Sensors and New Techniques

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In this lecture

- Sensor-based systems for VOC analysis
- Outline of sensor operation
- Sensors commonly found in electronic noses
- Sample handling, data analysis
- Illustration: Cranfield University “VapourGuard”

Sensor-based systems

- Typical laboratory methods for air monitoring (e.g. TD-GC-MS) are laboratory-bound
- Potential of sensor-based systems
  - Field use
  - Cost-effective
  - Rapid
  - Less operator training
- However, still need to be referred to laboratory analytical techniques
- Electronic nose or “e-nose”

What is e-nose?

- Instrument for monitoring volatile odour patterns
- Utilises one or more sensors
- Bench or portable
- Generates a pattern from the response of several component sensors to a (usually complex) odour
- Sensors typically have overlapping partial specificities to a wide range of compounds
- Not really an analysis method – no compound identification
- But useful for comparing different systems or samples and categorising them
- Responds to sample attributes to produce a “fingerprint” – useful for complex samples

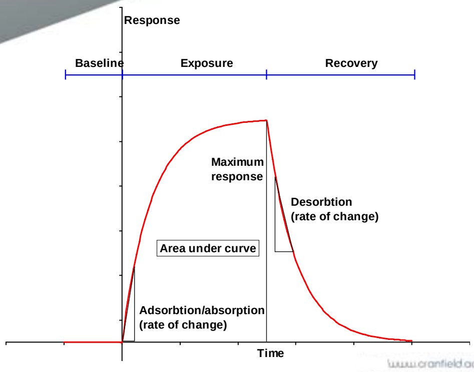
Electronic nose

- Sample delivery system
- Gas sensor array
- Signal acquisition system
- Data-logging capability
- Means of pattern recognition

Gas sensor

A chemical gas sensor can be described as a device, which upon exposure to a gaseous chemical compound or mixture of chemical compounds, alters one or more of its physical properties (e.g. mass, electrical conductivity, or capacitance) in a way that can be measured and quantified directly or indirectly.

Representative sensor response



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Gas sensor types

- Electrochemical
- Optical
  - Infrared
  - Coated fibre
- Piezoelectric (gravimetric)
  - Bulk acoustic wave/quartz crystal microbalance (BAW/QCM)
  - Surface acoustic wave (SAW)
- Conducting polymer
  - Instrinsically conducting polymer
  - Conducting polymer composite
- Metal oxide semiconductor field-effect transistor (MOSFET)
- Metal-oxide semiconductor (MOS)

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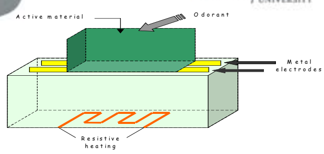
Conducting Polymer Sensors



- Typically polymers of pyrrole, aniline or aromatic and heteroaromatic materials
- Intrinsically conducting: linear backbone from unsaturated monomers which is then doped
- Conducting polymer composites: conducting particles (e.g. carbon) in insulating matrix
- Odorants diffuse into the polymer causing its properties to change – typically expansion
- This in turn causes a change in conductivity measurable as an electrical signal

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Conducting polymer sensors

Advantages

- Room temperature operation
- Rapid response
- Good baseline recovery
- Sensitivity ppb/ppm range for a range of organic compounds (alcohols, aldehydes and ketones; fatty acids)
- Can manipulate sensors to enhance selectivity

Disadvantages

- Very sensitive to water vapour
- Prone to ageing and drift
- Poor manufacturing reproducibility – variation between sensors
- Short lifetime due to polymer oxidation

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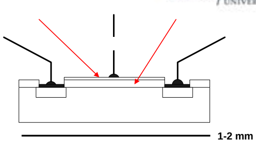
MOSFET sensors



- Metal-oxide semiconductor field-effect transistor (MOSFET) acts as an electronic switch – controlled by a "gate"
- Field-effect transistor with catalytic metal (e.g. Pt) as the gate contact
- Interaction of gas with the catalyst changes the operation of the MOSFET – typically changing the switching threshold
- Results in an electrical signal
- Operating temperature around 120 °C
- Sensitivity in the ppb range

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MOSFET sensors

Advantages

- Small
- Good reproducibility
- CMOS devices so easy to interface
- Low cost

Disadvantages

- Drift
- Baseline instability
- Control of flow and operating temperature are critical

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Metal oxide semiconductors

- In 1953, found that adsorption of a gas onto the surface of a metal oxide semiconductor produced a large change in its electrical resistance
- Led to development of metal oxide semiconductor sensor (MOS) technology.
- Commercially exploited for only a few oxides due to the requirement for a unique combination of resistivity, magnitude of resistance change in gas (sensitivity) and humidity effects.
- Two types:
  - n-type – respond to reducing gases (e.g. tin oxide)
  - p- type – respond to oxidising gases (e.g. nickel oxide)
- Most common oxides for n-type: chromium, titanium, tungsten, tin

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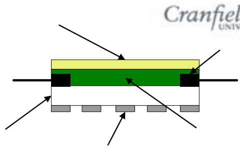
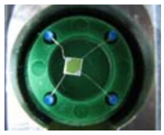
Metal oxide sensors



- Ceramic substrate
- Oxide doped onto the upper surface
- Intercalated platinum heating element (lower surface)
  - Operating temperatures 300 – 600ºC
  - Optimum temperature for VapourGuard 420ºC, determined using MtBE and benzene
- Sorbtion/desorption of volatiles changes resistance
  - Numerous reactions and processes
  - Compound-dependent
  - Resulting signal transduced and measured
- Major limitation is response time
  - Minutes to reach full-scale response
  - VapourGuard uses a different approach



