Chapter 6

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

Reference textbooks*:*

- Spinelle, L. et al, *“Review of Portable and Low-Cost Sensors for the Ambient Air Monitoring of Benzene and Other Volatile Organic Compounds”*, Sensors, 2017, 17, 1520

6.1 CLASSIFICATION AND SOURCES OF VOCS

Non-methane volatile organic compounds

The general category of **non-methane volatile organic compounds** (NMVOCs) includes organic compounds, such as **hydrocarbons** (alkanes, alkenes and aromatics), **halocarbons** (e.g. trichloroethylene) and **oxygenates** (alcohols, aldehydes and ketones).

The VOCs originate from anthropogenic and biogenic sources; many species are important reactants in the formation of **photochemical smog**.

The reactive species are readily oxidized by hydroxyl radical (OH), forming a complex mixture of peroxy radicals which oxidize NO to NO_2 without consuming O_3 and thus **allowing O_3 to increase** in the daytime atmospheric boundary layer.

The compositions, concentrations, and reactivities of the VOCs which compose biogenic and anthropogenic emissions vary greatly. The **hydrocarbons VOCs are emitted during the production, refining, and use of petroleum fuels**. In urban areas, mobile sources contribute the greatest amount of reactive emissions.

6.1 CLASSIFICATION AND SOURCES OF VOCS

Non-methane volatile organic compounds

Mixing ratios of the individual hydrocarbons VOCs vary greatly, from several parts per trillion by volume (pptv) to several parts per billion by volume (ppbv).

Variations in the reactivities are also substantial.

Isoprene (2-methyl butadiene), which is emitted by deciduous vegetation, has an atmospheric lifetime with respect to oxidation by OH of about 20 min in polluted air.

Monoterpenes ($C_{10}H_{16}$), which are emitted from coniferous trees, react extremely rapidly with OH and O_3 and have lifetimes of minutes.

The atmospheric lifetimes of 2-methylpropene, 2-methylbutane, and the **xylenes**, which are found in vehicle emissions, are approximately 30 min, 7 h, and 1.5 h, respectively.

Oxidation of the terpenes and monoaromatic hydrocarbons produce hygroscopic aerosols which influence **radiative forcing of Earth's climate.**

6.1 CLASSIFICATION AND SOURCES OF VOCS

Non-methane volatile organic compounds

Methanol, **ethanol**, and methyl tertiary butyl ether (MTBE) are **oxygenated VOCs** added to fuels to decrease tailpipe emissions of hydrocarbons and CO.

Some alcohols, aldehydes, and ketones are emitted from **biogenic sources**; others are also produced in the atmosphere through photochemical oxidation.

The levels of some of the light oxygenated VOCs (e.g., acetaldehyde, methanol, ethanol, and acetone) are substantial. In the **rural atmosphere, these can dominate the VOCs distribution**. Although the reactivity of acetaldehyde is very high, the other OxHCs have lifetimes of several days or more, facilitating global-scale transport and enabling the species to contribute to oxidant formation in remote areas.

Organic acids like formic and acetic acids are generated by anthropogenic and biogenic sources, and these are **very soluble in water, and represent the major acidic species in rainwater of remote areas.**

6.1 CLASSIFICATION AND SOURCES OF VOCS

Non-methane volatile organic compounds

The halogenated VOCs include the **chlorofluorocarbons** (CFCs) and their replacements, the **hydrochlorofluorocarbons** (HCFCs) and the **hydrofluorocarbons** (HFCs).

The CFCs have been used as propellants, refrigerants, and blowing agents for producing polyurethane foam. These are chemically inert in the troposphere and thus have **very long atmospheric lifetimes**.

However, their very rapid decomposition in the stratosphere leads to stratospheric ozone depletion. CFCs are also considered as **powerful greenhouse gases**.

The HCFCs and HFCs were manufactured as CFC substitutes. Addition of an extractable H to the molecule makes them more reactive and thus more easily removed from the atmosphere by oxidation.

6.1 CLASSIFICATION AND SOURCES OF VOCS

BTEX group

BTEX is the abbreviation for a group of VOCs consisting of **benzene**, **toluene**, **ethylbenzene**, and **o-, p-, and m-xylenes**.

The presence of BTEX in the environment is caused mainly by the **industrial use** as solvents and in the **production of organic chemicals** such as rubbers, plastics, resins, nylon, lubricants, dyes, detergents, drugs, pesticides, paints, lacquers, and adhesives.

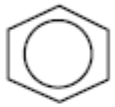
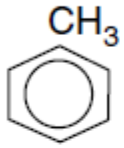
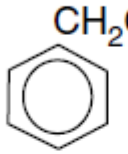
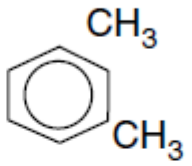
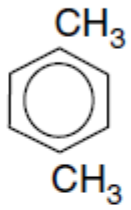
BTEX contamination is also related to petroleum due to the high concentration in gasolines and in other derivate products such as diesel fuel, lubricating, and heating oil.

The characteristics and the uses of BTEX can cause them to be present in many environments. This represents a **hazard to the environment itself as well as to public health**. That is the reason why these are priority pollutants in environmental organizations.

6.1 CLASSIFICATION AND SOURCES OF VOCS

BTEX group

TABLE 14.1
Physicochemical Properties of BTEX Compounds

Property	Benzene	Toluene	Ethylbenzene	*m*-Xylene	*p*-Xylene
Chemical structure					
CAS number	71-43-2	108-88-3	100-41-4	108-38-3	106-42-3
Molecular weight (g/mol)	78.11	92.13	106.16	106.16	106.16
Water solubility (g/l)	0.7	0.5	0.2	0.2	0.2
Vapor pressure (hPa 20°C)	101	29	9.3	8	8.2
Density (20°C g/ml)	0.8786	0.8669	0.8670	0.8642	0.8611
Octanol–water partition coefficient K_{ow} 20°C	135	489	1412	—	1510
Henry's law constant (atm cm^3/mol)	126	340	528	—	831
Melting point (°C)	−11	−95	−95.01	−47.4	13–14
Boiling point (°C)	80.1	110.6	136.2	139.1	138.35

6.1 CLASSIFICATION AND SOURCES OF VOCS

BTEX group

Benzene is recognized as the most toxic compound among BTEX, because it has been proved that breathing very high concentrations of benzene in air can cause death and that long-term exposure to lower levels causes leukemia.

The Occupational Safety and Health Administration (OSHA) has set a permissible **exposure limit of 1 ppm in the workplace during an 8-h day if 40 h a week are worked.** For water, the U.S. Environmental Protection Agency (EPA) has set the maximum permissible level for benzene in drinking water at 5 mg/l, while in Europe a maximum concentration of 1 mg/l is allowed. In air, the maximum limit recommended by the European Community is 10 mg/l.

Toluene is less toxic compared to benzene. Whereas very high concentration exposures are needed to cause death, moderate ones may affect the nervous system. There is no evidence for the carcinogenicity of toluene.

For air, the OSHA has set a limit of **200 ppm in the workplace** and the EPA's drinking water limit is set at 1 mg/l.

6.1 CLASSIFICATION AND SOURCES OF VOCS

BTEX group

Ethylbenzene. Ethylbenzene's toxicity is low and there is no evidence that it causes cancer.

EPA drinking water and OSHA occupational exposure limits are set at 0.7 mg/l and **100 ppm** (8 h/day per 40 h/week), respectively.

Xylenes. Like toluene, high concentration exposures to xylene can cause death, while moderate ones can affect the brain. No evidence for the carcinogenicity of xylene is found.

EPA drinking water and OSHA occupational exposure limits are set at 10 and **100 ppm** (8 h/day per 40 h/week), respectively.

6.1 CLASSIFICATION AND SOURCES OF VOCS

BTEX group

Inquinante: C6H6

NomeCentralina	Comune	Provincia	Valore
Bari - Caldarola	Bari	Bari	0,5
Bari - Cavour	Bari	Bari	-
Bari - CUS	Bari	Bari	0,8
Molfetta - Verdi	Molfetta	Bari	0,9
Monopoli - Aldo Moro	Monopoli	Bari	0,5
Monopoli - Liceo ..	Monopoli	Bari	0,8
Andria - Vaccina	Andria	BAT	0,8
Barletta - Casardi	Barletta	BAT	0,5
Brindisi - SISRI	Brindisi	Brindisi	0,6
Brindisi - Terminal ..	Brindisi	Brindisi	0,7
Brindisi - Via dei Mille	Brindisi	Brindisi	0,7
Brindisi - Via Taranto	Brindisi	Brindisi	0,7
Ceglie Messapica	Ceglie Messapica	Brindisi	1,1
Francavilla Fontana	Francavilla Fontana	Brindisi	2
Torchiarolo - Don ..	Torchiarolo	Brindisi	2,2
Candela - Scuola	Candela	Foggia	-
Foggia - Rosati	Foggia	Foggia	0,5
Manfredonia - ..	Manfredonia	Foggia	0,5

Inquinante: C6H6

NomeCentralina	Comune	Provincia	Valore
Cokeria	Taranto	ILVA	18
Direzione	Taranto	ILVA	20
Meteo Parchi	Taranto	ILVA	3,8
Portineria C	Taranto	ILVA	-
Riv1	Taranto	ILVA	0,8
Tamburi - Via Orsini	Taranto	ILVA	3,4
Galatina-Colacem	Galatina	Lecce	0,5
Lecce - Garigliano	Lecce	Lecce	0,6
Lecce - Libertini	Lecce	Lecce	0,6
Martina Franca	Martina Franca	Taranto	1,3
Massafra	Massafra	Taranto	1,4
Taranto - Alto Adige	Taranto	Taranto	1,2
Taranto - CISI	Taranto	Taranto	0,5
Taranto - Machiavelli	Taranto	Taranto	2,4

http://old.arpa.puglia.it/web/guest/qariainq2

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Non-optical-based sensors for VOCs detection

A large number of VOCs sensors based on non-optical techniques are available, and many of them are commercially available.

- Photo-ionization detectors (PID)
- Electrochemical sensors (amperometric or potentiometric)
- Metal oxide sensors (MOx)
- Gas chromatograph coupled with mass spectrometers (GC-MS), including also portable or micro-gas chromatograph (µGC)

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Photo ionization detector

Photo-ionization detectors (PIDs) use high-energy photons, typically in the ultraviolet (UV) range.

The use of UV light to excite the molecules results in the ionization of gas molecules. The energy of the photons is typically in the range of **10 eV**, so that only gases with low ionization energy e.g., organic vapor, can be ionized. The main air constituents, **oxygen** and **nitrogen**, **do not form ions** at this photon energy.

The resulting ions produce an **electric current proportional to the signal output of the detector**. More molecules are presents in the air, more ions are produced, and higher will be the resulting current. Finally, the ions recombine after the detector to reform the original molecules.

Intrinsically, **PIDs sensors not selective** as they ionize everything with an ionization energy less than or equal to the lamp output.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Photo ionization detector

Table 1. Sensitivity of PID sensors for the measurement of benzene or other VOCs.

Model	Manufacturer	LoD for Benzene, ppm	Sensitivity for IBE, V/ppm	Selectivity, Known Interferents	Stability, Drift	Range for IBE, ppm	t_{90}, s
ppb MiniPiD white	Ion Science	0.5	0.025	VOCs with IP lower than the lamp output are detected. Interference from humidity and temperature	calibration periodicity < 1 month	0.001–40	2
piD-TECH eVx Blue 045-014	Baseline-Mocon	0.25	1.125			0.0005–2	a few seconds
piD-TECH plus, 043-235	Baseline-Mocon	2.5	0.125			0–20	<5
PID-AH for VOCs	Alphasense LTD	0.5	>0.020			0.0005–50	<3
Multi-PID 2	Dräger	0.050	Not relevant	Benzene absorption tube	No data	0.100–2000	3
Model 102+	PID Analysers	0.001	Not relevant	All VOCs with IP < 9.6, 10.2 or 11.7 eV	No data	0.001–20	1
VOC-Traq	Baseline-Mocon	0.005	Not relevant	VOCs with IP < 10.6 eV	No data	0.010–20	10
Club	Ion Science	0.0005	Not relevant	All VOCs with IP < 10.0 eV	No data	0.001–5000	13
Tiger Select benzene	Ion Science	0.010 (resolution 0.001)	Not relevant	Use benzene pre-filter	No data	0.001–5000	<2
AdvancedSense DirectSens IAQ	Graywolf	0.0025	Not relevant	VOCs with IP < 10.6 eV	No data	0.005–20	<60
UltraRAE 3000	RAE Systems	50	Not relevant	9.8 eV lamp and benzene tube	No data	0.050–200 (benzene)	60
ppbRAE 3000	RAE Systems	Resolution 1 with 10.6 eV lamp		VOCs with IP < 10.6/9.8 eV	No data	0.001–10	2

IBE: isobutylene, IP: ionization potential [27], t_{90}: time response, time for reaching 90% of final value.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Voltammetric detector

A **voltammetric sensor** is made of a measuring and a counter electrodes together with an additional reference electrode. The gaseous species to be measured diffuses trough the sensor's membranes and to the measuring electrode. A direct electron transfer takes place which produce an internal current which gives a measured **electric current proportional to the gas concentrations**.

These are low cost, low power, compact sensors and in general, their **response time is about 120 s** depending on the air temperature.

To measure a VOC with electrochemical cells it is typically necessary to **optimize the electrochemical sensor to the target VOC**. In fact, amperometric sensors show **poor selectivity** and a limit of detection down to the **high ppb range**.

This type of sensors can be tuned to a specific target gas in many ways. One of the most logical way is to **target a specific chemical reaction** of the electrochemical reaction controlling the selectivity. Some physical characteristics of the diffusion barrier (e.g., **porosity** or **pore distribution**) can be adjusted for specific molecules, in addition to the bias voltage between the reference and the counter electrode, the type of electrolyte, the material of the measuring electrode etc. which impact the selectivity such types of gas sensor.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Voltammetric detector

Usually, these sensors provide high compactness and have a very **low electrical consumption** owing to the low electrical current signal generated. The main power requirement is the amplification of the very low-level signal required to read the measurement.

Most of the amperometric sensors need **humidity** to function properly, as certain electrolytes can be damaged by very low humidity, leading to a bias in the measurements. Solid-state material-based sensors are not so dependent on ambient humidity.

The **temperature** also has an influence on the sensor response, but this interference can be modelled and compensated.

Wind velocity, in particular in ambient air applications, can also have an influence on the chemical equilibrium on the or the **diffusion** through the membrane of these sensors.

