iSOCS Short Course 2016

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Introduction to Chemical Sensing

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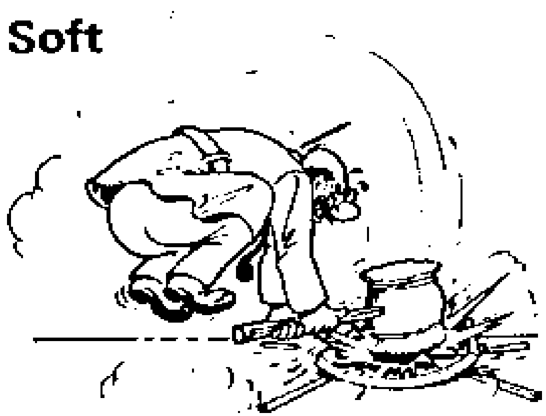
iSOCS
International Society for
Olfaction and Chemical Sensing

Measurement science

Provides the "tools" and the "eyes" scientists and engineers require

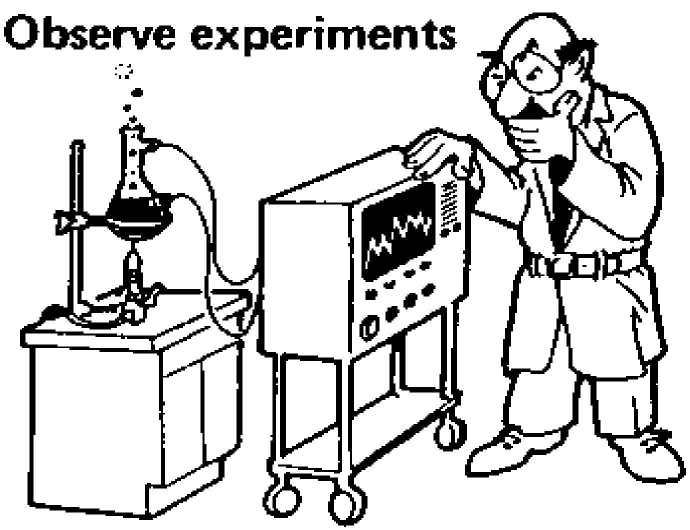
1 Characterize materials

Soft



Brittle

2 Observe experiments

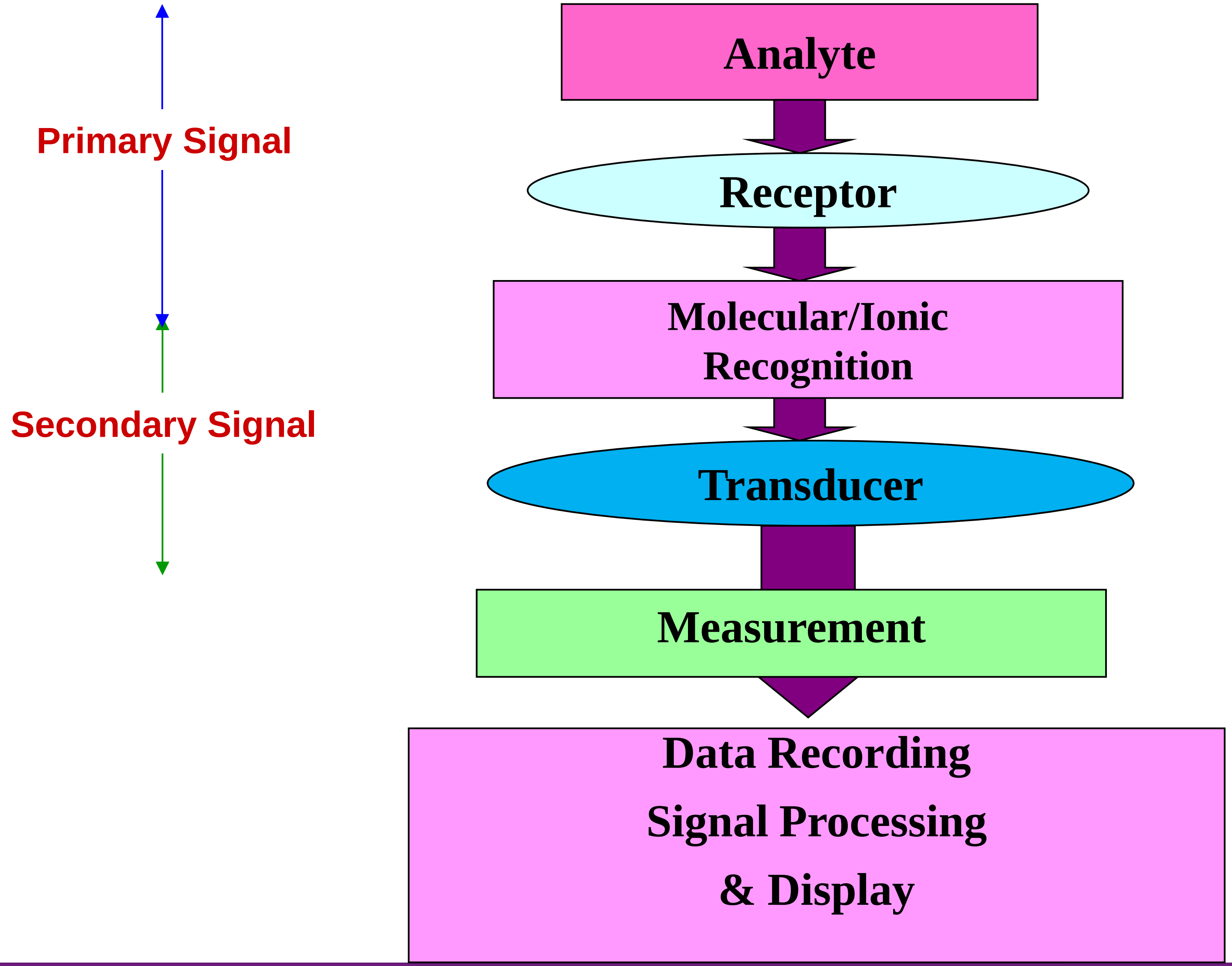


Outline

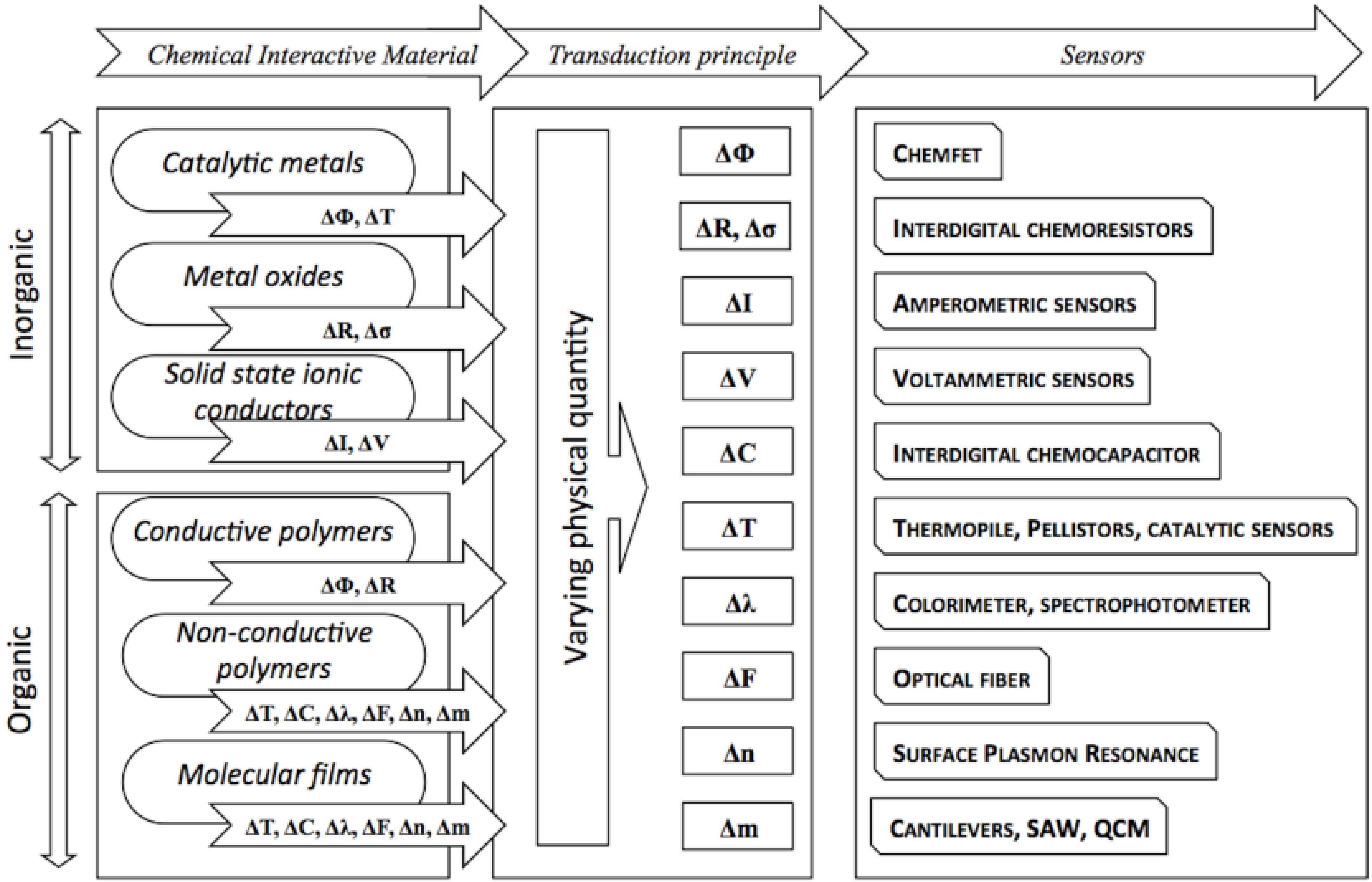
- Chemical Sensor Technologies
- Array based chemical sensing – electronic noses
- Biosensors
- Electronic Tongue
- Bioinspired sensing systems

Definition - Sensors and Transducers

