UMONS
Université de Mons

Volatile Organic Compounds (VOC) Detection & Measurement Techniques

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6th European workshop on VOC's
Dunkerque, June 23rd

MateriaNova
MATERIALS R&D CENTRE

B-SENS

Context

What are Volatile Organic Compounds?

All organic compounds (except methane) having a vapor pressure > 0.01 kPa at 293.15 K or having a corresponding volatility in particular conditions

In pratice, the most studied VOC's are:
Benzene, toluene, ethylbenzene, xylene (called BTEX)
Formaldehyde, acetaldehyde

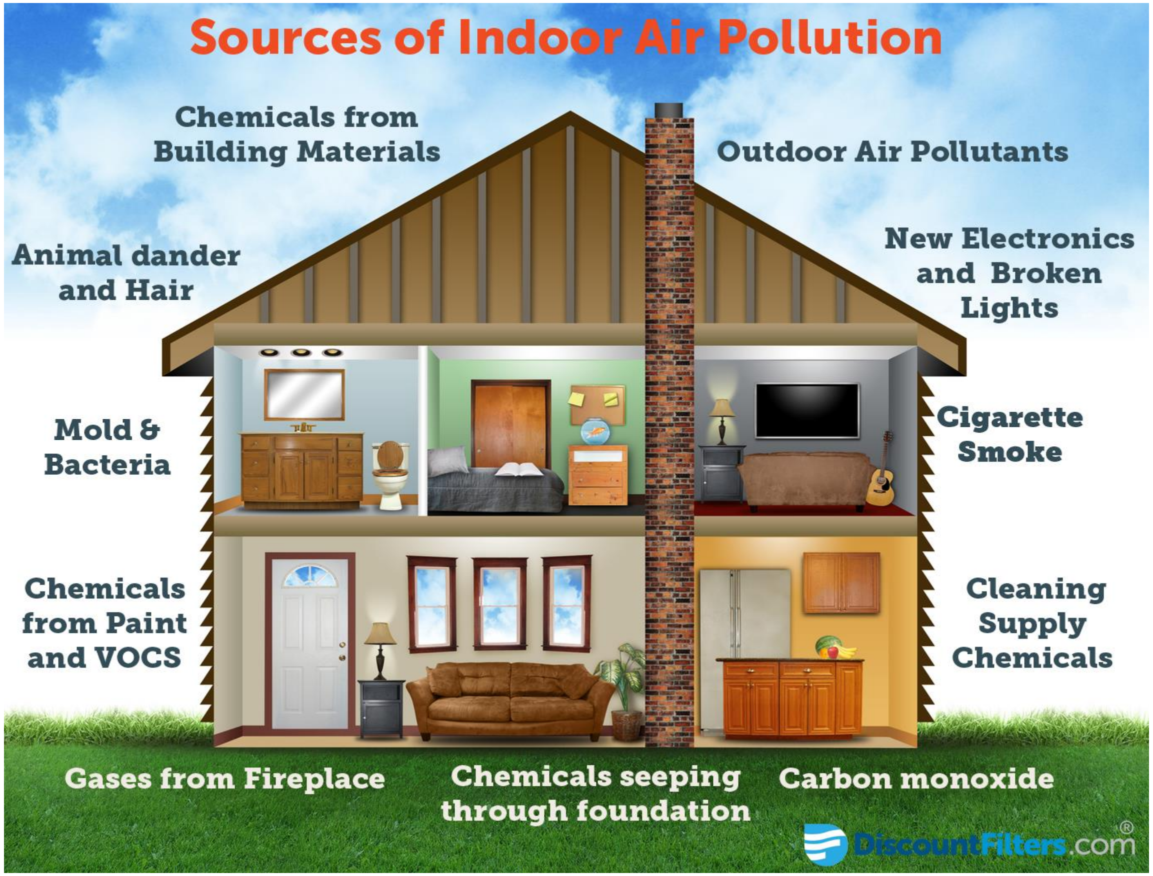
Sources

Transport (combustibles, combustions)

Industry (solvents, combustions)

Agriculture

Domestic applications (paints, pesticides, glues, etc…)



Nuisances for environnement and health: asthma, lung attack, cancer

Responsible of the sick building syndrome

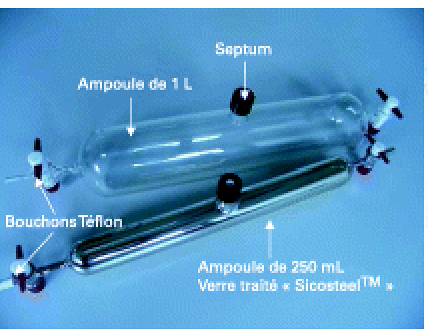
=> Efforts to reduce the pollution

=> Measurement of the concentration in VOC for preventive actions

Main analysis methods

SAMPLING + LAB

~~preconcentration~~ preconcentration



NO SAMPLING **ON FIELD**

accumulation direct

Choice of the method depends on:
concentration levels, response time and accuracy