In general, this kind of sensors show **long-term instability** with performances drift needing for **recalibration**.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Voltammetric detector

Table 2. Sensitivity response time and limit of detection of the commercially available amperometric sensors.

Model	Supplier	LoD, ppm	Sensitivity, μA/ppm	Selectivity, Known Interferents	Stability, Drift in ppm	Range, ppm	t_{90}, s
3ETO CiTiceL	City Technology	0.1 (Resolution)	2.75 ± 0.5	CO, HC, and VOCs	Zero: 2, Baseline: 0–1, Span: <5%/year	0–20	<140
4ETO CiTiceL	City Technology	0.1 (Resolution)	1.9 ± 0.5	VOCs in general	Zero: 4, Baseline: 0–3, Span: <5%/year	0–20	<120
7ETO CiTiceL	City Technology	0.1 (Resolution)	2.25 ± 0.65	Ethanol ≈ 55%; MEK ≈ 10%; Toluene ≈ 20%; CO ≈ 40%	Zero: 2, Baseline: 0–1, Span: <5%/year	0–20	<140
ETO-A1	Alphasense LTD	0.1	2.0 to 3.2	The bias voltage is set for ETO and needs adjusting for other VOCs	No data	0–100	<150
ETO-B1	Alphasense LTD	0.1	2.0 to 3.2		No data	0–100	<150
ETO/M-10	MembraporAG	0.05 (Resolution)	2.0 ± 0.5		Zero: no data, Baseline: 0–1, Span: <2%/month	0–10	<140
ETO/C-20	Membrapor AG	0.1 (Resolution)	2.5 ± 0.6	Interference evaluated for a list of VOCs	Zero: no data, Baseline: 0–1, Span: <2%/month	0–20	<140
EC4-10-ETO	SGX Sensortech	0.1 (Resolution)	1.9 ± 0.8	CO, HC, and VOCs	Zero: −0.2–2.5 μA, Baseline: 0–2, Span: <2%/month	0–10	<120

ETO: ethylene oxides, C2H5OH: ethanol, MEK: methyl ethyl ketone ($CH_3C(O)CH_2CH_3$).

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

MOx detector

Resistive sensors are usually smaller compared to amperometric ones, with a size of a few millimeters and a weight about a few grams. A **high temperature** is needed for the reactions to take place at a faster rate.

This kind of sensors are **like PID not specific to individual organic compounds**. Moreover, these sensors do additionally respond to inorganic reducing and oxidizing gases like e.g., CO or NOx. To improve their selectivity, manufacturers typically incorporate different dopants or filters.

Temperature and humidity are also important interferents of the signal and have to be controlled or measured with precision so they can be extracted, and their influence can be modelled. The main issue for this type of sensor is the **long-term stability**. In fact, the response changes over time and the sensors needs to be recalibrated more regularly.

The gas desorption tends to be very slow, increasing the length of time needed to make a measurement. The times can be as high as 45 min but in most of the cases, their **response time is in the range of the minutes.**

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

MOx detector

Compared to PIDs, MOx sensors are generally **compact**, **low cost** but need **higher power**. MOx sensors also respond to inorganic gases, so one should not use them to measure low concentrations of VOCs where gases such as NO, NO_2 or CO are also present in higher concentrations. Thus, when using Mox sensors, information about long-term stability, **cross-sensitivity** to gaseous interfering compounds and humidity sensitivity is also important in order to correct sensor response. MOx sensors are advisable when sensing VOCs that are not measured by PIDs (e.g., many CFCs).

A few studies show that the most sensitive oxides for VOCs include the four following types: WO_3, SnO_2, In_2O_2 and ZnO.

Several methods have been studied to **improve the selectivity** of MOx VOCs sensors. For example, using physical or chemical filters, doping of the sensitive element, combining of several detection systems on the same matrix (electronic noses), or the operation of sensors under different temperatures or dynamic regimes.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

MOx detector

- Green synthesis approach for the preparation of WO_3 nanomaterials.
- Porous materials composed of polycrystalline WO_3 nanoparticles prepared using two methods: aqueous solution of sodium chloride (WO_3-1) and upon exposure to water vapor (WO_3-2)

From the journal:
Journal of Materials Chemistry A

doi.org/10.1039/D0TA06418A

A novel approach for green synthesis of WO_3 nanomaterials and their highly selective chemical sensing properties†

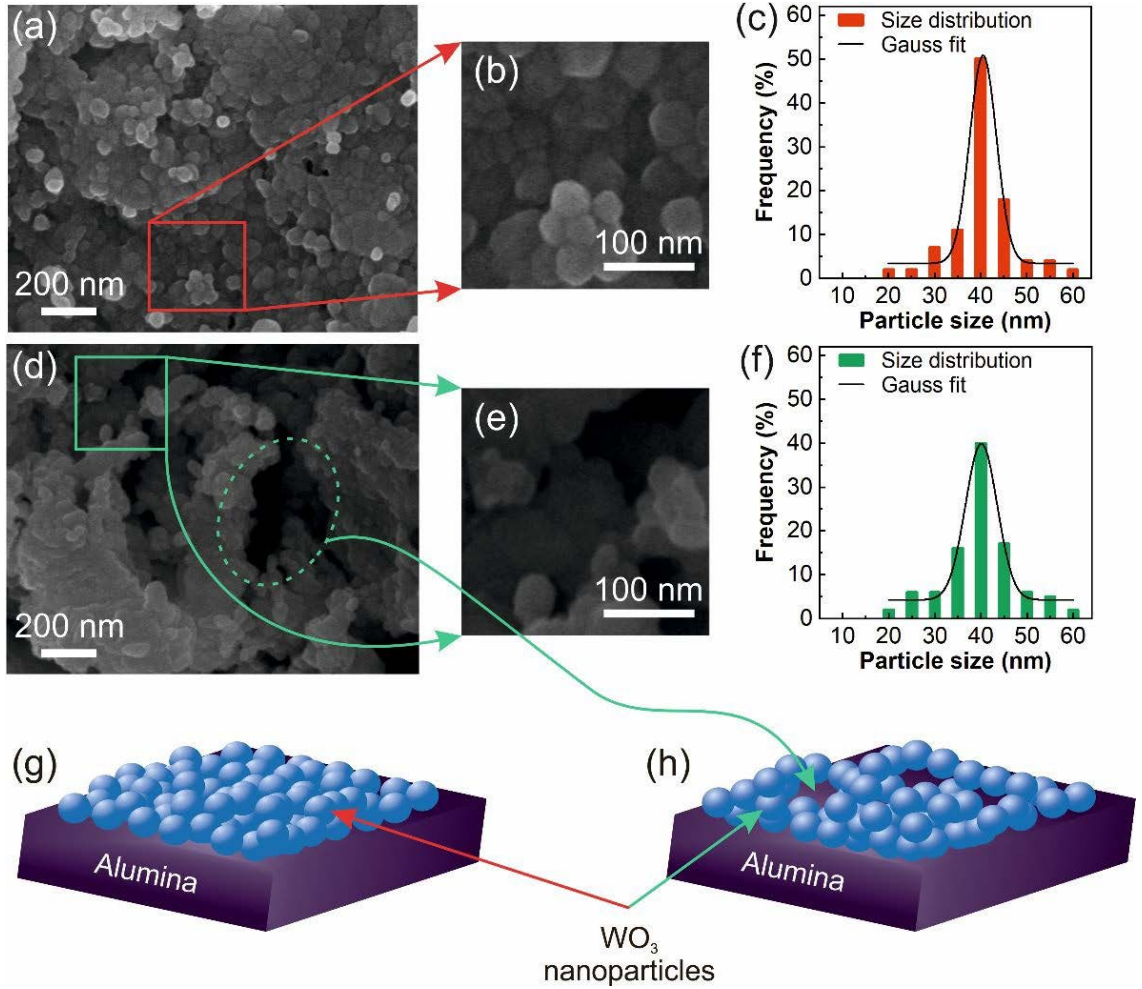
Check for updates

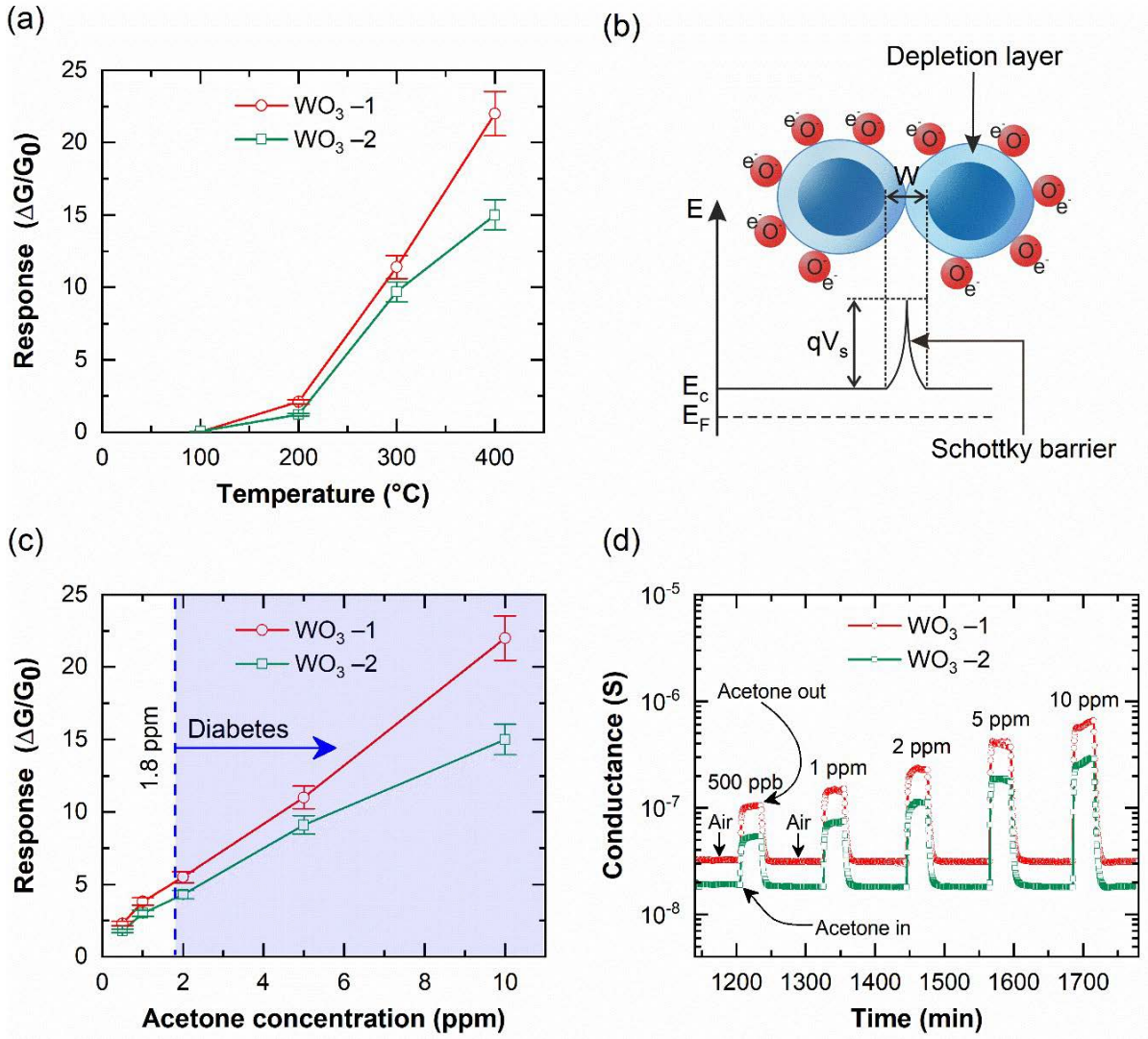
Vardan Galstyan, *a Nicola Poli,a Annalisa D'Arco, bc Salvatore Macis,c Stefano Lupi cd and Elisabetta Comini a

- Good selective response to acetone compared to different interfering gases.
- Limits of detection of the samples prepared in sodium chloride-containing water and upon exposure to water vapor are 170 and 220 ppb, respectively.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

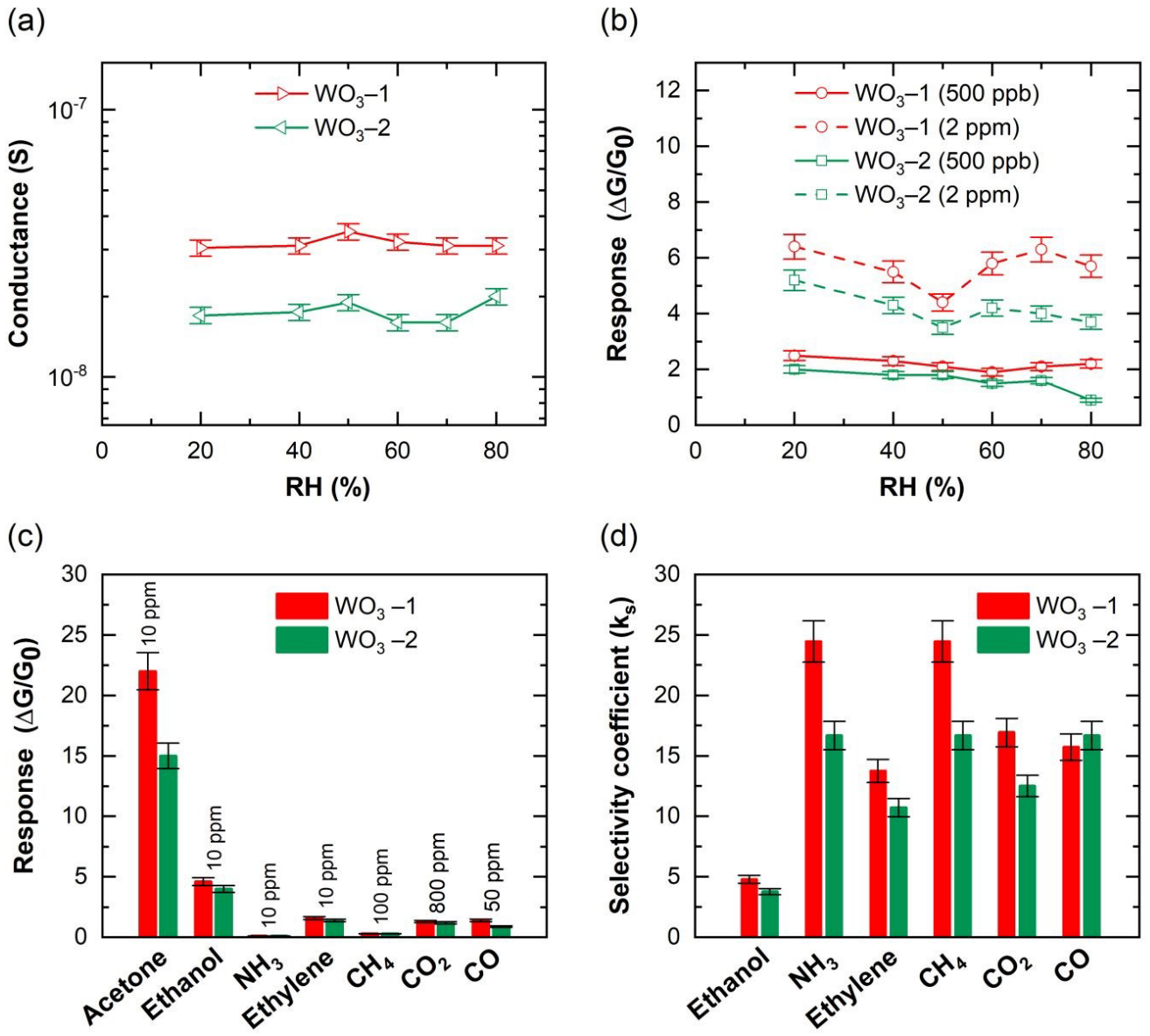
MOx detector





6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

MOx detector



6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

MOx detector

- Yolk-shell SnO_2@SnO_2 structures with hierarchical architecture and penetrable multi-walled surfaces and cuboctahedral shape.
- Secondary building blocks consisting of numerous nanoparticles.