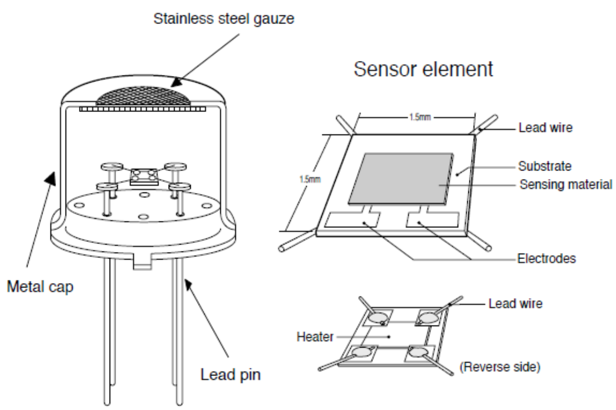
- Chemical sensors consist of a recognition element that is sensitive to stimuli produced by various chemical compounds (analyte) and a transduction element that generates a signal whose magnitude is functionally related to the concentration of the analyte.

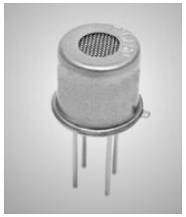

Primary Signal
Secondary Signal
Analyte
Receptor
Molecular/Ionic Recognition
Transducer
Measurement
Data Recording
Signal Processing
& Display

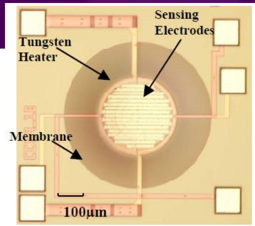
Transduction principles



Common Gas Sensing Technologies





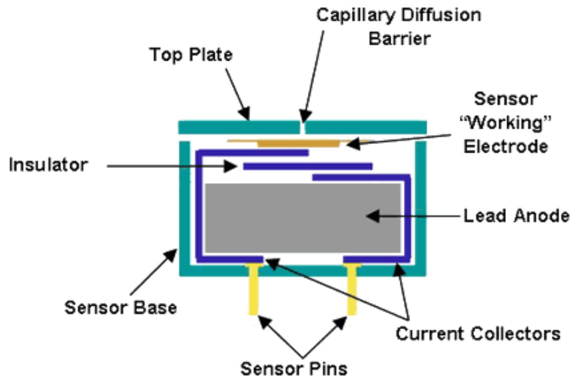


Multi pixel gas sensor
Sensirion

Micro hotplates (Cambridge CMOS Sensors)