Main characteristics

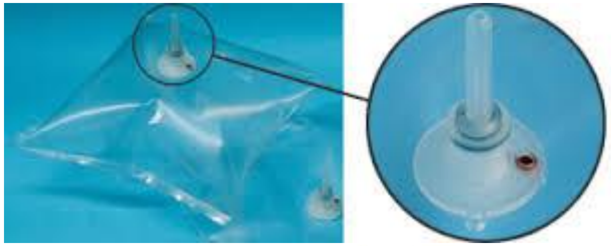
	SAMPLING + LAB		NO SAMPLING ON FIELD	
	~~preconcentration~~	preconcentration	accumulation	direct
+	Allows a very complete analysis Accurate Low detection limit	Accurate Low detection limit	Low detection limit Not expensive Accurate	Fast Real time Not expensive Reusable
−	Slow Expensive	Slow Expensive	Slow Average values	Higher detection limit Lower accuracy

Sampling without preconcentration

Bags

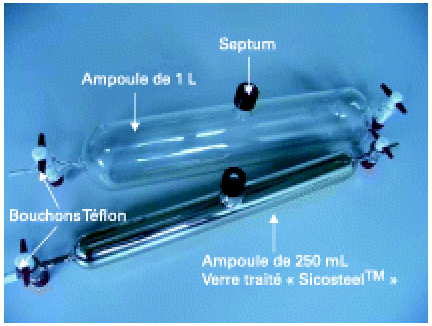
Teflon FEP (hexafluoropropylène/tetrafluoroethylene),
Mylar (polyester), Tedlar (PVF)
Nalophan (polyethyleneterephtalate)

Allow sampling of large volumes (from 2 to 100 l)
NF EN 13725 (2003),



Glass tubes

Avoid losses by adsorption on the walls
Small volumes (<3 l)

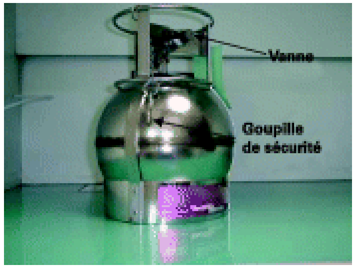


Analysis by
GC-MS
FTIR

Canisters

Stainless steel convered with CrO_3

Easy transport but problems of gas reactions

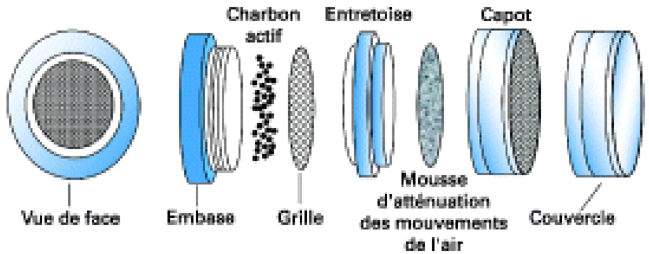


Sampling with preconcentration

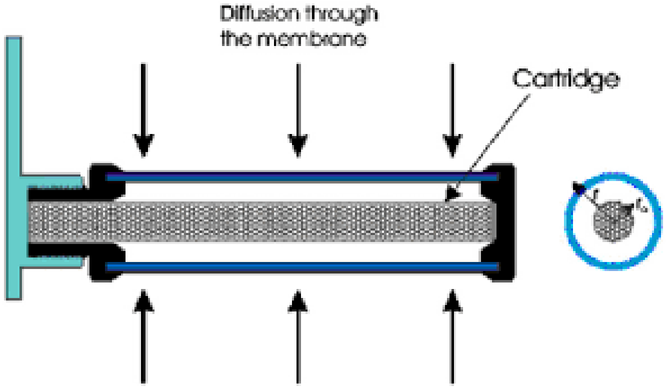
Adsorption on a cartridge filled with adsorbant

Active adsorption with a pump

Passive adsorption (diffusion)