Sensors and Actuators B 231 (2016) 365–375

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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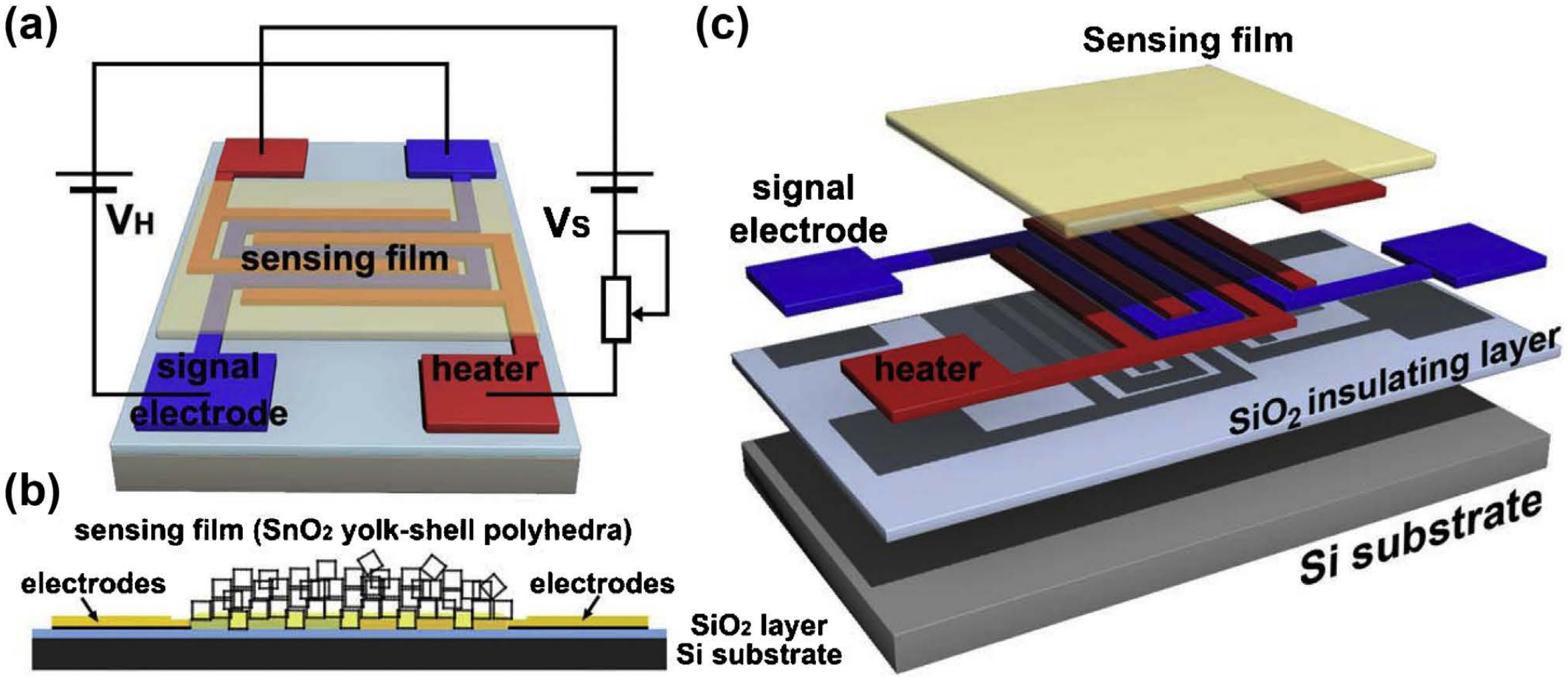
Multistep synthesis of non-spherical SnO_2@SnO_2 yolk-shell cuboctahedra with nanoparticle-assembled porous structure for toluene detection

Yifei Bing[a], Chang Liu[a], Liang Qiao[b], Yi Zeng[a,*], Shansheng Yu[a], Zhongzhu Liang[c], Junping Liu[a], Jingze Luo[a], Weitao Zheng[a,*]

- Sensor based on SnO_2 products for Toluene detection. Excellent sensing performances with a response of 28.6–20 ppm toluene at the optimal working temperature of 250°C.
- Response time and recovery time of 1.8 and 4.1 s, respectively, were demonstrated.

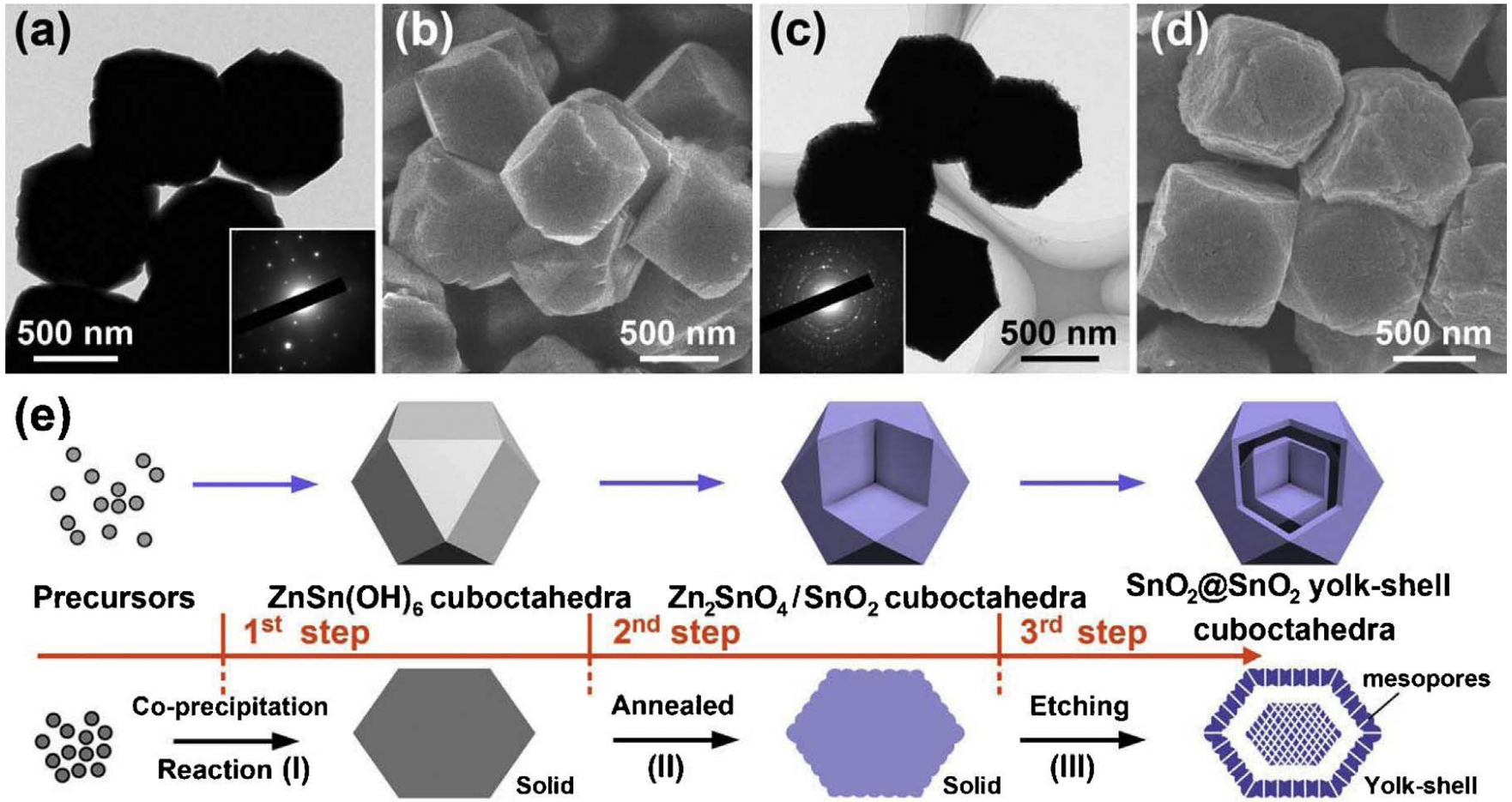
6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

MOx detector



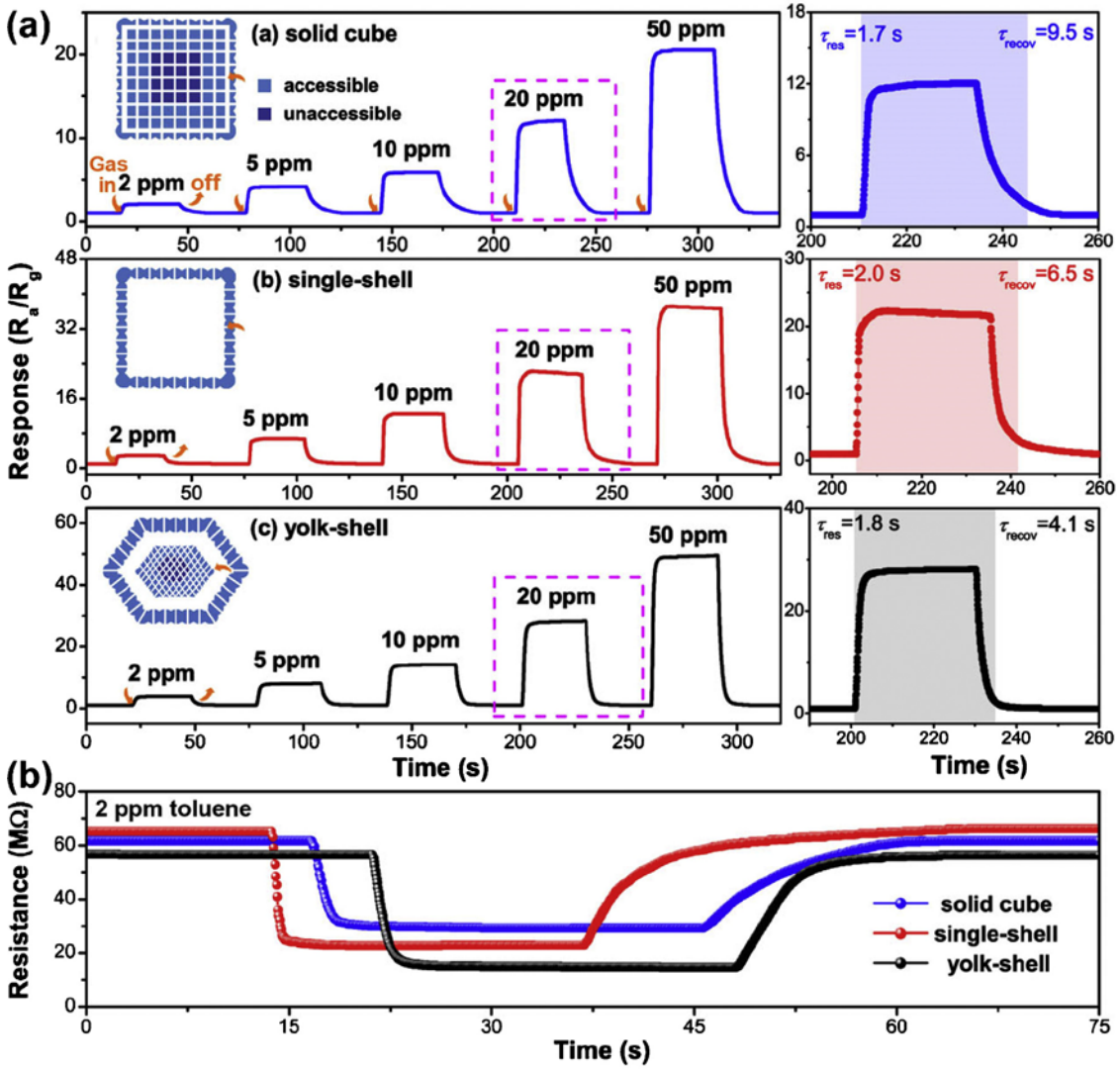
6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