Other Sensors
MeMs Pellistor
Infra-red Sensors
Pellistor Sensors
Thermal Conductivity Sensors

Metal Oxide Sensors (Figaro Ltd, FIS, Synkera, Applied Sensors)



Photoionisation detectors
Ion Sense etc

Electrochemical Gas Sensors, Alphasense, ATI, SGS SensorTech etc

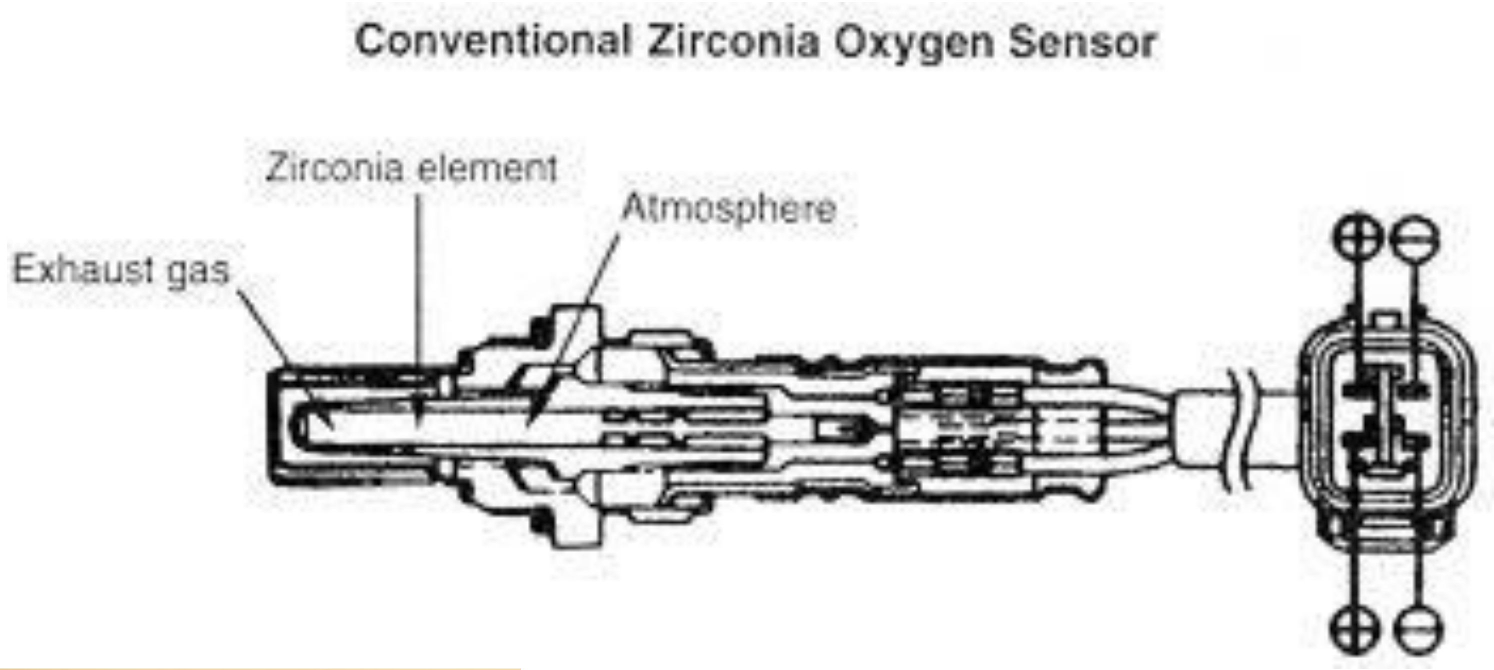
Gas Sensors - Applications

- Controlled combustion (automobile, industrial furnaces)
- Toxic and inflammable gas detection (leakages)
- Electronic noses for air-quality monitoring, food quality and medical diagnosis

Sensing Principles

- Electrochemical (solid electrolyte and amperometric)
- Catalytic combustion (hot-wire)
- Semiconductor (conduction)

ZrO_2 oxygen sensor



Bosch (Germany) and NTK (Japan) are largest manufacturers of so-called lambda sensors.

Solid electrolyte gas sensors

- Modern automobiles monitor combustion efficiency using a galvanic oxygen sensor in the exhaust manifold.
- This sensor measures the oxygen pressure of the exhaust gas.
- The potential between two electrodes depends solely on the ratio of the partial pressures of oxygen at each electrode, separated by an oxygen ion conductor; zirconia.
- The chemical reactions (electron transfer) at each electrode are the same but in reverse of one another; at one electrode the reduced form of the chemical particle is being oxidised (releasing electrons) and at the other electrode the oxidised form is being reduced (accepting electrons).
- The voltage output of the sensor is sent in a feedback loop to control the air/fuel mixture for optimised combustion.