Doc SKC



Doc Radiello

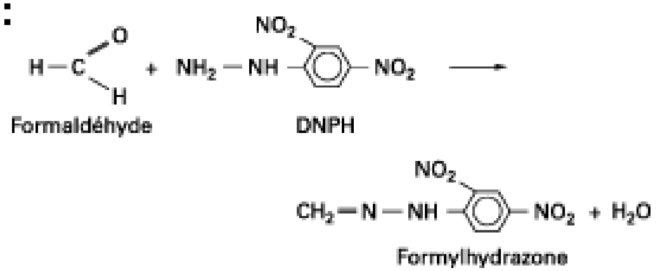
Sampling with preconcentration

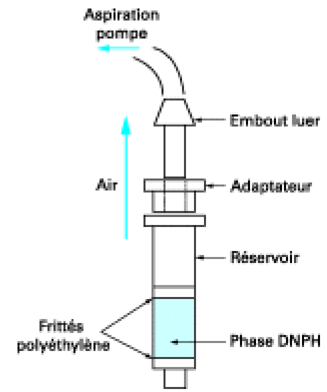
Materials

Distinction beween carbonylated (aldehydes and ketones) and non carbonylated

Materials for carbonylated gases:

Specific reaction with DNPH





Reading of the results by Liquid Phase Chromatography

Materials for non carbonylated gases:

Porous materials with high specific surface area
Active charcoal,
Tenax
….

Reading by Programmed Thermal Desorption in a special equipment (detection by MS or FID).

Accumulation methods

Principle

The target gases are ad(b)sorbed in a solid material and accumulate or react with a specific reagent.
It results in a **permanent** physical or chemical change of the material properties that can be measured separatly.

Act as **dosimeters** and are not real time.
For average concentrations during the exposure period.

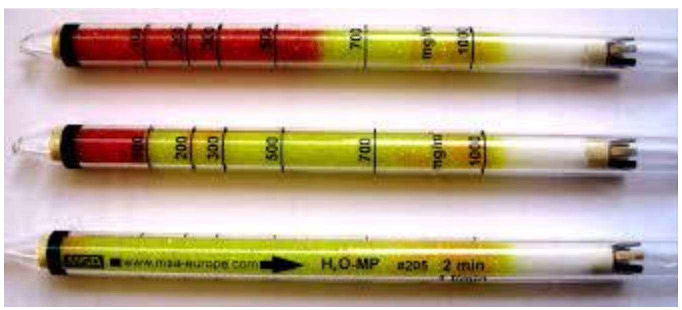
Not reusable!

Measured properties

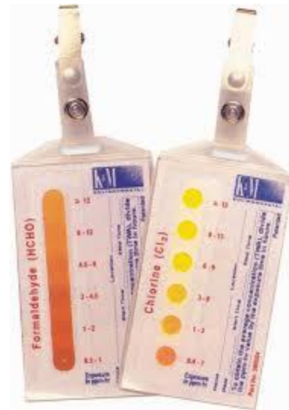
Mass (increase of mass or thickness of a rectangular sample)
Refractive index
Colour
Permittivity
Conductivity

Colorimetric methods

Reactive tubes



Badges



Front of VOC Chek 575

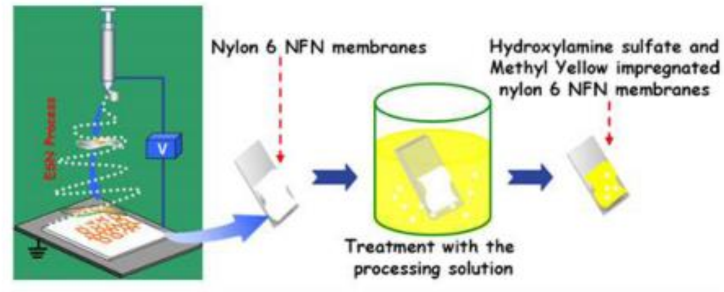
Back of VOC Chek 575 Sampler designed for easier analysis

Direct

Indirect

Colorimetric methods

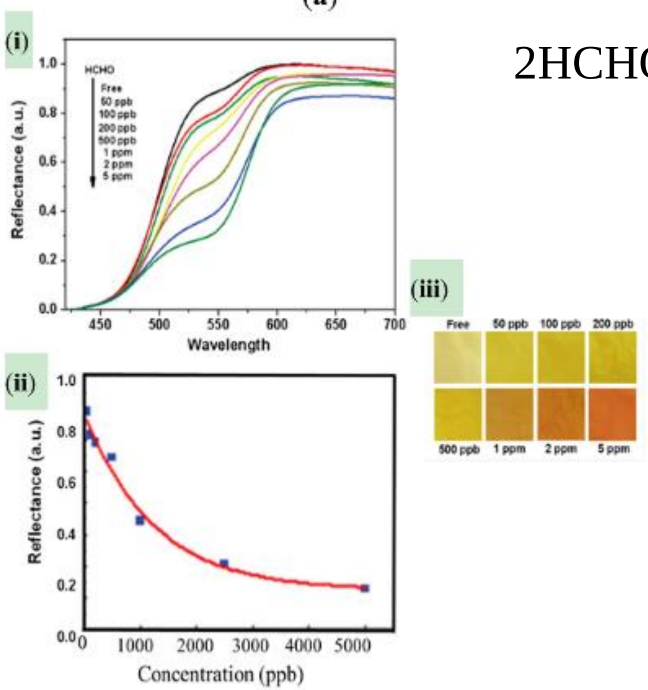
Example with formaldehyde



(a)

