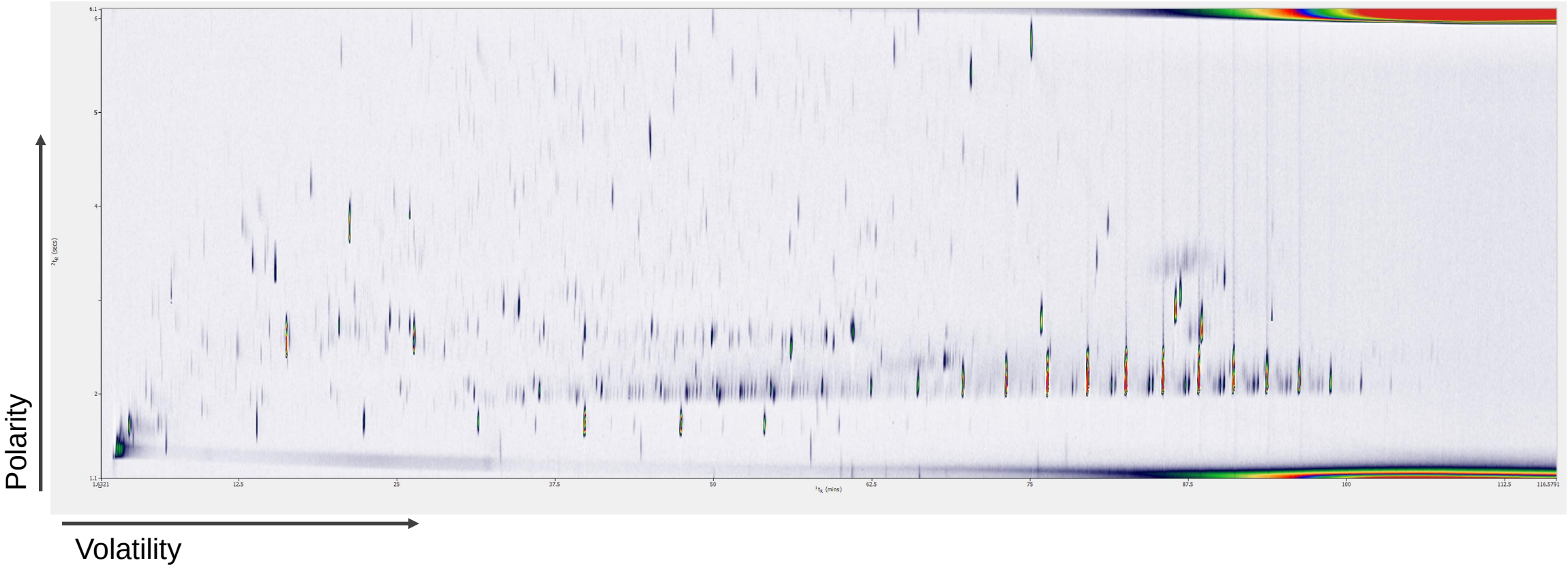
Real-Time Advanced Air Source Management Network (R-AASMAN) software



Source: http://www.raasman.com/dashboard/realtime_source

Future work

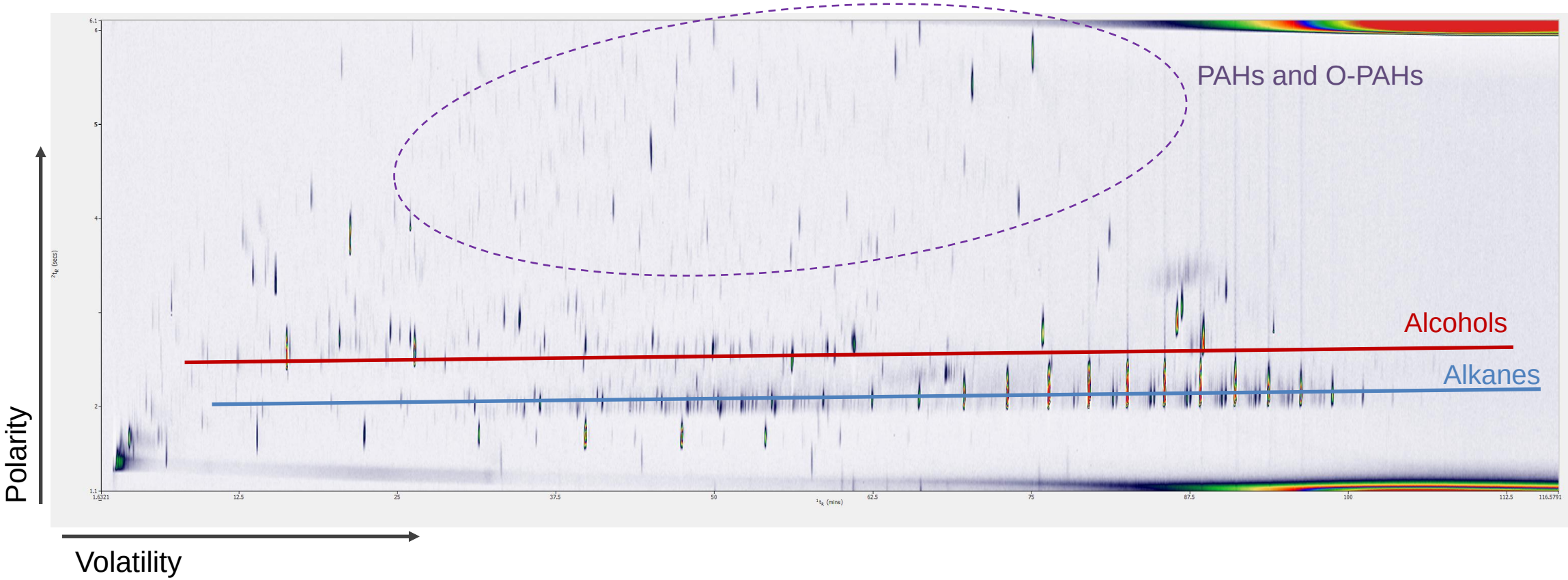
Tackling sample complexity via GC×GC–TOF MS



- Enhanced separation of chemical classes for greater detail on sample composition

Future work

Tackling sample complexity via GC×GC–TOF MS



- Enhanced separation of chemical classes for greater detail on sample composition

Summary

- There is a wealth of information available in chemical fingerprinting of PM2.5
- Online monitoring simplifies sample preparation and analysis of PM2.5 and provides real-time data
- The described system analyses SOA adsorbed onto PM2.5 particles using specially-modified TD filter tubes
- Provides improved monitoring and forecasting of air quality to accelerate anti-pollution strategies.

Acknowledgements

- **Bob Green, James Ogden & Ian Biggs**
  (SepSolve Analytical)
- **Stephen Davies and Ricci Underhill**
  (Markes International)
- **Vikas Tomas and Rajender Kalsain**
  (AVV Technologies, India)
- **Dr Dhirendra Singh**
  (Airshed Planning, India)
- **Prof Mukesh Sharma**
  (Indian Institute of Technology (IIT) Kanpur, India)

Contact SepSolve

Email: hello@sepsolve.com

Tel.: +44 (0)1733 669222

Web: www.sepsolve.com

Twitter: @SepSolve

LinkedIn: www.linkedin.com/company/sepsolve-analytical