ZrO_2 sensor operating principle

Electrochemical cell line notation

P_{O2} (ref), Pt|Y_2O_3-ZrO_2 |Pt, P_{O2} (test)

Half-cell reactions

$4e^- + O_{2(test)} \rightarrow 2O_2^{2-}$

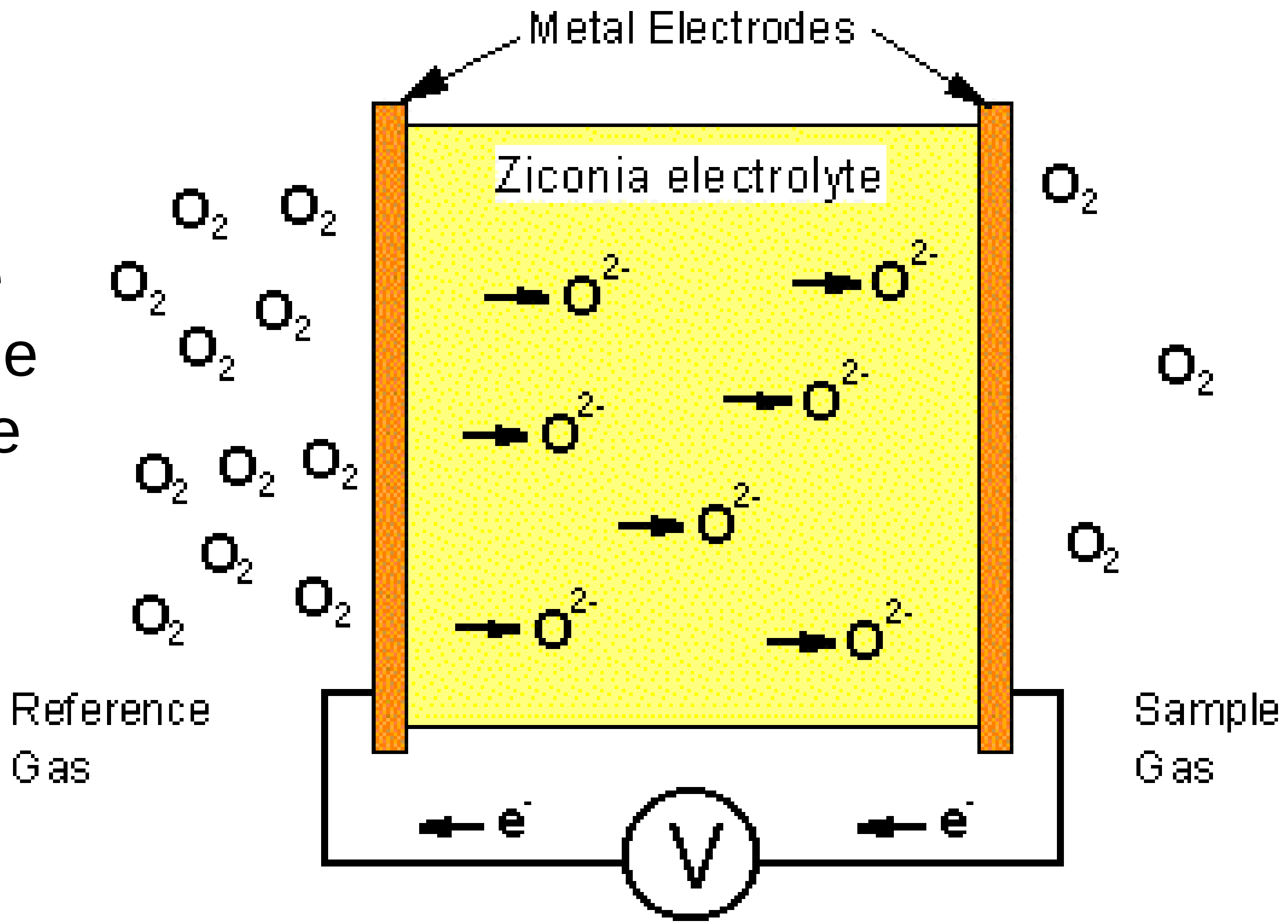
$2O_2^{2-} \rightarrow 4e^- + O_{2(ref)}$

NERNST Equation

$$E = \left(\frac{RT}{4F}\right)\ln\left(\frac{P_{O_{2(ref)}}}{P_{O_{2(test)}}}\right)$$

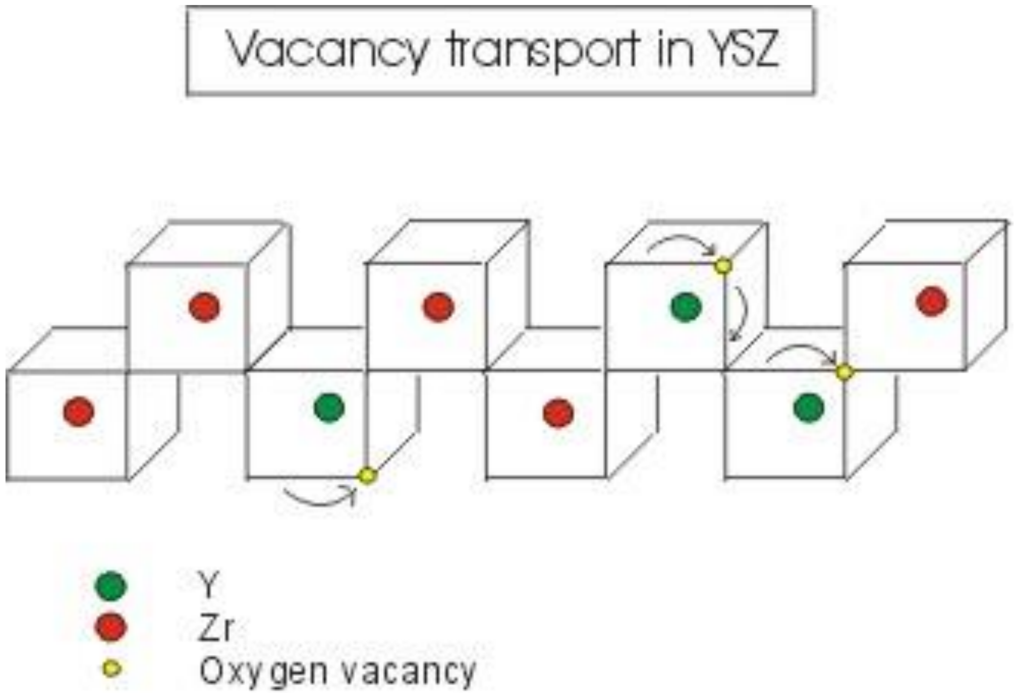
Mechanism

In order for the zirconium oxide sensor to function, the oxides must be mobile. To make the oxides more mobile and the sensor more stable, the zirconium oxide is doped with yttrium oxide and heated above 450C.



Why dope?