$$2HCHO + (NH_2OH)_2 \cdot H_2SO_4 \rightarrow 2H_2C{=}NOH + H_2SO_4 + 2H_2O$$

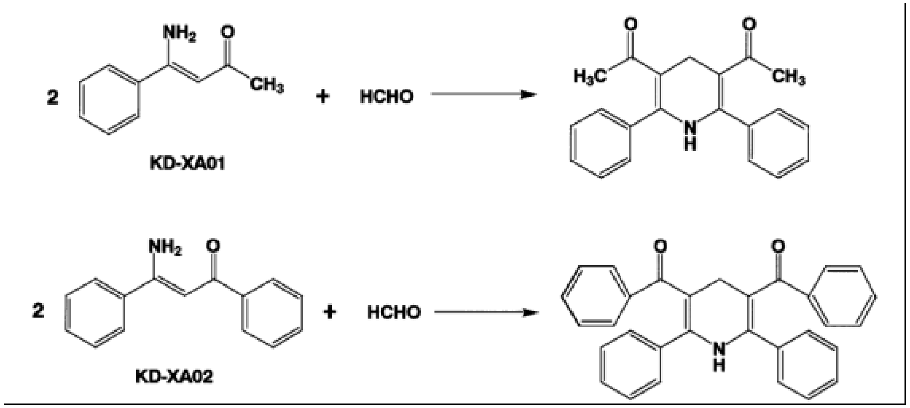
Use of a pH indicator

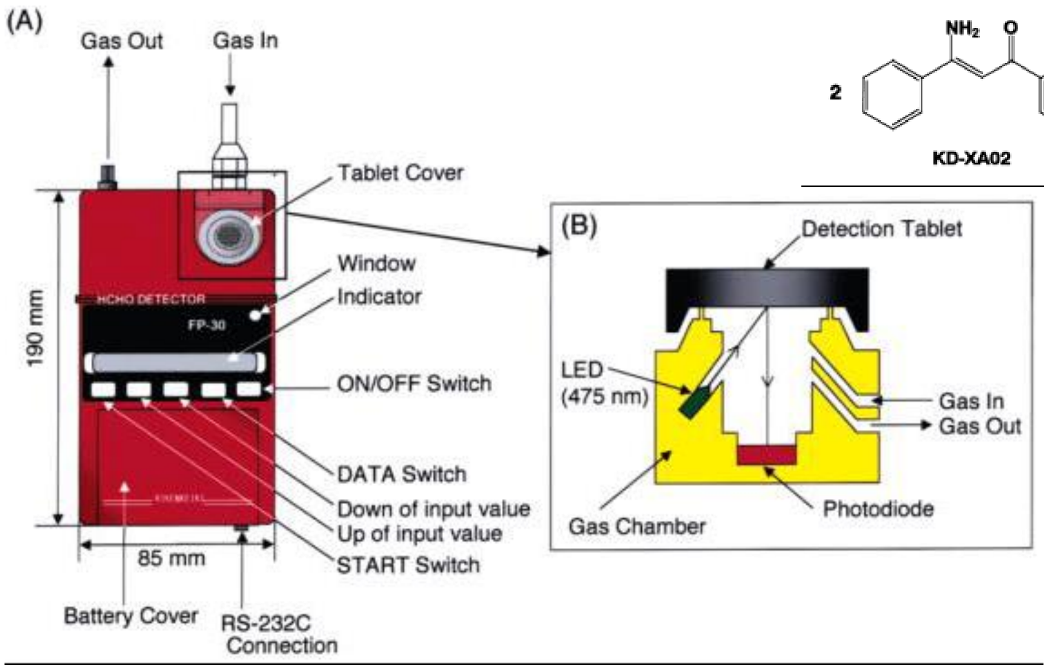


(b)

Colorimetric methods

Formaldehyde detector with pumping system for immediate reading





Pumping time adjusted to concentration

Suzuki, Y.; Nakano, N.; Suzuki, K.*Environ. Sci. Technol.* **2003**, *37*, 5695–5700

Sensors, detectors and analysers

Systems for direct, reversible and real time readings.

fix

portable

Various physicochemical principles are used:

Photo Ionization Detectors
Electrochemical cells
Semiconductors

Systems can combine several sensors

Others

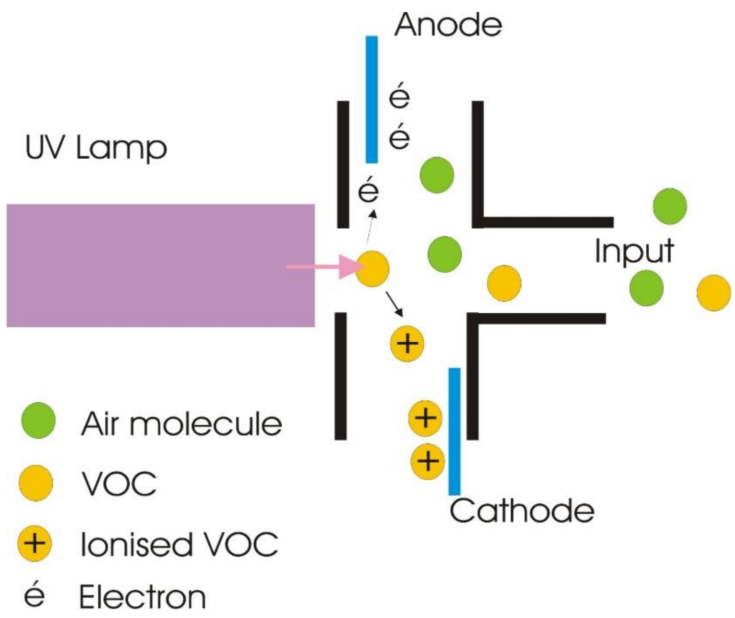
AQ EXPERT

Specifications

Parameter	Sensor	Range	Res.	Accuracy
CO_2	NDIR	0 - 5,000 ppm	1 ppm	±2% of rdg. ±10 ppm
CO_2	NDIR	0 - 20%	0.1%	±3% of rdg.
CO[1]	Electrochemical	0 - 200 ppm	0.1 ppm	±4% of rdg. ±0.5 ppm
% RH	Thin Film Capacitive	5 - 95% RH	0.1% RH	±2% RH
Ambient Temperature	Pt100	-40 - 257°F (-40 - 125°C)	0.1°C/F	±2°F (32-140°F) (± 0.4°C [0-60°C])
VOCs	PID	0 - 20,000 ppb (0 - 46,000 µg/m³)	1 ppb (1 µg/m³)	±10 % of rdg. ± 20 ppb
VOCs	PID	0 - 200 ppm (0 - 460 mg/m³)	1 ppm (1 mg/m³)	±10 % of rdg. ± 2 ppm
O_2	Electrochemical	0 - 25%	0.1%	±0.1% vol rdg.
Ozone (O_3)	Electrochemical	0 - 5 ppm	1 ppb	
H_2S[1]	Electrochemical	0 - 100 ppm	1 ppm	±4% of rdg. ± 0.5 ppm
CH_2O[2,3]	Electrochemical	0 - 10,000 ppb	1 ppb	±5% of rdg. ± 50 ppb
NO[1]	Electrochemical	0 - 250 ppm	0.1 ppm	±4% of rdg. ±0.5 ppm
NO_2[1]	Electrochemical	0 - 20 ppm	0.1 ppm	±4% of rdg. ±0.5 ppm
SO_2[1]	Electrochemical	0 - 20 ppm	0.1 ppm	±4% of rdg. ±0.5 ppm
Barometric Pressure	Solid State	260 - 1260 mbar	1 mbar	±2 mbar
Differential Pressure	Bridge	±40.0 inH_2O (±100 mbar)	0.1 inH_2O (0.25 mbar)	±1% of rdg.
Temperature Type K T1 & T2	Tc K	0 - 2000°F (0 - 1100°C)	1°C/F	±2% of rdg.
Air Velocity	Calculated	0 - 300 ft/sec	1 ft/sec	
Electromagnetic compatibility		EN 61326-1, Portable Equipment		

Photoionization detectors (PID)

Based on the detection of ions produced by the impact of high energy photons (UV ~10 eV)
The ions are collected on electrodes and the current is proportional to the gas concentration.



Sensitivity depends on molecular weight of the molecule (less sensitive for smaller molecules) (difficult for formaldehyde)

Photoionization detectors (PID)

Can be very sensitive (< 1 ppm)
Typical concentration ranges 0-20 ppm (LOD 20 ppb) or 0-1000 ppm

Not selective

Rapid (response time ~10s)