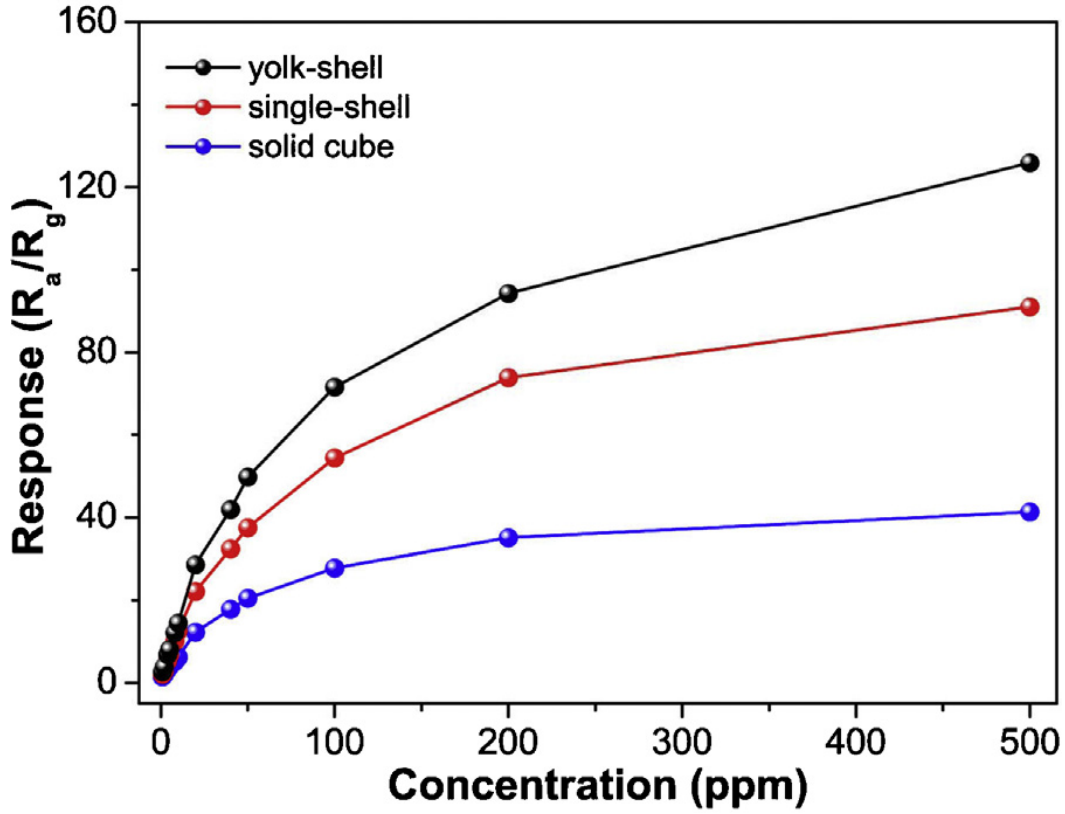
MOx detector



6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

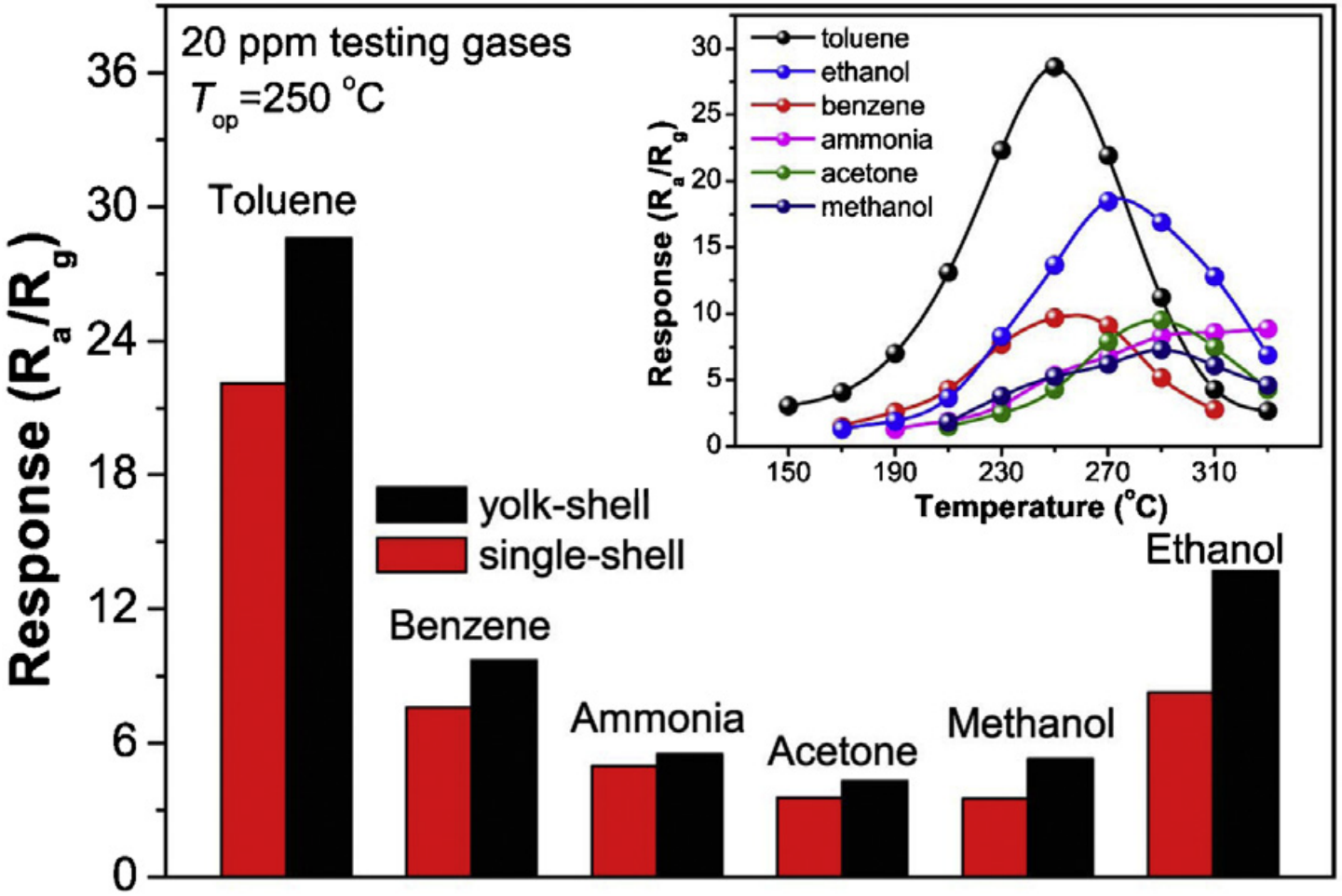
MOx detector





6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

MOx detector



6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

MOx detector

Table 3. Sensitivity response time and limit of detection of the commercially available MOx sensors.

Models	Manufacturers	LoD, ppm	Sensitivity log(Rs/R_0)/log(ppm)	Selectivity, Known Interferents	Stability, Drift	Range, ppm	t_{90}, s
VM	Aeroqual	Res.: 0.001	No data	negative response with oxidising gases, positive response with combustible gases	No data	0–25	60
iAQ-100	AppliedSensor	VOC + CO_2: 350	No data	alcohols, aldehydes, aliphatic hydrocarbons, amines, aromatic HC, CO, CH_4, LPG, Ketones, Organic acids	No data	VOC + CO_2: 350–2000	15 min
iAQ-2000	„	No data	No data		No data	CO_2: 450–2000	15 min
iAQ-engine	„	CO_2: 450	No data		No data	CO_2: 450–2000	15 min
AS-MLV	„	About 1	No data		No data	CO_2: 450–2000	seconds
TGS 2201	FIGARO USA	i-butane: <1	i-butane: −0.26	CO, H_2, CH_3OH, other HC, with similar sensitivity, NO_2, SO_2 and H_2S according to load resistance	No data	i-butane: 2–100	No data
TGS 2600	„	i-butane: <1	i-butane: −0.24	CH_4, CO, i-butane, Et-OH, $(CH_3)_2CO$, H_2	No data	i-butane: 1–100	No data
TGS 2602	„	toluene: <1	Toluene: −0.6		No data	toluene: 1–30	No data
TGS 8100	„	toluene: <1	i-butane: −0.14		No data	i-butane: 1–30	No data
TGS 822	„	benzene: <50	Benzene: −0.67	CH_4, CO, i-butane, n-hexane, ethanol, acetone	No data	benzene: 50–5000	No data
SP3_AQ2	FIS	<1	CO: −0.4	VOCs	No data	EtOH: 0.1 to 100	No data
MICS-5121/5521	SGX Sensortech	No data	CO: −0.59	reducing gases such as CO, HC and VOCs	No data	CO: 1–1000	No data
MICS-VZ-87	SGX Sensortech	No data	CO: −0.59	VOCs and CO_2	No data	CO_2: 400–1000	15 min
GGS 1330T	UST Umwelt-sensortechnik	No data	CH_4: −0.186	H_2 and CO	No data	CH_4: −0–1000	No data
GGS 2330T	„	No data	CO: −0.361	CH_4 hydrogen and alcohol	No data	CO: 0–1000	No data
GGS 3330T	„	No data	CH_4: −0.227	C1-C8 hydrocarbon, CO and H_2	No data	CH_4: −0–1000	No data
GGS 8330T	UST Umwelt-sensortechnik	No data	EtOH: −0.227	CH_4, CO and H_2	No data	EtOH: 0–1000	No data
VOC Sensor (P/n 731)	Synkera Technologies	No data	EtOH: −1.166	Isobutylene (200%), CO (30%), H_2 (10%), CH_4 (2%), NO_2 Negative Resp. CH_2O (0%)	No data	EtOH: 75–700	<60
SENS 3000, SENS-IT, ETL2000	Unitec Srl	Resolution: 0.1 µg/m^3!	No data	No data	<2.5%/6 months	benzene: 0–0.030	<3

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Chromatographic methods for VOCs detection

Chromatographic techniques represent the **golden reference** for VOCs detection, due to their capability of high selectivity and high sensitivity, with **detection limits reaching the part-per-trillion** range.

Multiple configuration of column, oven and detector can be employed to target VOCs. However, the **main drawbacks are the measurement time required and the relevant instrument footprint**.

For on-field detection, **portable gas chromatographs** used for the determination of VOCs in air quality assessment can be classified into miniaturized chromatographic systems, **micro gas chromatographs** (μGC) or lab-on-a-chip type (LOC) and portable gas chromatograph analyzers.

Low power consumption sample processing, column programming, detection systems and data handling have been combined to reduce the size and weight of GCs for portable use. Of course, the advantages of portability comes with the **disadvantages of reduced selectivity and sensitivity**.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Chromatographic methods for VOCs detection

Selection of the appropriate VOC-sampling method depends upon the **physicochemical properties** of the **target analytes**. Samples are collected for VOCs analysis in containers, on solid sorbents, or in a scrubbing solution. The VOC analytes which are amenable to processing by thermal methods are **injected directly**, **preconcentrated** from whole-air samples, or **desorbed** thermally from sorbent cartridges and analyzed by gas chromatography (GC).

Gas chromatographic analysis can be by **one-dimensional** or **two-dimensional** approaches. The choice of a detection system is based on **selectivity** and **sensitivity** to a particular class of VOCs.

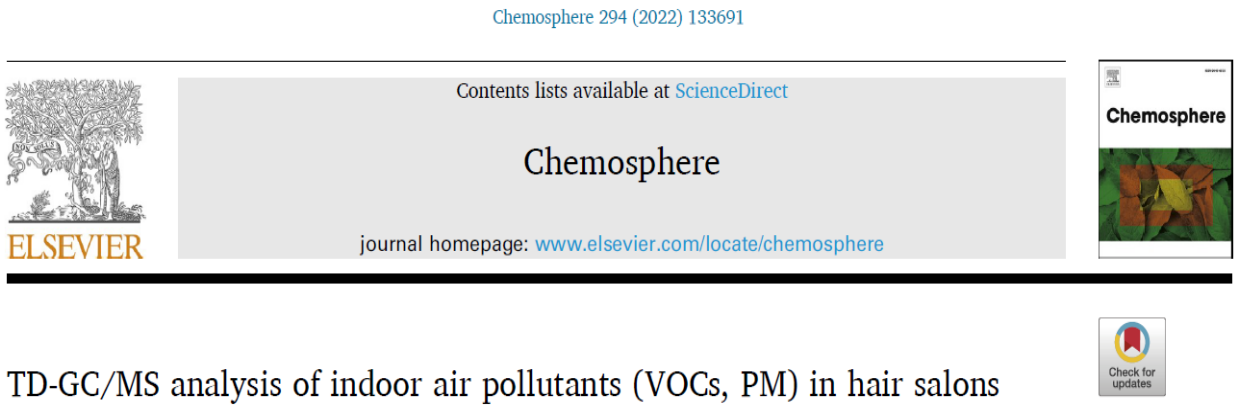
Detectors based on principles of operation such as flame ionization, electron capture, reduction of a gas by the analyte, photoionization, and helium ionization are used to quantify VOCs by GC. **Mass spectrometers** are interfaced to GCs for positive confirmation of molecular composition and also for quantification.

Sampling and analytic instrumentation which use the various methodologies have been deployed on surface, balloon, and aircraft platforms to measure the temporal and spatial variability of atmospheric VOCs.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Chromatographic methods for VOCs detection

- Indoor air analysis in 5 hair salons to identify the main VOCs produced or activities responsible for the respective indoor pollution.
- The chemical analysis took place inside the salon environment by monitoring the emitted VOCs, as well as the PM of 1, 2.5, 4, and 10 μm diameter.