The yttria dopant introduces a defect into the zirconia crystal that leaves voids. In the solid zirconia, some Zr^{4+} ions are replaced by Y^{3+} ions so that oxygen vacancies are created which allow the oxide anion, O^{2-}, to move in the solid, giving a solid electrolyte.



Other solid electrolyte sensors

Same principle applies to producing cells sensitive to hydrogen gas and/or humidity (using perovskite oxides based on $SrCeO_3$ as proton conductors).

Research is underway to identify other oxides for detection of hydrocarbons, CO_2, CO, NO_X and SO_X

Amperometric Sensors

Amperometric Oxygen Sensors

Similar to the solid electrolyte sensors.

An oxygen cell can simply be considered as an enclosure which holds a flat PTFE tape coated with an active catalyst (Pt), the cathode, and a block of lead metal, the anode.

This enclosure is airtight apart from a small capillary at the top of the cell which allows oxygen access to the working electrode. The two electrodes are connected, via current collectors, to the pins which protrude externally and allow the sensor to be electronically connected to an instrument. The entire cell is filled with conductive electrolyte which allows transfer of ionic species between the electrodes

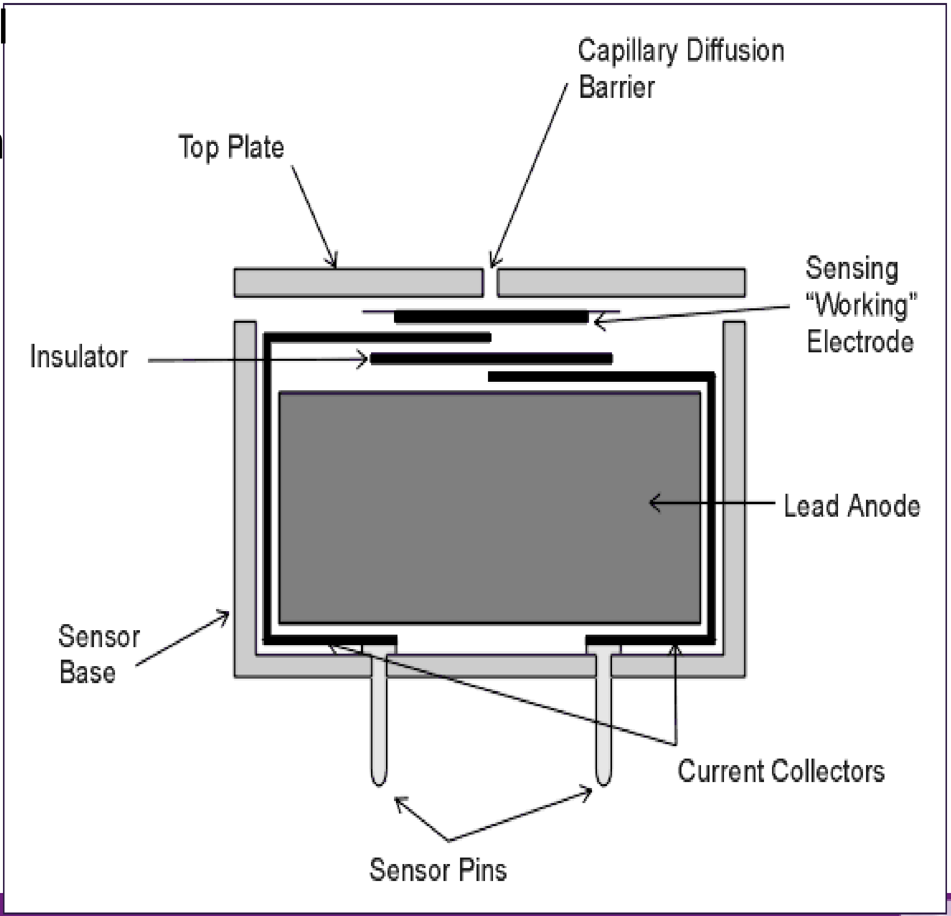
Amperometric cell principles

The rate at which oxygen can enter the cell is controlled by the size of the capillary hole at the top of the sensor. When oxygen reaches the working electrode, it is reduced:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The hydroxyls migrate through the electrolyte to the lead anode where they are involved in the oxidation of the metal:

$$2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$$



Amperometric Sensors

The signal from a capillary controlled oxygen sensor is non-linear and follows the following relationship with the fractional oxygen concentration (C);

$$\text{Signal} = \text{constant}\{\ln [\ 1/(1-C)\ ]\}$$

In practice, the output from the cells are effectively linear up to 30% oxygen.

Newer amperometric cells utilise three electrodes, one of which functions as a reference electrode (no current flowing through it) to improve response by maintaining a fixed potential at the working electrode. This yields linear responses and wider dynamic ranges.

Toxic Gas Sensors

The reactions that take place at the electrodes in a carbon monoxide sensor are:

Sensing: $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$

Counter: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall reaction is: $CO + \frac{1}{2}O_2 \rightarrow CO_2$

Similar reactions take place for all other toxic gases that are capable of being electrochemically oxidised or reduced (H_2S,Cl_2).

Interferences

- An auxiliary electrode can assist in overcoming cross interference from other gases. Typically carbon monoxide sensors show a significant response to hydrogen which can make the accurate measurement of CO difficult when hydrogen is present.
- However, using a sensor with an auxiliary electrode all of the CO and some of the H_2 reacts on the sensing electrode leaving only H_2 to react with the auxiliary electrode. Once the ratio of the responses on each electrode in known, a H_2 –compensated signal can be obtained by subtracting the auxiliary signal from the sensing electrode signal with an analogue circuit or using a microprocessor with appropriate software.