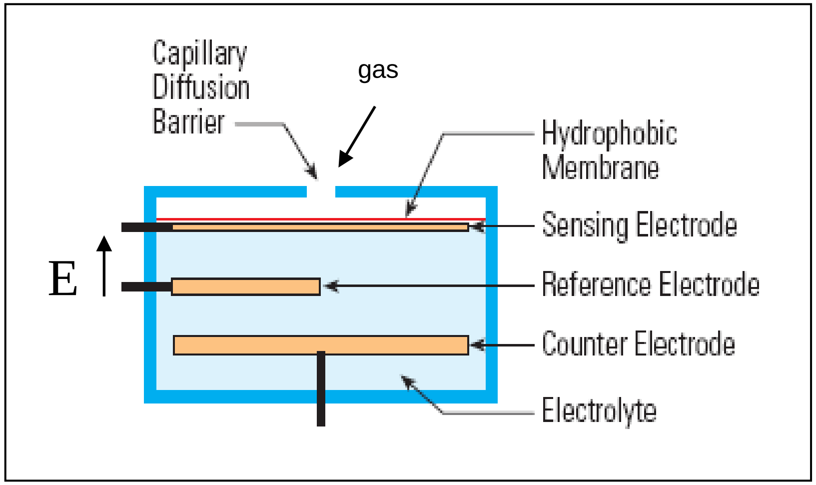
Regular calibration needed

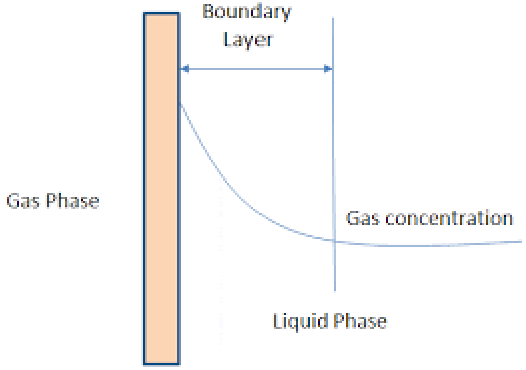
Can be portable

Most used for rapid screening

Electrochemical sensors

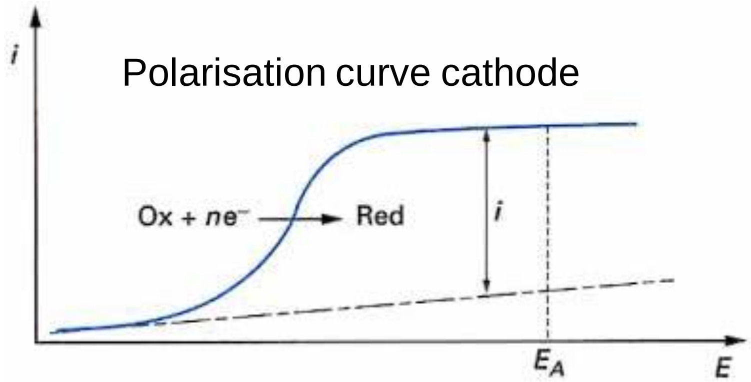
Amperometric sensors based on the limiting current measurement





If diffusion barrier mass flow of Ox ÷ C_{ox}

=> Current i ÷ C_{ox}



Current i ÷ mass flow of Ox

Signal = current through the cell ÷ C_{gas}

Electrochemical sensors

Typical concentration ranges 0-20 ppm (LOD 1 ppm)

Can be selective

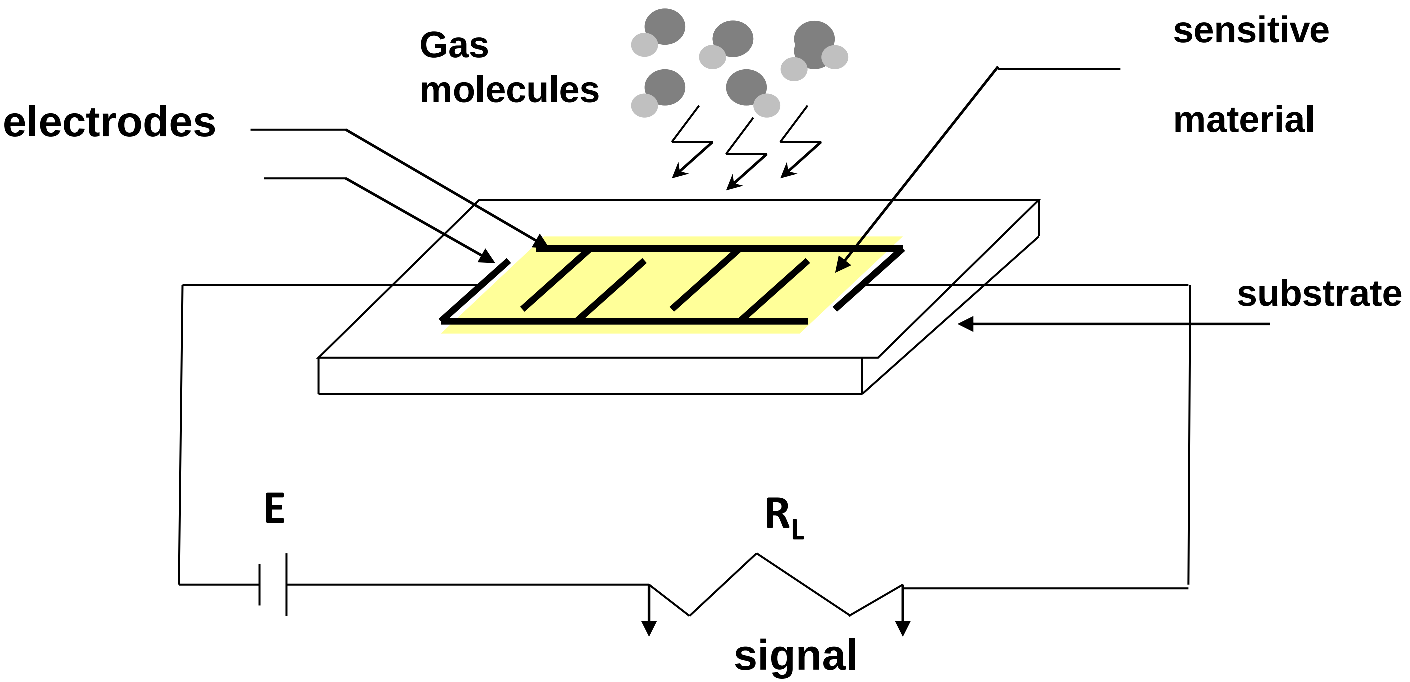
Rapid (response time ~10s)