Chemosphere 294 (2022) 133691

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

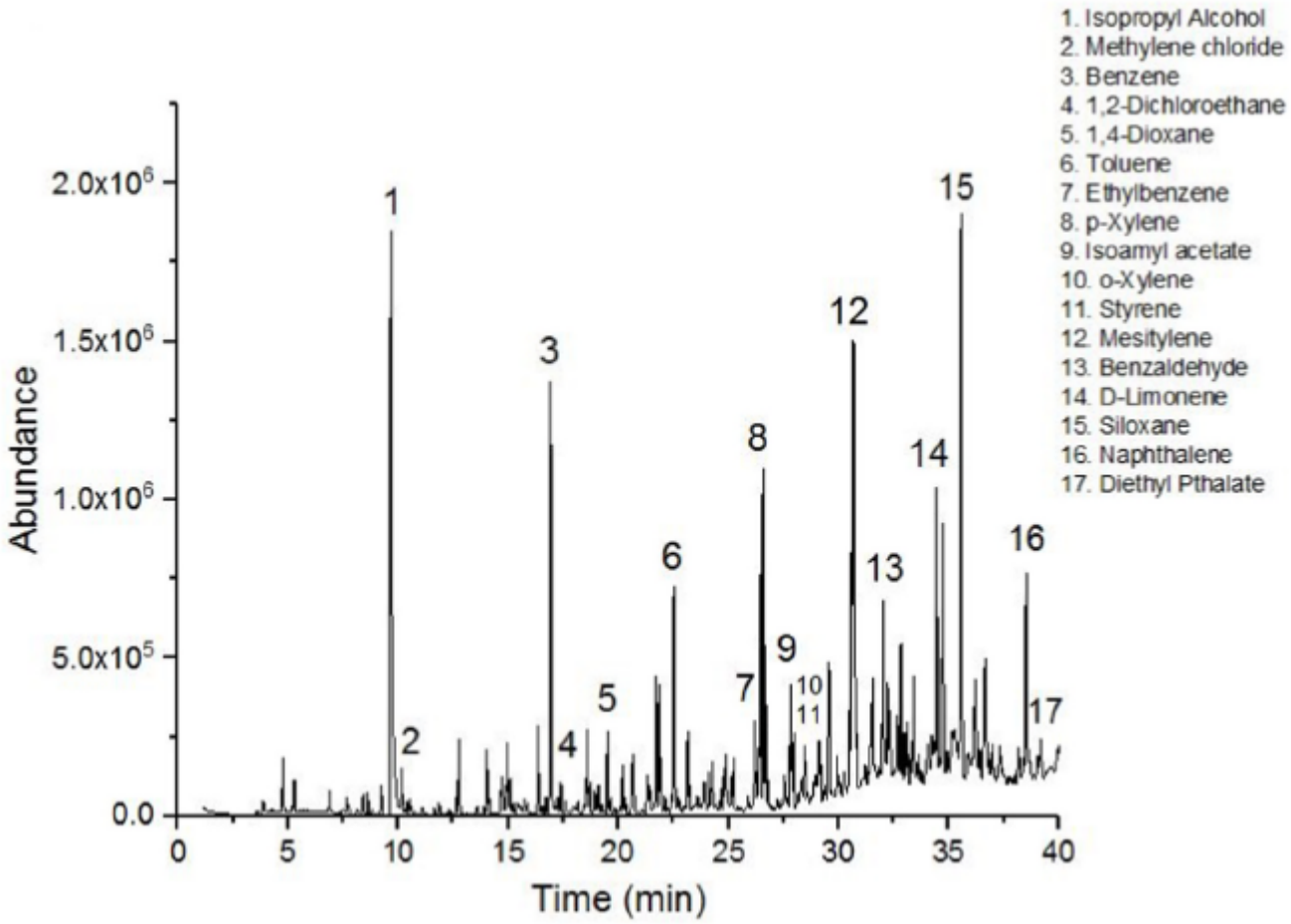
TD-GC/MS analysis of indoor air pollutants (VOCs, PM) in hair salons

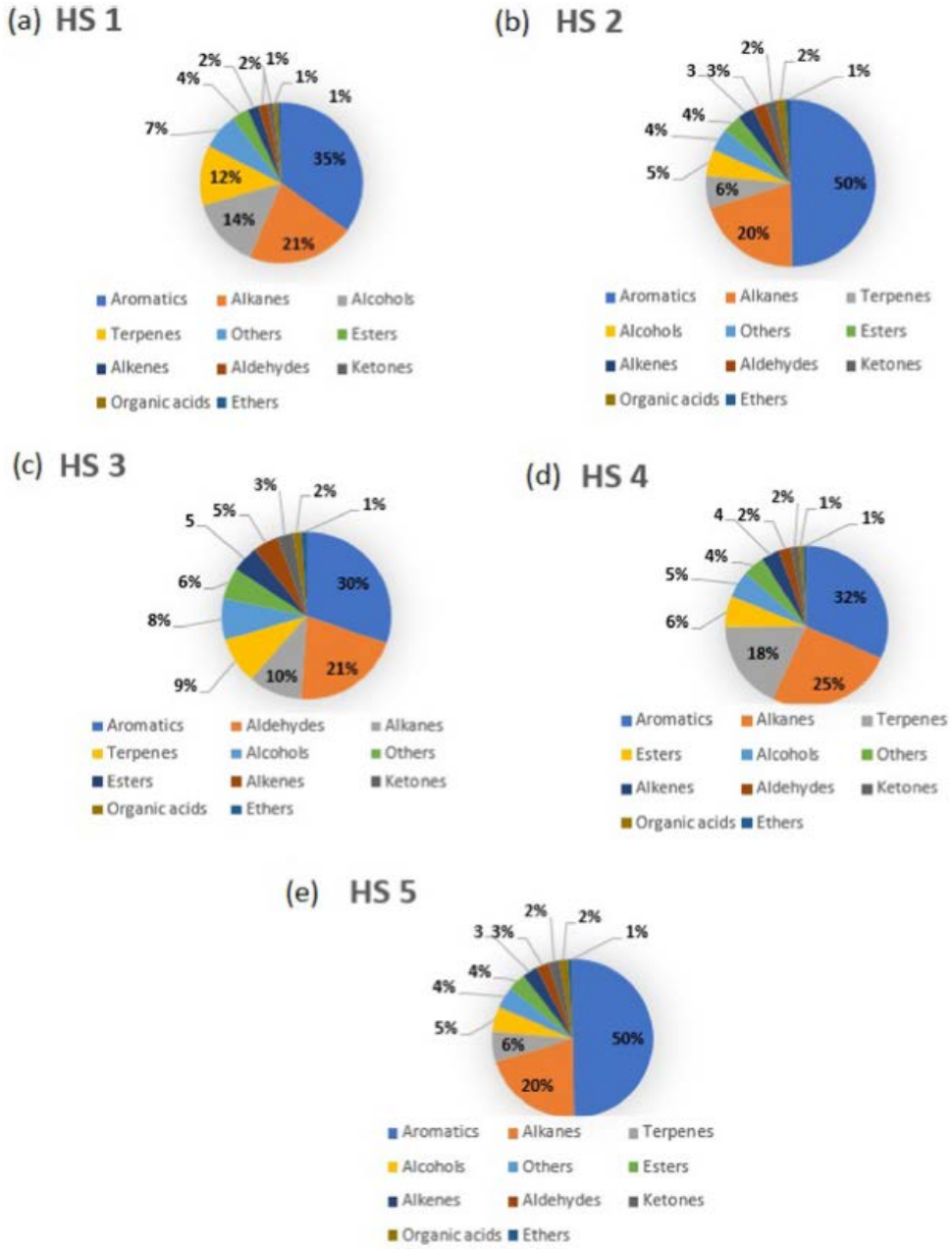
Chrystalla Kaikiti, Marinos Stylianou, Agapios Agapiou *

- The sampling of VOCs was performed by adsorption of pollutants on sorbent tubes, analyzed using a thermal desorption unit coupled to gas chromatography/mass spectrometry (TD-GC/MS).
- Among the main compounds detected there was benzene, toluene, ethylbenzene, and xylenes, known as BTEX, as well as, diethyl phthalate, 1,4-dioxane, etc. More than 50 VOCs were identified (occurrence ≥60%) and 14 of them were quantified.

6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Chromatographic methods for VOCs detection





6.2 VOCS ANALYSIS WITH NON-OPTICAL METHODS

Chromatographic methods for VOCs detection

Calibration curves, LOD, LOQ, and determined concentrations values (μg m-3) of selected VOCs in samples collected from the hair salons indoor air.

VOCs	Equation	Correlation coefficient (R^2)	Concentration range per calibration curve (ppb_v)	LOD (ppb_v)	LOQ (ppb_v)	Concentration range (average) (ppb_v)
Benzene	$y = 13{,}706\ x + 3 \times 10^6$	0.9910	1–350	0.068	0.206	50-120 (88)
Toluene	$y = 872.91\ x + 331{,}742$	0.9980	5–2500	0.446	1.35	402-1594 (941)
p-Xylene	$y = 1877.4\ x - 60{,}848$	0.9930	1–1000	0.101	0.308	288-502 (372)
o-Xylene	$y = 792.38\ x - 17{,}859$	0.9933	0.5–350	0.099	0.300	52-95 (79)
Styrene	$y = 771.88\ x + 81{,}272$	0.9924	1–750	0.106	0.321	158-330 (294)
Mesitylene	$y = 823.97\ x - 69{,}517$	0.9900	0.5–750	0.121	0.367	79-281 (108)
Ethylbenzene	$y = 905.97\ x - 20{,}507$	0.9990	0.5–750	0.038	0.114	58-202 (98)
Methylene chloride	$y = 2531.7\ x - 331{,}266$	0.9900	0.5–350	0.121	0.367	34-87 (68)
Naphthalene	$y = 513.29\ x + 2231$	0.9996	0.3–350	0.025	0.075	10-13 (12)
Isoamyl acetate	$y = 1110.2\ x + 30{,}265$	0.9925	1–650	0.076	0.230	266-564 (341)
1,4-Dioxane	$y = 7216.4\ x + 13{,}487$	0.9901	1–750	0.015	0.045	46-402 (147)
Diethyl Phthalate	$y = 331.04\ x - 25{,}862$	0.9983	0.3–150	0.041	0.125	3-44 (21)
Benzaldehyde	$y = 495.11\ x + 39{,}605$	0.9921	0.5–750	0.108	0.326	93-234 (103)
1,2-Dichloroethane	$y = 129.85\ x - 8624.5$	0.9960	1–350	0.077	0.232	63-99 (76)

6.3 VOCS ANALYSIS WITH OPTICAL METHODS

Absorption spectroscopy for VOCs detection

Optical absorption spectroscopy represents a promising alternative to traditional sensors for VOCs detection, particularly for its capability to discriminating between different substances with a high accuracy.

Infrared spectroscopy, and in particular the region of mid-IR, is characterized by numerous absorption lines allowing the different VOCs to be recognized. This ensures a **high selectivity and sensitivity** for ambient-level detection (typically in the ppm range) of common hazardous air pollutants, which are typically strong IR absorbers.

The **real-time monitoring** represents a challenging issue, in particular in occupational and environmental safety and health security. Notable examples such as open-path FTIR have demonstrated the ability of **vibrational spectroscopy** to analyze ambient air in situ and in real time, making it a good candidate for implementing portable devices.

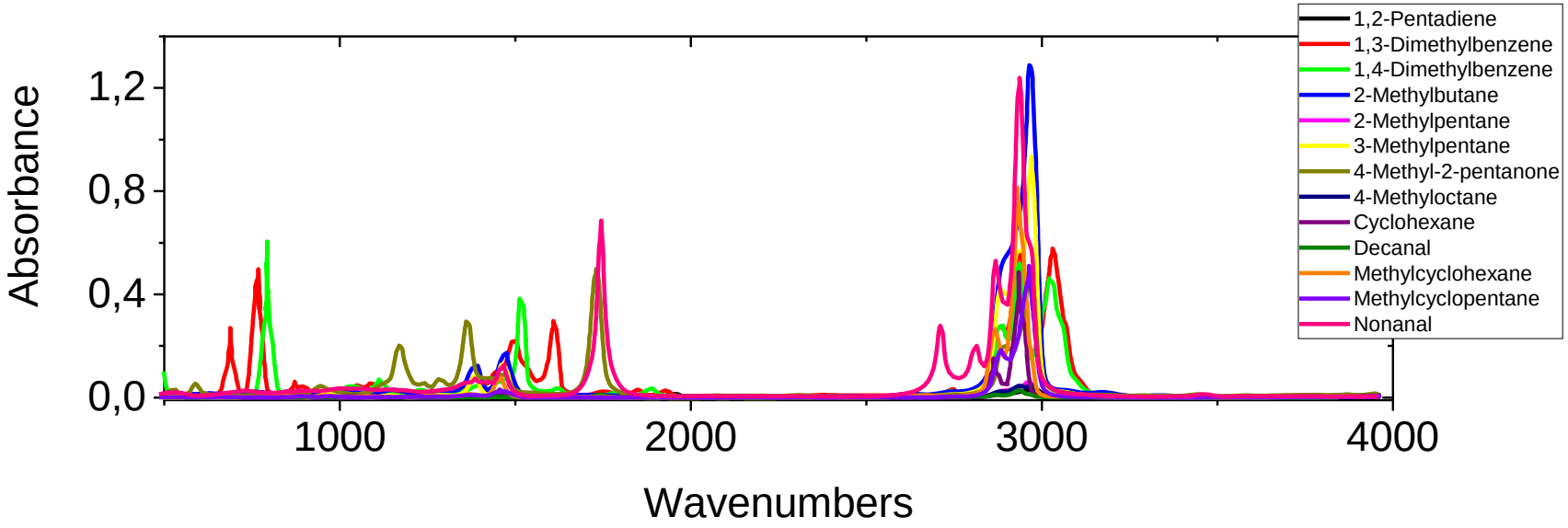
6.3 VOCS ANALYSIS WITH OPTICAL METHODS

FTIR spectroscopy for VOCs detection

FTIR-based sensors allow for the identification and quantification of VOCs target by means of their "spectral fingerprint".

However, **spectral overlap occurs** due to the similar composition of these molecules (e.g., multiple C-H bond in almost all the relevant VOC molecules).

For this reason, FTIR spectroscopy benefit from the **large spectral interval** to be investigated (typically 400 – 8000 cm^{-1}) even in case of **low resolution** (few cm^{-1}).

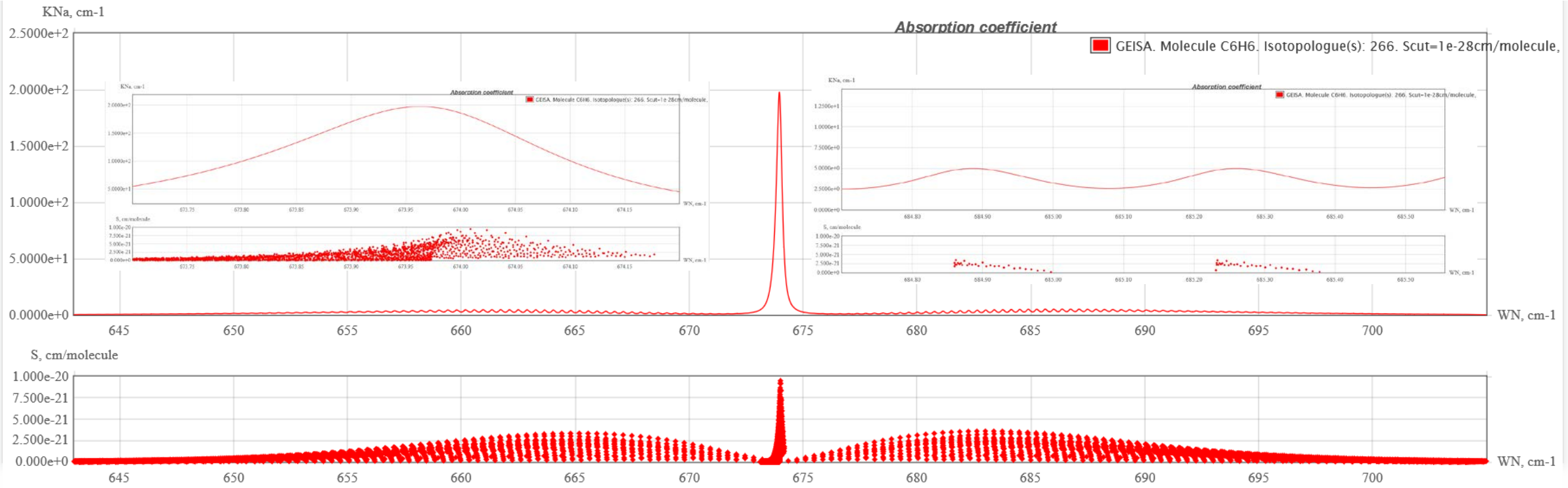


6.3 VOCS ANALYSIS WITH OPTICAL METHODS

FTIR spectroscopy for VOCs detection

Being complex molecules, characterized by multiple chemical bonds, VOCs point out multiple absorption features in the IR region, with a **high density of absorption lines within the band**.