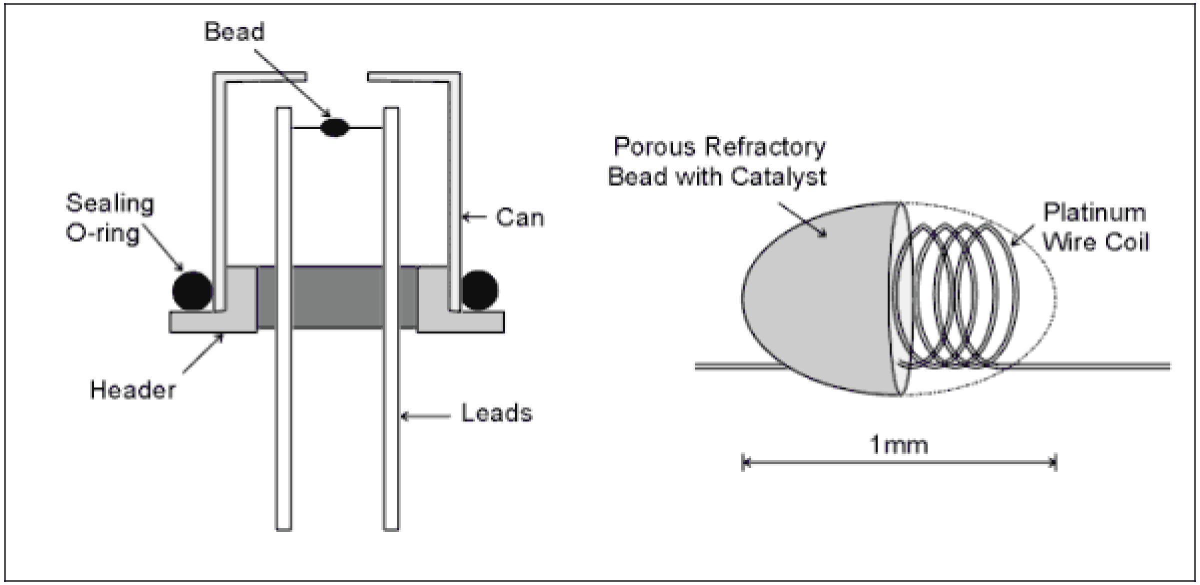
Applications

- Oxygen: Typical applications include the measurement of oxygen deficiency in confined spaces such as tunnels, mines or chemical plant or for the analysis of combustion gases in flues and chimney stacks. Amperometric oxygen sensors are also used in patient monitoring .

- CO: Sensors are available for a wide range of applications, including residential safety, fire detection (smouldering fires), and industrial safety devices.

- Toxic gases: Personal and industrial safety. Flue gas emission monitoring.

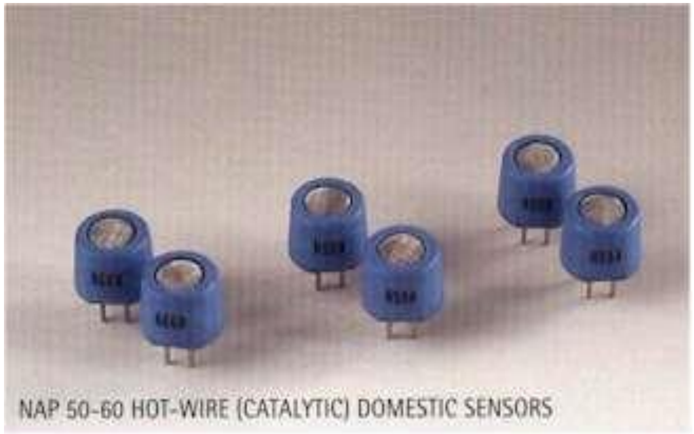
Catalytic combustion sensors



A pellistor element is simply a platinum wire coil, coated with a catalytic slurry of an inert base material (e.g. alumina) and a metal catalyst which accelerates the oxidation reaction. This type of element is known as the "sensitive" element. There are a number of catalyst materials available and the precise type and mix is carefully chosen to optimise sensor performance.

Pellistor systems

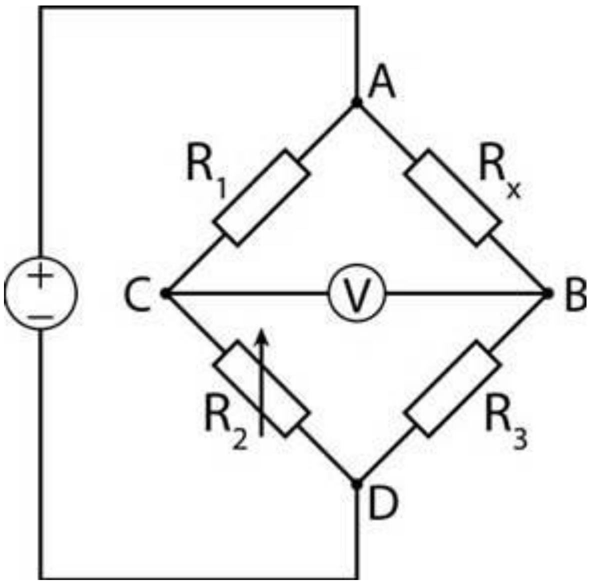
- The standard sensor consists of a matched pair of elements, typically referred to as a detector and compensator (reference element). The detector comprises a platinum wire coil embedded within a bead of catalytic material. The compensator is similar except that the bead does not contain catalytic material and as a consequence is inert.
- Both elements are normally operated in a Wheatstone bridge circuit, that will produce an output only if the resistance of the detector differs from that of the compensator.



Pellistor Principles

- The bridge is supplied with a constant dc voltage that heats the elements to 500-550° C.
- A chemical reaction (oxidation) occurs when a combustible gas reaches the sensing element. This increases the temperature of the element. This T rise is transmitted to the platinum heater coil which causes an increase in the resistance of the wire.
- The inert element is unaffected and this results in an electrical unbalance in the bridge circuit and a detectable output signal is obtained. The output voltage level depends on the type of the detected gas, but shows an excellent linearity with the gas concentration level.

Pellistor Principles



Theoretically $dV=(dR \times V)/4R$

where $dR=k \times a \times m \times Q/C$

dV	Output voltage
R	Resistance value of sensor in clean air
V	Bridge supply voltage
dR	Resistance value variation of the heater
k	Constant
m	Gas concentration
a	Thermal coefficient of heater material
C	Thermal capacity of sensor
Q	Molecular heat of combustion of gas

Pellistor Applications

- Catalytic gas sensors (pellistors) are an industry standard for the detection of flammable gas.
- Catalytic sensors will oxidise most combustible vapours and as such offer a true "explosimeter".
- Their sensitivity to different substances varies, depending on the combustibility of the substance. The sensitivity of a catalytic sensor is defined as its relative sensitivity to methane.
- It is thus important to identify which substances are most likely to be present and to set the sensitivity of the finished detector in accordance with the substance that has the lowest relative sensitivity.