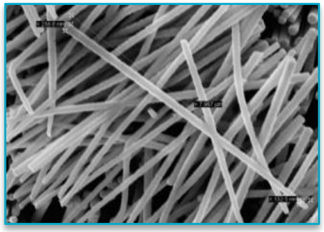
Regular calibration needed (lifetime < 2 y)

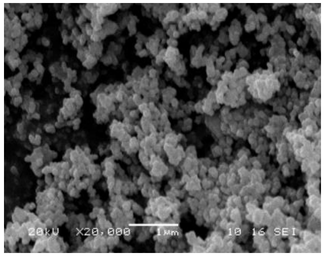
Can be portable

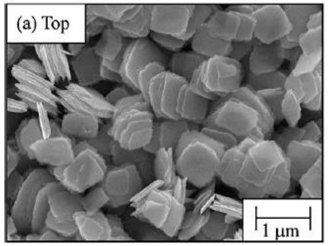
Mostly used for alarms

Semiconductor based gas sensors



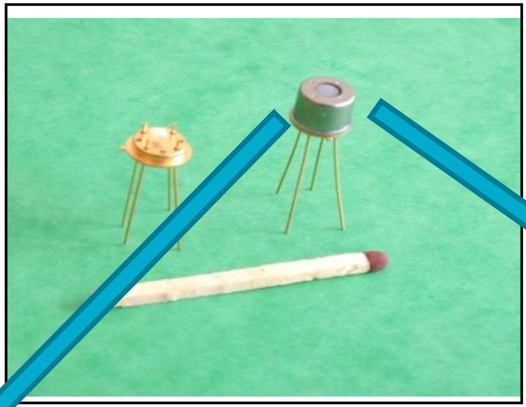




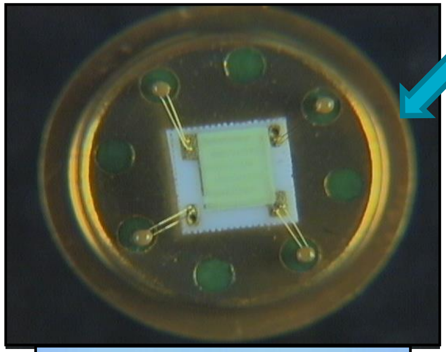


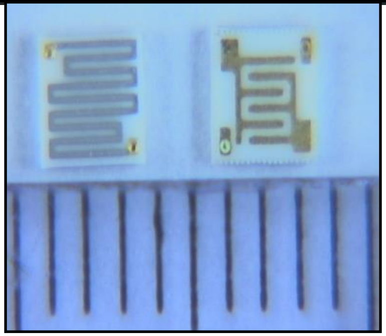
- Gas adsorption induces electrical conductivity variations $\Delta\sigma = f(C_{gas})$
- Resistance measurement = C_{gas} measurement