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Metal oxide sensors

The CAP25

- General-purpose air quality monitoring sensor
- (Was) commercially available, inexpensive
- Non-specific
- Chromium-titanium oxide - proprietary mixture
- Intended for hazardous solvent detection at 10ppm and above
- Integration of fluidics, electronics and chemometrics enable use at sub-ppm concentrations
- Used in the VapourGuard

≈10mm

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VapourGuard

- Designed and built at Cranfield University
- Proof-of-concept device for fuel product discrimination
- Detection/speciation of leaks from underground storage tanks
- Mains-powered, portable
- Software controls and data logging

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Problems and advantages of MMOS sensors

- High power requirement due to high operating temperature
- Can be fouled by some compounds, reducing sensitivity & lifespan
- Full-scale response can be measured in minutes

BUT:

- Can affect sensitivity/specificity by changing temperature
- Less sensitive to water vapour
- Sensitive to a wide range of compounds

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Sample handling and delivery

- Sample handling directly affects observed sensor response
- Laboratory-based – headspace
- Field-based – pumps and pipes
- Temperature, flow rate and humidity may all be important

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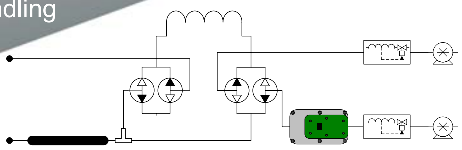
VapourGuard sample handling



- Single sensor
- Two-channel device using two shuttle valves
  - Sample arm
  - Sensor arm
- Aspirates air sample – known volume; controlled rate
- Sample loop – sampling and sensing flow rates can be different
- Flow rate across sensor is constant
- Sample is never static (though its speed changes)
- Reference gas – atmospheric air drawn through hydrocarbon trap
- Inert materials for flow path – High-purity PtFE

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VapourGuard sample handling

- Sensor chamber and "piggyback" circuit board
- Chamber is heated to 40ºC
- Minimum dead volume
- Circuit board acts as top seal
- Proximity of pre-amplifier to sensor minimises EMI

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MFC

Sample port

Sensor chamber

Sample MFC

Sensor MFC

Pump

Pump

Data analysis

- Most commonly used is multivariate data analysis techniques
  - Principal Components Analysis (PCA)
  - Discriminant Function Analysis (DFA)
  - Artificial Neural Networks (ANN)
- Aim is to reduce data dimensionality
- Initial data reduction is often a prerequisite

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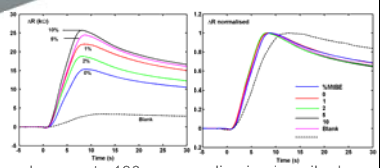
Data analysis
Normalisation



- Response of VapourGuard sensor to 100ppm gasoline in air, spiked with various amounts of the oxygenate methyl tertiary butyl ether (MtBE) (0 – 10% v/v)
- Clear visible difference between samples in left-hand graph
  - Different response amplitude
  - Probably related to relatively high volatility of MtBE compared to gasoline
  - Cannot easily control sample concentration in the field
- Process the data to remove the effect of absolute concentration
- Can we still tell these signals apart if we normalise them to zero baseline and unity amplitude?

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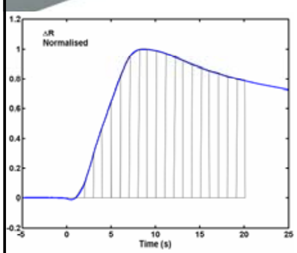
Data analysis
Data reduction by segmentation



- Divide into segments (first 20 seconds into 1-second segments)
- Mean amplitude of each segment
- Rate of change (slope) of each segment by linear regression
- Easy to implement
- Flexible
- No *a priori* assumptions
- Arbitrary but effective

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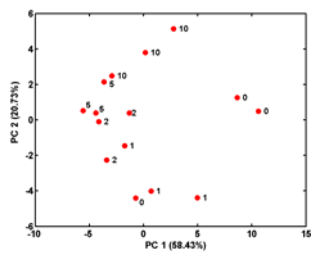
MtBE in gasoline

- Labels show %MtBE in ULG-95
- Normalised data
- Clusters relate to MtBE content



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Fuel discrimination

Soil microcosms

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- Duran bottle (100 ml) with sample bag sealed to top
- Artificial soil: mix of clay, compost and sand
- Add water (20% of dry weight) for "artificial mud"
- Gasoline, diesel or kerosene (1000 mg/kg): 3 replicates
- Bag filled with zero-grade air
- Analysed after 24 hours

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Fuel discrimination

Soil microcosms

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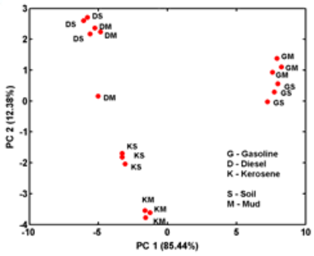

- Normalised data – blank samples not shown
- Clusters based on fuel type
- Presence of water makes little difference

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Conclusions

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- Electronic noses can provide a cost-effective solution for measurement of VOCs in air
- Need to be referred to analytical techniques
- No one class of sensor is suitable for all applications
- General considerations for sensor selection
  - Cost
  - Power consumption
  - Susceptibility to ambient conditions and fouling
  - Stability and ageing
  - Reproducibility
  - Selectivity
- But sensitivity less likely to be an issue

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Conclusions

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- To be useful, a sensor must form part of a system into which it must fit
- E-nose is a device for delivering a sample to a sensor
- Observed performance is strongly dependent on the system
  - Sample handling, sensor properties, data processing
- Sensors can be "persuaded" to do far more than they were designed to do (or less!)
- Trade-off between specificity and information?
- Arrays of cheap, highly-specific sensors?

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