Semiconductor gas sensors

Most widely studied area of solid-state gas sensors is that based on semiconducting oxides.

- The discovery in 1953 that adsorption of a gas onto the surface of a metal oxide semiconductor produced a large change in its electrical resistance signalled the advent of mixed metal oxide semiconductor sensor (MMOS) technology. The effect is 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.
- Amongst the oxides which are used as MMOS sensors are

  ZnO_2, TiO_2, Cr_2TiO_3, WO_3 and SnO_2.

MMOS

- The resistance change is caused by a loss or a gain of surface electrons as a result of adsorbed oxygen reacting with the target gas.
- If the oxide is an n-type, there is either a donation (reducing gas) or subtraction (oxidising gas) of electrons from the conduction band. The result is that n-type oxides increase their resistance when oxidising gases such as NO_2, O_3 are present while reducing gases such as CO, CH_4, EtOH lead to a reduction in resistance.
- The converse is true for p-type oxides, such as Cr_2TiO_3. Unlike some other gas sensing technologies, for MMOS the magnitude of change in electrical resistance is a direct measure of the concentration of the target gas.

MMOS applications

- A TiO_2 MMOS has been in wide use as an oxygen sensor in automobiles (notably Ford and Nissan).
- SnO_2-based sensors are used for most other gas sensors.
- Figaro Engineering USA is the leading supplier of these sensors (for applications including residential and commercial/ industrial alarms for toxic and explosive gases, breath alcohol checkers, automatic cooking controls for microwave ovens, air quality/ventilation control systems for both homes and automobiles. Etc).

SnO_2 Sensors

In the case of SnO_2 sensors, which are n-type semiconductors, the chemistry occuring on the surface involves two main reactions.

- Chemisorption of oxygen:

  $$O_2 + 2e^- \rightarrow 2O^-_{ads}$$

- Removal by reducing gas:

  $$R + O^-_{ads} \rightarrow RO_{des} + e^-$$

- In the first case the surface conductivity decreases (resistivity increases), whilst the reverse occurs upon introduction of a reducing gas.

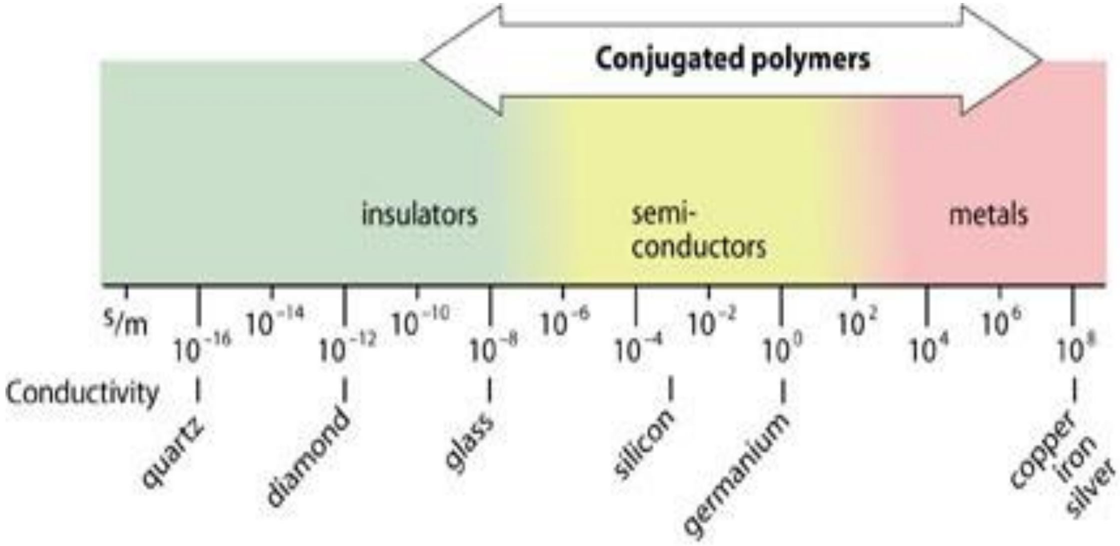
MMOS sensors

- Since the change in electrical resistance in the sensing oxide to the analyte gas is caused by a surface reaction, commercial gas sensors use highly porous oxide layers, which are either printed down or deposited onto alumina chips, to provde maximum surface area.
- A heater track is also present usually on the backside of the chip as both the interference from humidity is minimised and the speed of response is increased upon heating.

MMOS selectivity

- MMOS sensors do not normally discriminate between different target gases.
- As such, considerable care is taken to ensure the microstructure of the oxide, its thickness and its running temperature are optimised to improve selectivity.
- In addition, selectivity is further enhanced through the use of catalytic additives to the oxide, protective coatings and activated-carbon filters.