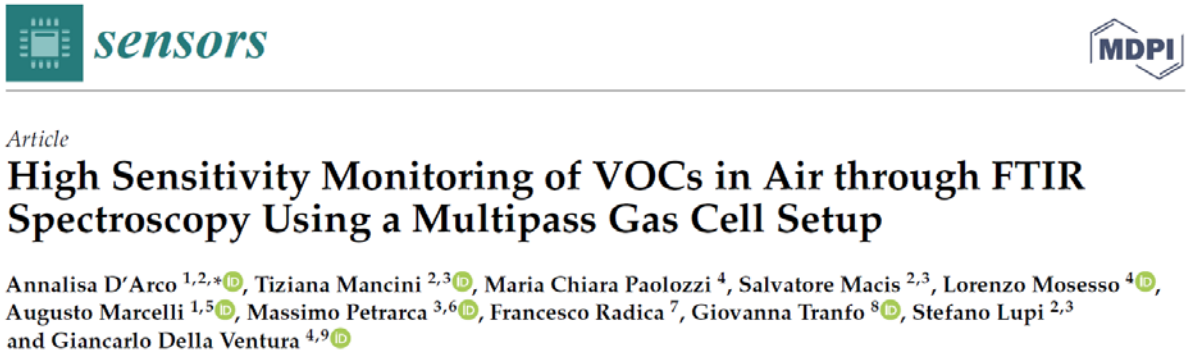
When operating at **ambient conditions** (i.e., ambient pressure and temperature), these features can't be easily separated, thus resulting in **unresolved bands** retracing the standard P-, Q-, and R- branches.



6.3 VOCS ANALYSIS WITH OPTICAL METHODS

FTIR spectroscopy for VOCs detection

- Fourier Transform Infrared (FTIR) spectroscopy as powerful tool for quantifying VOCs in air.
- Sensor calibrated for multiple compounds: styrene, acetone, ethanol and isopropanol

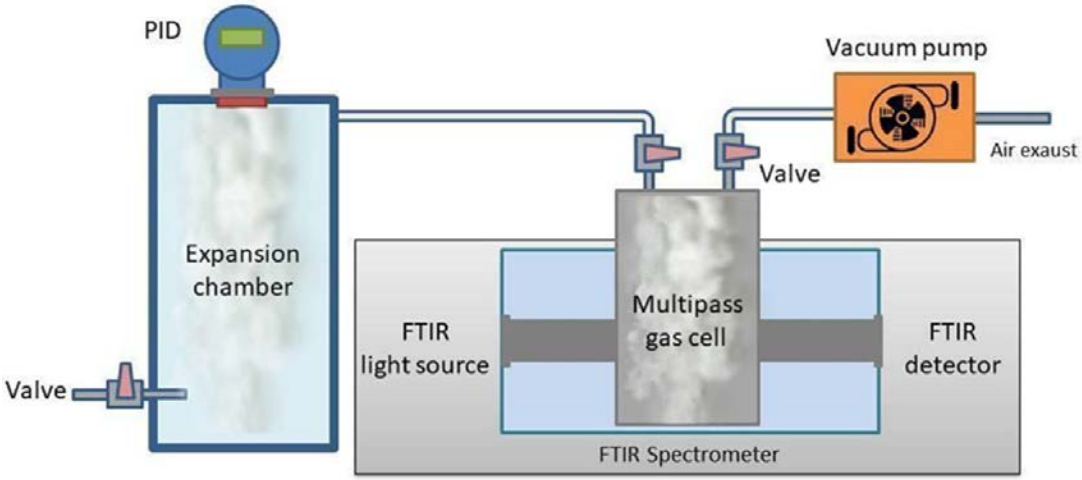


- With the aim of developing a new, and highly sensitive sensor system for VOCs monitoring, a multipass cell was used.
- As a result, the sensitivity of the FTIR-based system reached the part per million (ppm) level.

6.3 VOCS ANALYSIS WITH OPTICAL METHODS

FTIR spectroscopy for VOCs detection

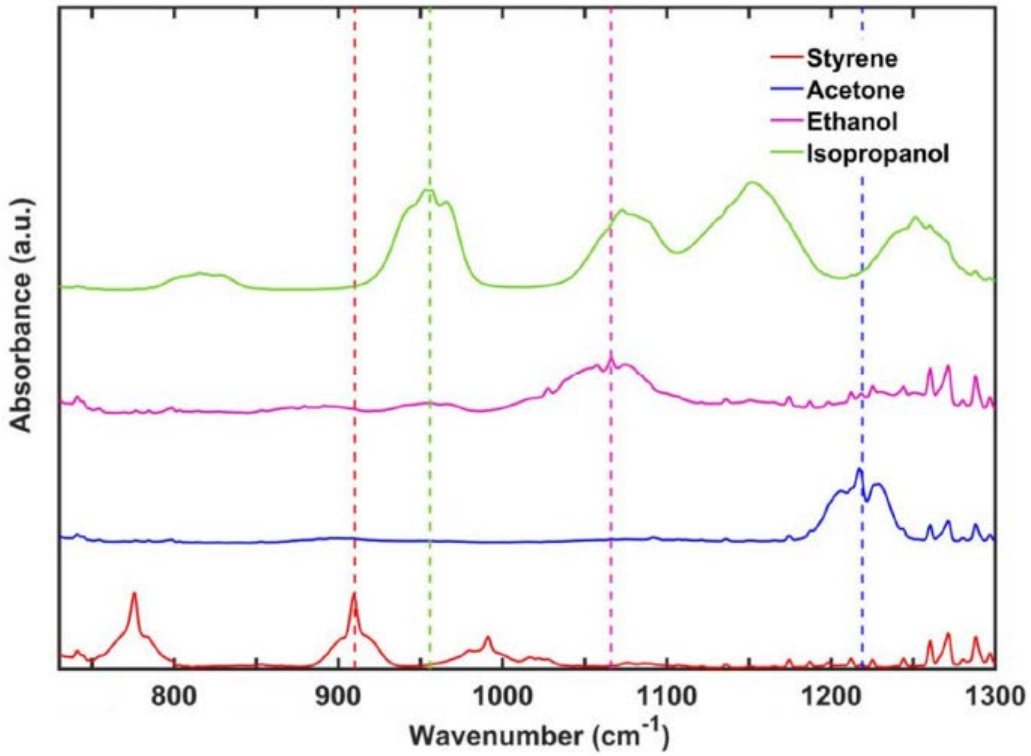
- FTIR measurements performed using a Bruker Vertex 70V
- GEMINI Mars Series Multi-Pass Gas Cells 2 L/10 M
- Commercial Photo-Ionization Detector (PID) sensor was installed for real-time referencing of the evaporated VOC

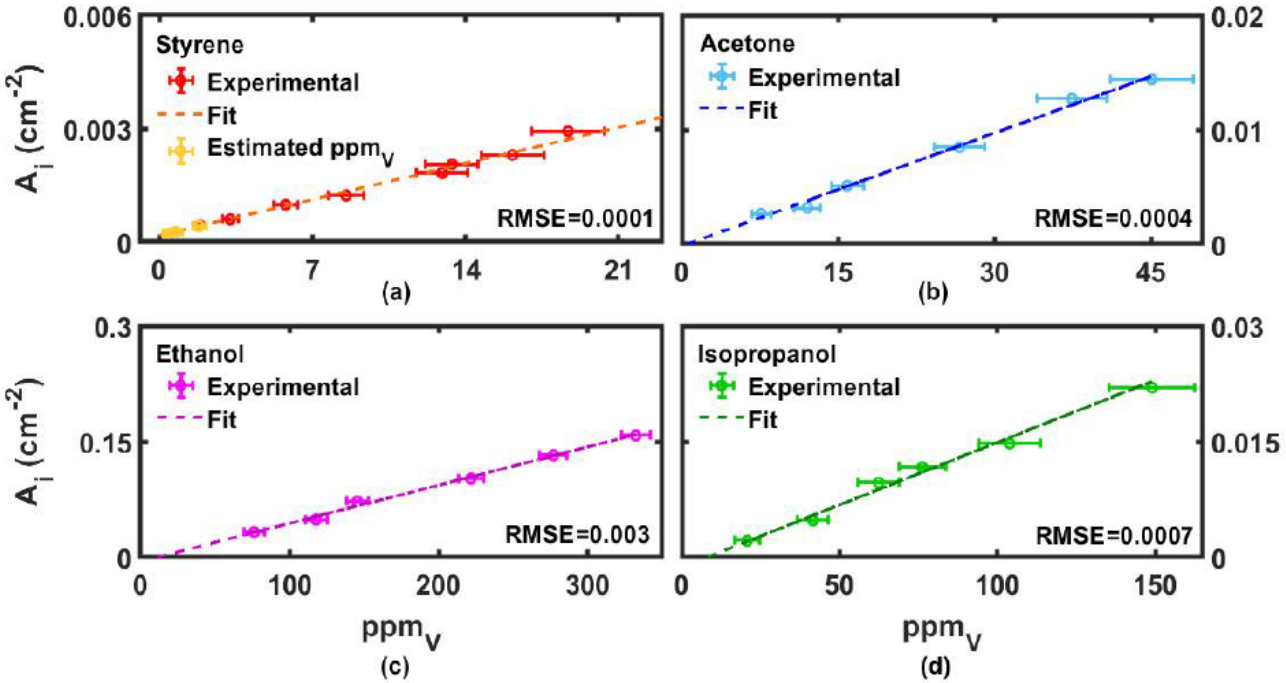


- 15 acquisitions collected for each gas sample, each spectrum being the average of 64 scans, with a nominal resolution of 2 cm^{-1} in the 400–5000 cm^{-1} frequency range.
- Baseline removal, spectral windows identification and peak integration performed using OPUS™ 8.2 software