Semiconductor based gas sensors

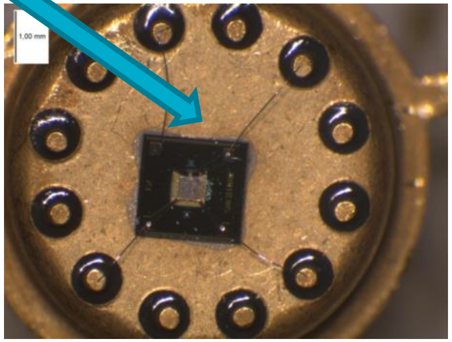


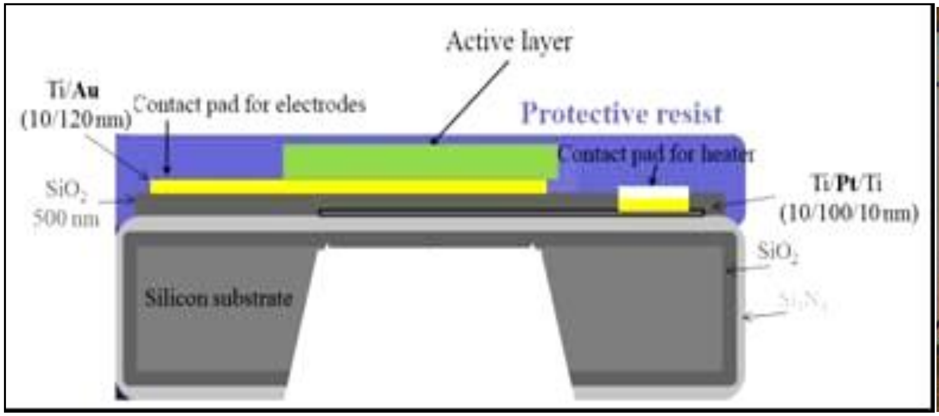
Ceramic substrate

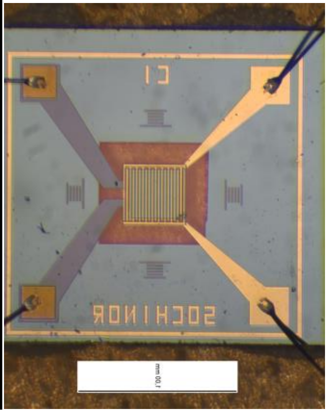




MEMS substrate
Microfabrication







Semiconductor based gas sensors

Very sensitive
Typical concentration ranges 0-2 ppm (LOD 10 ppb) for formaldehyde
0-100 ppm (LOD 1 ppm) for toluene

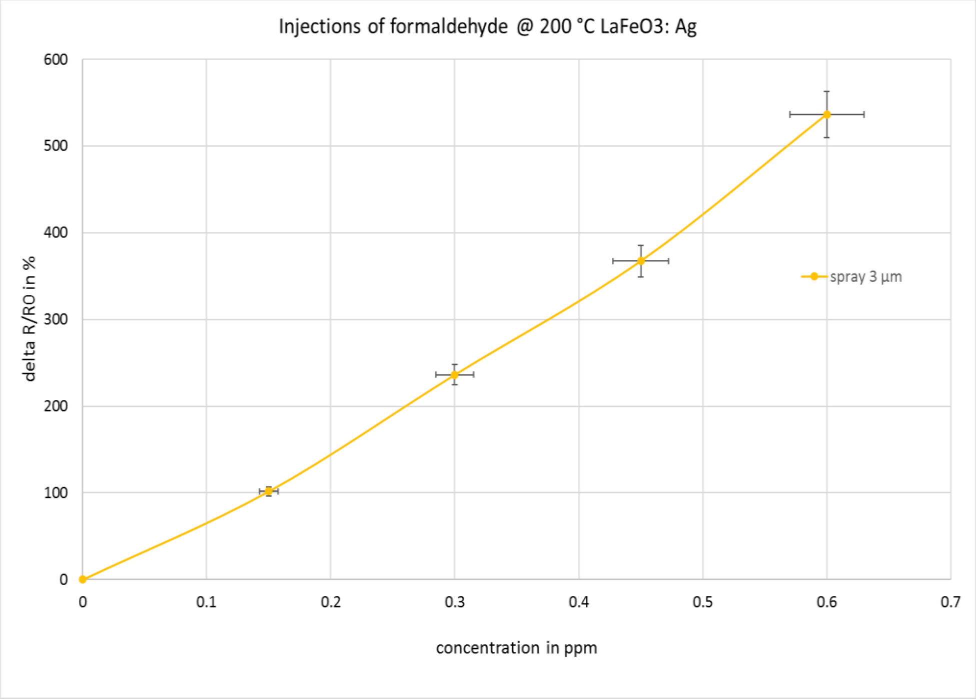
Poorly selective

Rapid (response time < 60s)

Easily inserted in electronic boards

Lifetime ~ 5 y

Mostly used for alarms



Conclusions

- Different technologies exist for the measurement of the VOC’s.
- In general, the most accurate are based on sampling and analysis in the lab but they are absolutely not real time and quite expensive.
- New technologies are now in development in the field of sensors and low cost detectors