6.3 VOCS ANALYSIS WITH OPTICAL METHODS

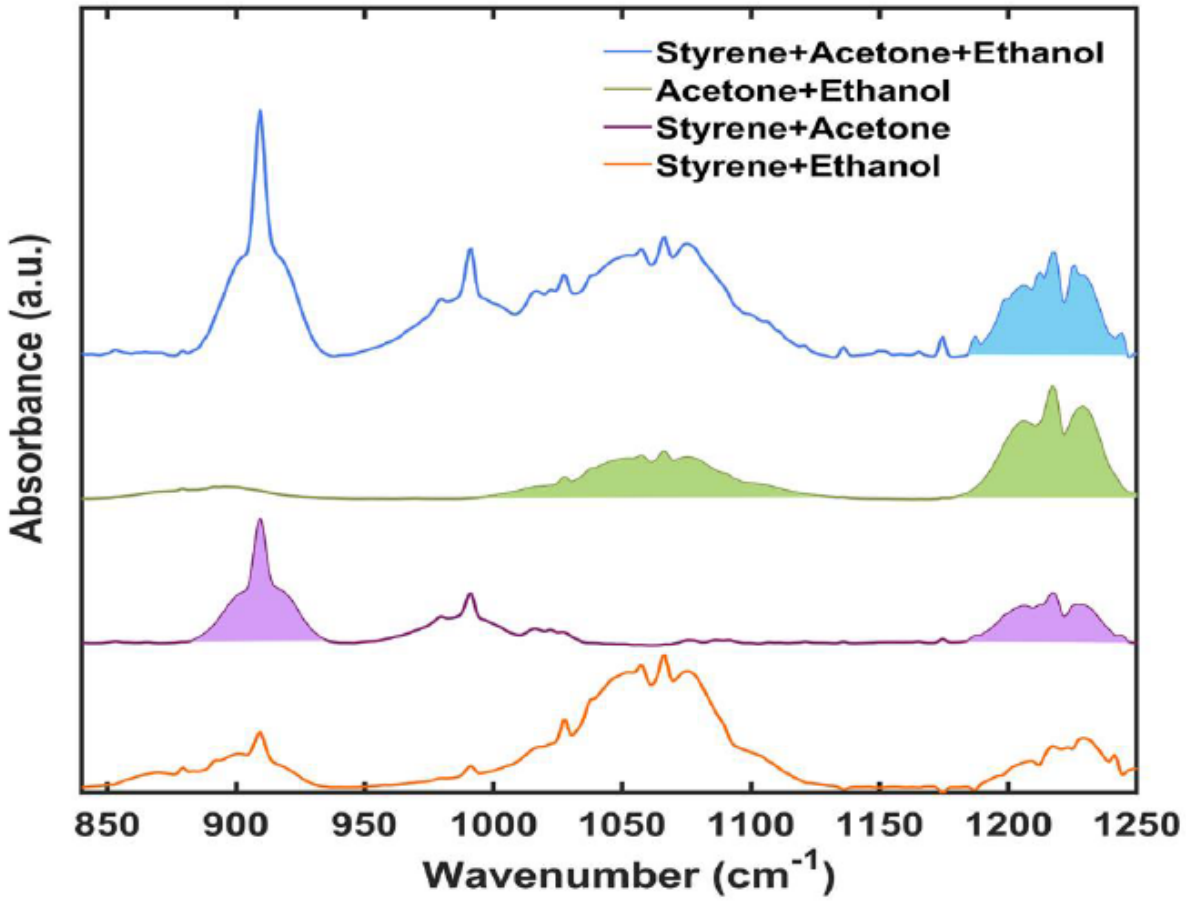
FTIR spectroscopy for VOCs detection

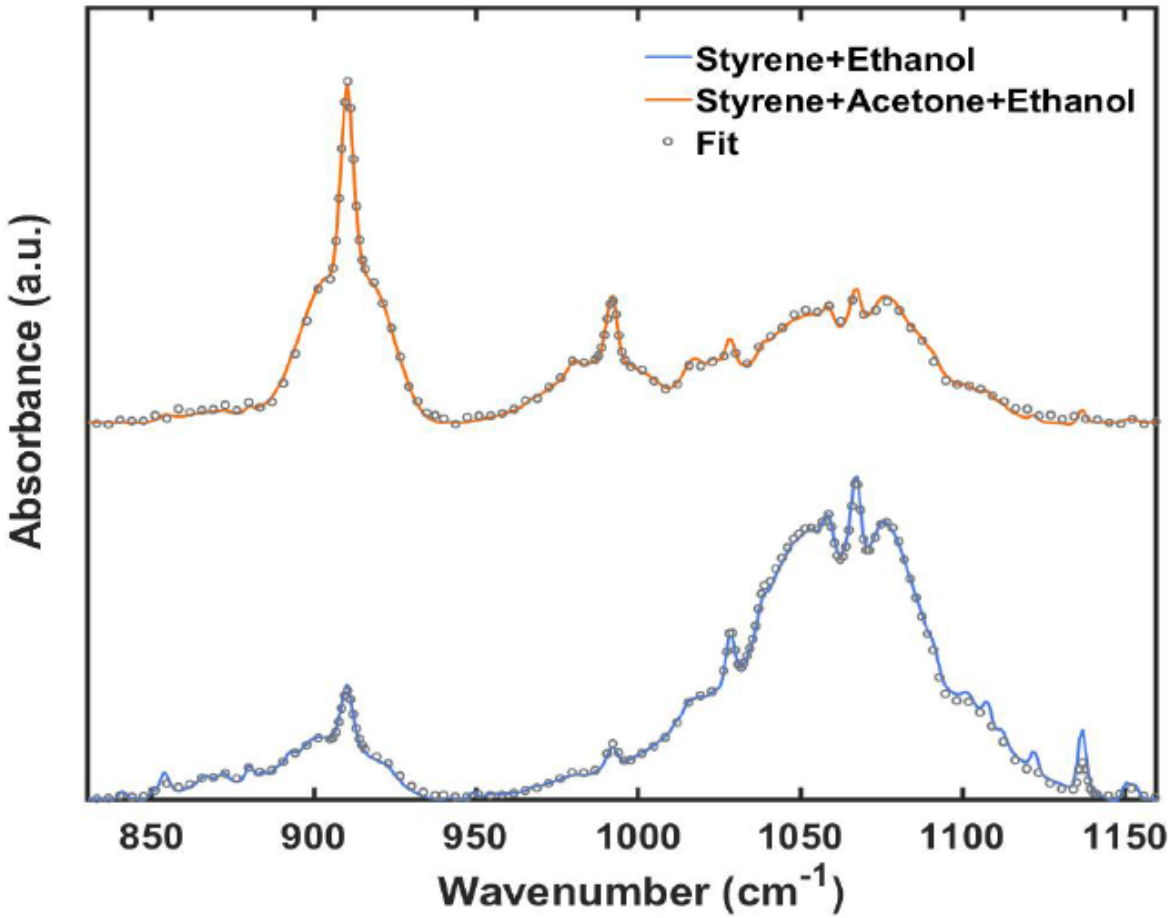




6.3 VOCS ANALYSIS WITH OPTICAL METHODS

FTIR spectroscopy for VOCs detection



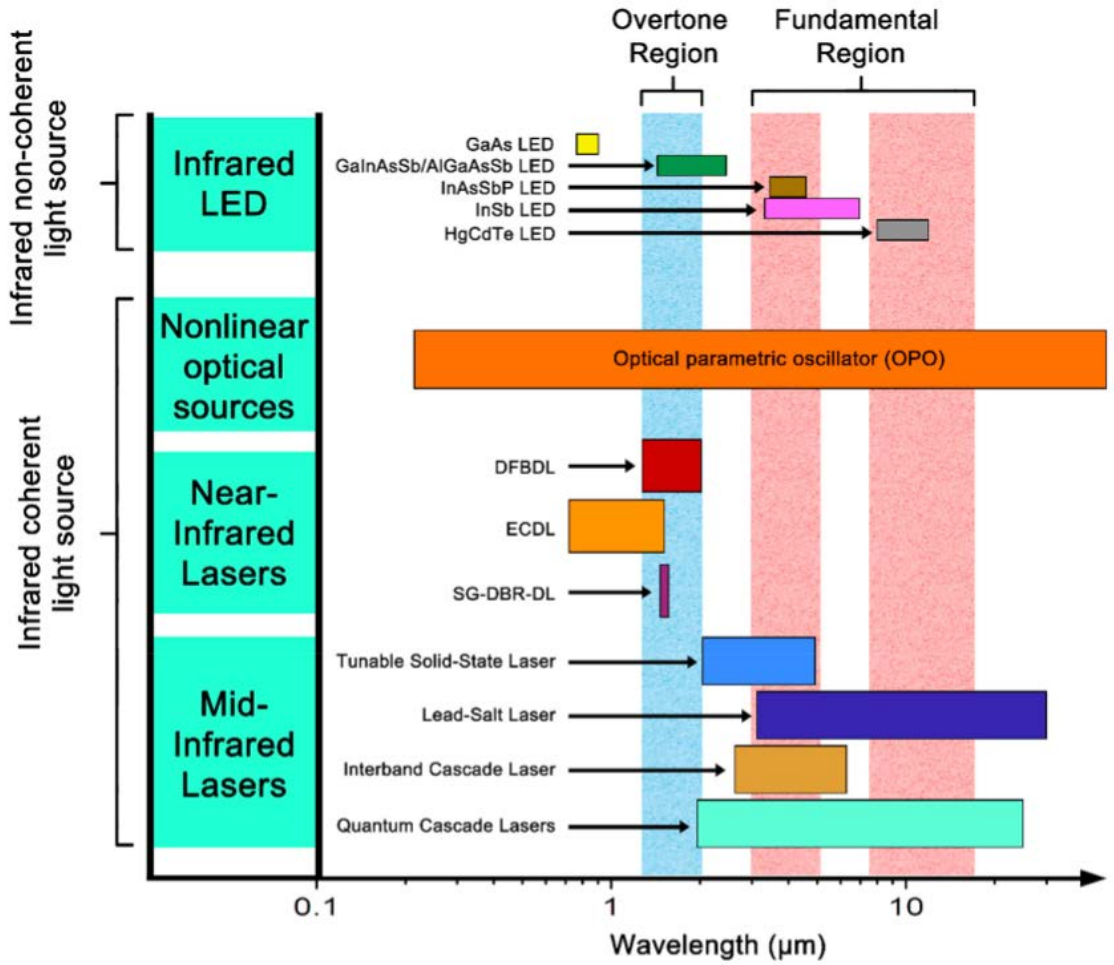


6.3 VOCS ANALYSIS WITH OPTICAL METHODS

QEPAS spectroscopy for VOCs detection

High resolution spectroscopy benefitting of the narrow emission linewidth of laser source is still a developing approach to VOCs detection.

In particular, for BTEX detection, several works reported on infrared sensors to exploit the **3.3 µm absorption range of these molecules** through techniques such as cavity-enhanced spectroscopy, and multi-pass absorption sensing via difference frequency generation. In this case, optical sensing techniques benefit from the **Interband Cascade Lasers (ICLs)** emitting in this region.

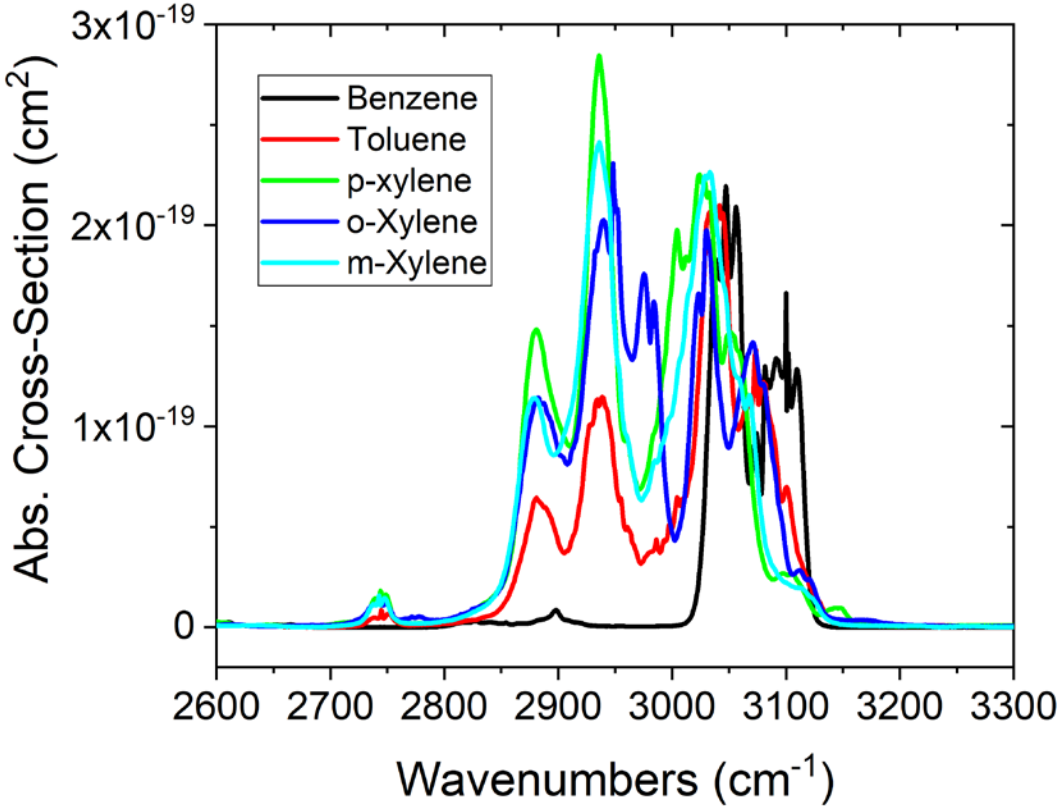


6.3 VOCS ANALYSIS WITH OPTICAL METHODS

QEPAS spectroscopy for VOCs detection

However, the detection of BTEX compounds, as well as the heavier alkanes like propane, butane, pentane, presents unique challenges stemming from their potential interferences among themselves or from other compounds.

The presence of **coexisting VOCs characterized by the same bonds can normally introduce spectral interferences** especially in the spectral region where the fundamental bands of IR transitions lie, resulting in overlapping absorption features or distorted signals.



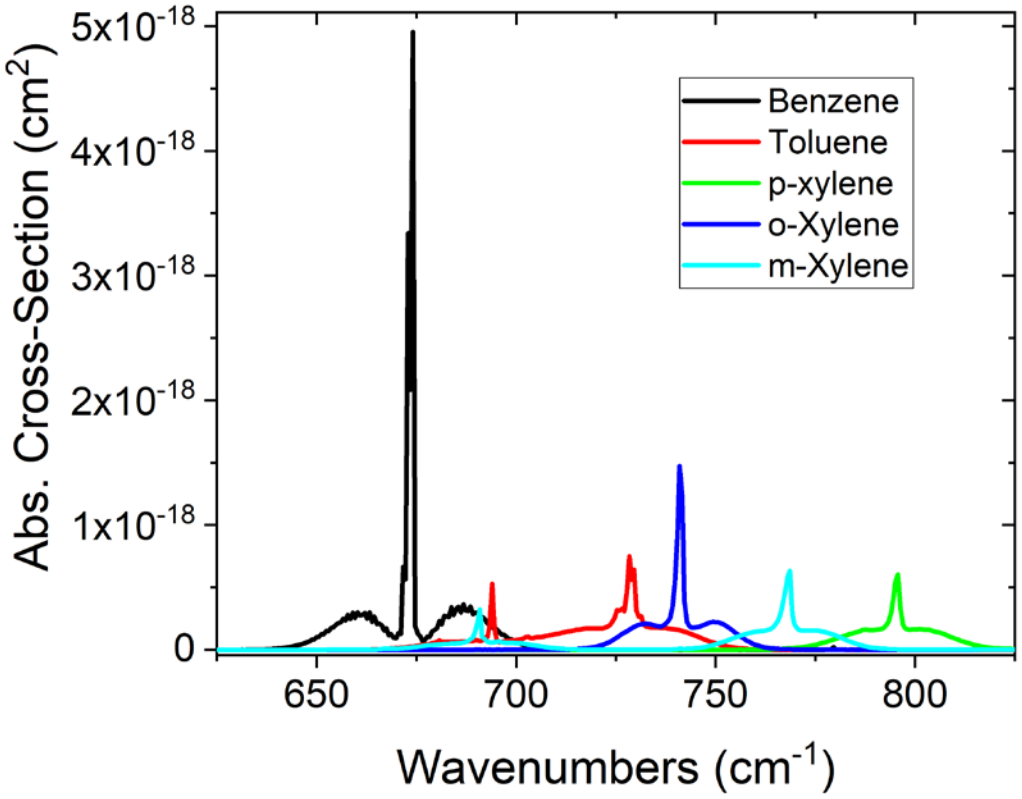
6.3 VOCS ANALYSIS WITH OPTICAL METHODS

QEPAS spectroscopy for VOCs detection

This issue of spectral interference should be eliminated at **longer wavelength** (13 µm – 15 µm) where BTEX and heavier hydrocarbons show distinct and **isolated absorption features**.

Recently, non-commercial long-wavelength QCLs emitting in the range 13 µm – 15 µm have been developed, to specifically target BTEX absorption features.

These devices would enable **accurate targeting of the absorption lines** associated with these compounds.

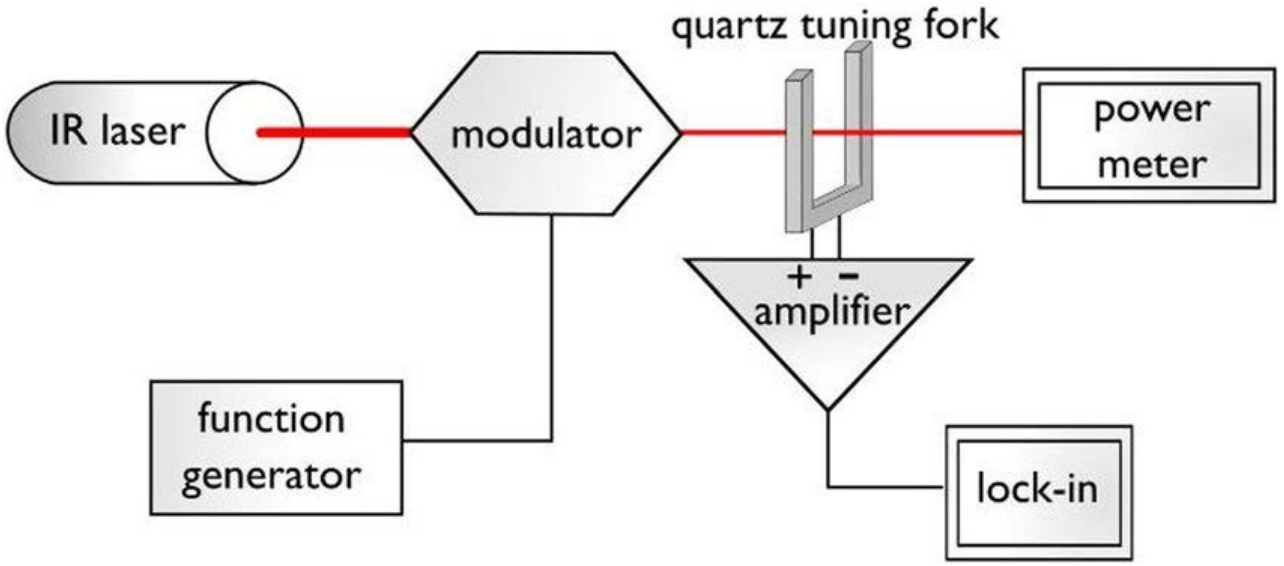


6.3 VOCS ANALYSIS WITH OPTICAL METHODS

QEPAS spectroscopy for VOCs detection

Unfortunately, the lack of **suitable laser sources** and **efficient photodetector** has limited the development of optical sensors at such long wavelengths.

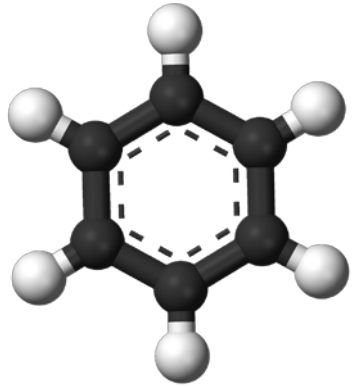
Being an **indirect detection** technique, **QEPAS remove the need for a photodetector** capable to operate at such long wavelength. The main features of this kind of sensor would make it a suitable alternative for **real-time, in situ detection** with high sensitivity and selectivity.

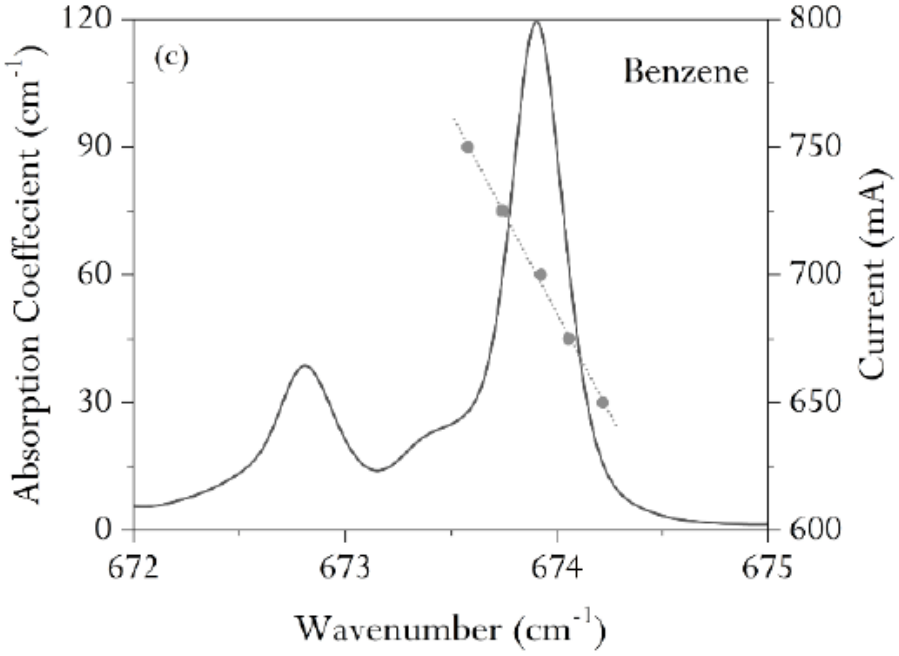


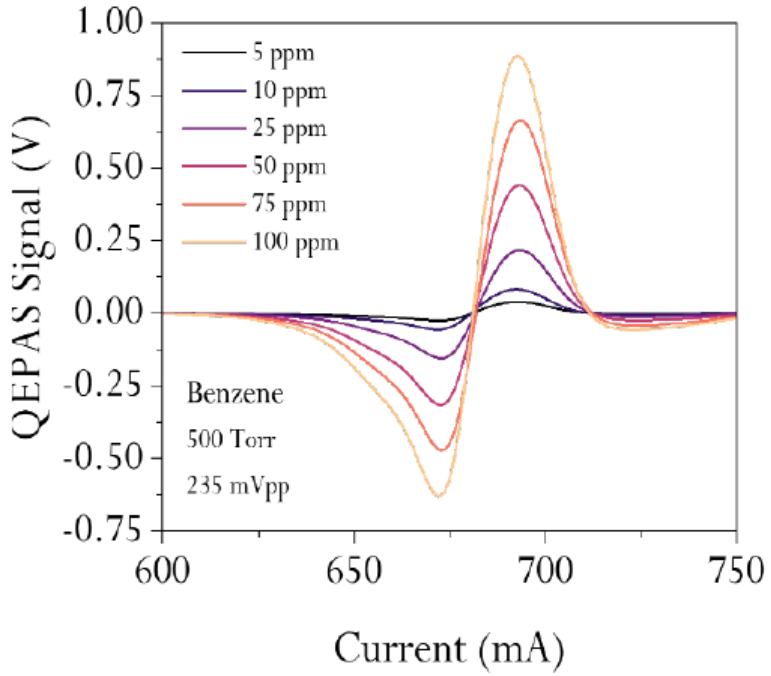
6.3 VOCS ANALYSIS WITH OPTICAL METHODS

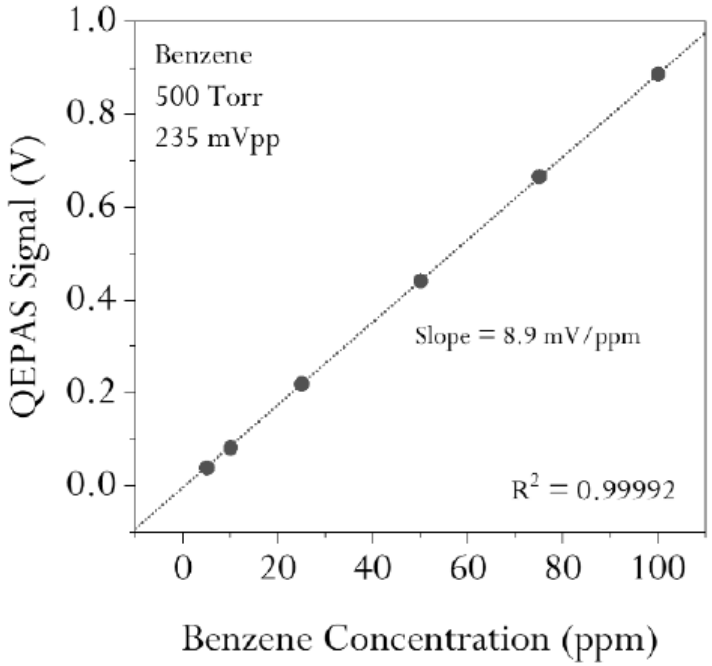
QEPAS spectroscopy for VOCs detection

- 2f-WM QEPAS Benzene detection at 674 cm^{-1} (14.8 µm)
- LOD = 13 ppb for real-time monitoring





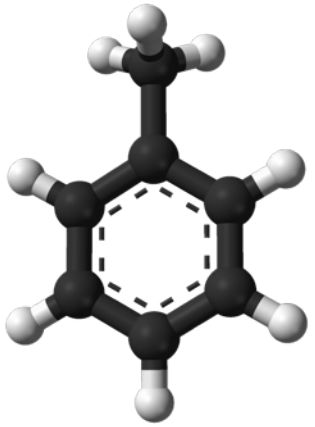


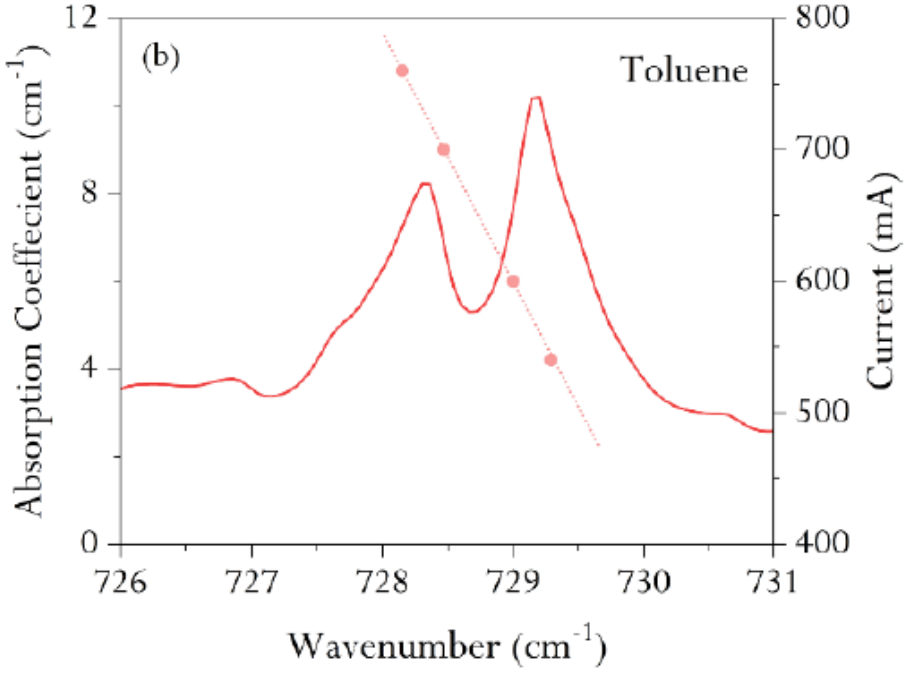


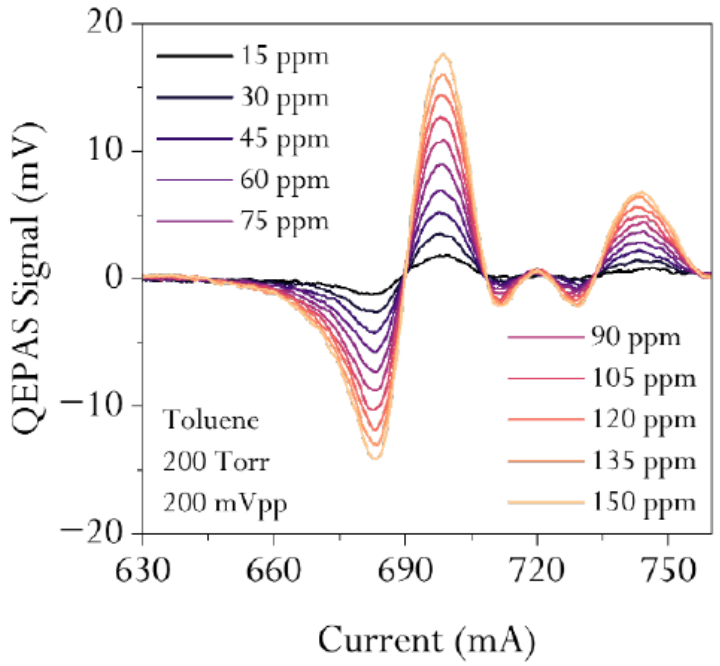
6.3 VOCS ANALYSIS WITH OPTICAL METHODS

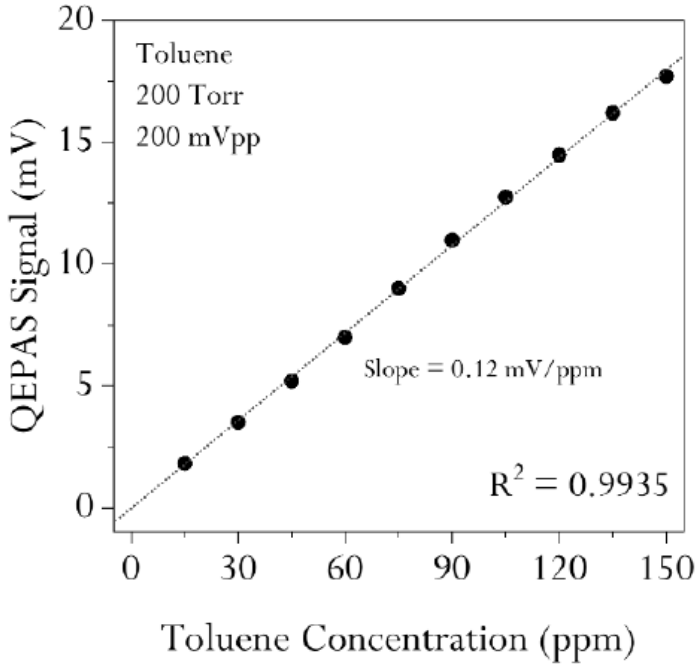
QEPAS spectroscopy for VOCs detection

- 2f-WM QEPAS Toluene detection at 729 cm^{-1} (13.7 µm)
- LOD = 375 ppb for real-time monitoring









6.3 VOCS ANALYSIS WITH OPTICAL METHODS

Recap of detection methods for VOCs detection

Detection method	Pros	Cons
Photon-ionization detectors	• Good sensitivity (ppm and below) • Low cost • Wide detection range	• No selectivity • Need for periodic recalibration
Electrochemical sensors	• Low power required • Good sensitivity (below ppm) • Good response time (~minute)	• Low selectivity • Narrow concentration range (tens of ppm) • Short instrument lifetime
MOx sensors	• Compact and low cost • Good sensitivity (ppm) • Good response time (~minute)	• Low selectivity • Prone to drift and instability • Short instrument lifetime
Chromatography-based sensors	• High sensitivity (below ppb) • Multiple VOCs detected at the same time (identification)	• Long response time (>20 mins) • Large instrument footprint • Expensive

6.3 VOCS ANALYSIS WITH OPTICAL METHODS

Recap of detection methods for VOCs detection

Detection method	Pros	Cons
FTIR spectroscopy	• Good sensitivity (ppm) • High selectivity • Fast response time (~seconds)	• Laboratory-based approach • Difficult to resolve features from “heavy” molecules
Photoacoustic spectroscopy	• High sensitivity (ppb) • High selectivity • Compact sensor • Real-time detection	• Isolated absorption features required • Need for high power laser in long wavelength (13-15 µm)