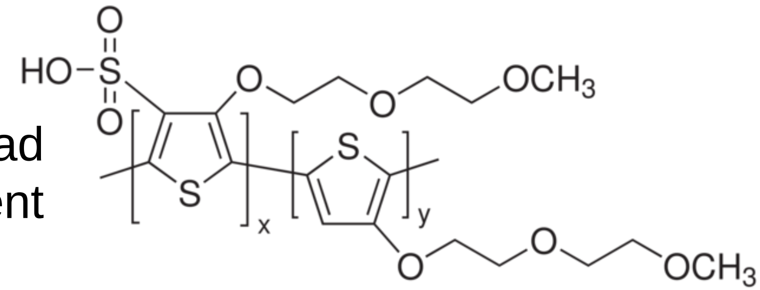
Organic Semiconductors

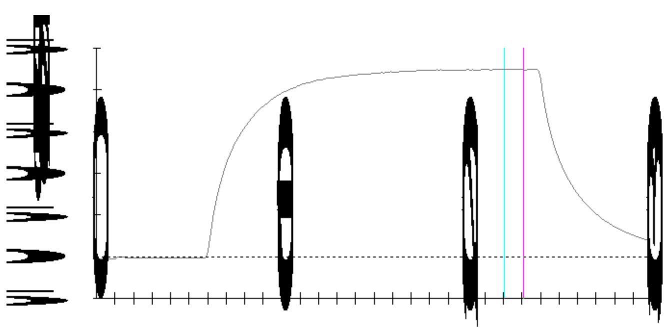


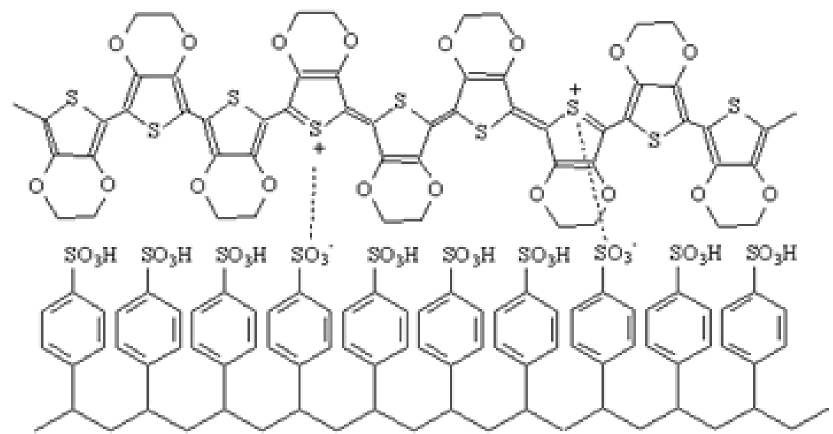
Conductivity of conductive polymers compared to those of other materials, from quartz (insulator) to copper (conductor). Polymers may also have conductivities corresponding to those of semiconductors.

Conducting polymers for Chemical Sensing

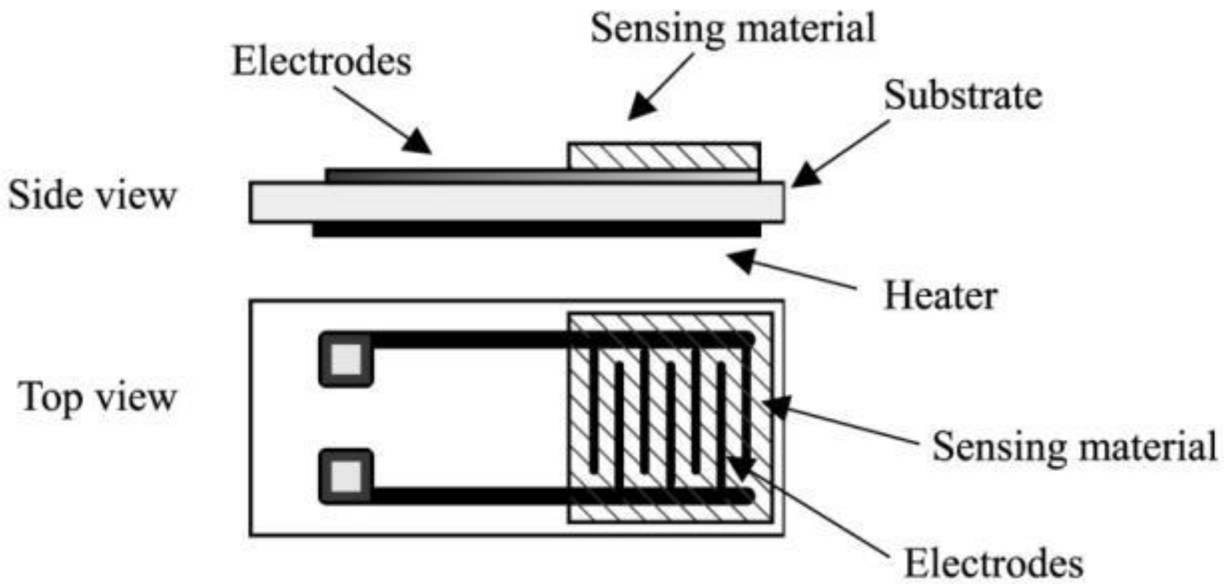
Organic Conducting polymers show broad and overlapping specificity to different volatile organic compounds

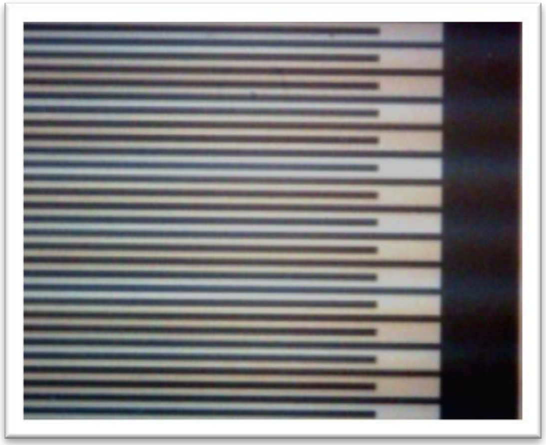




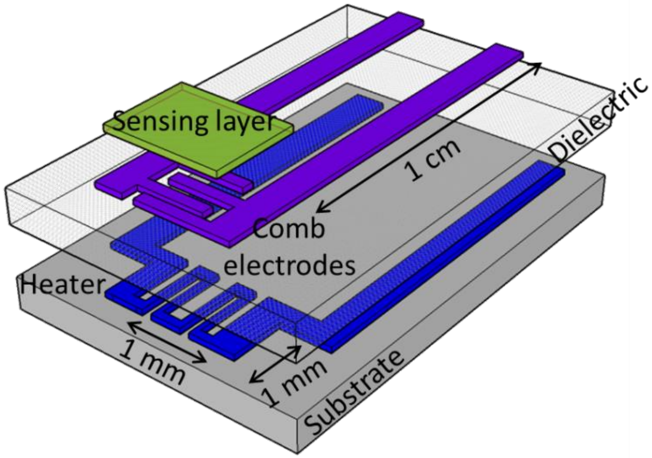


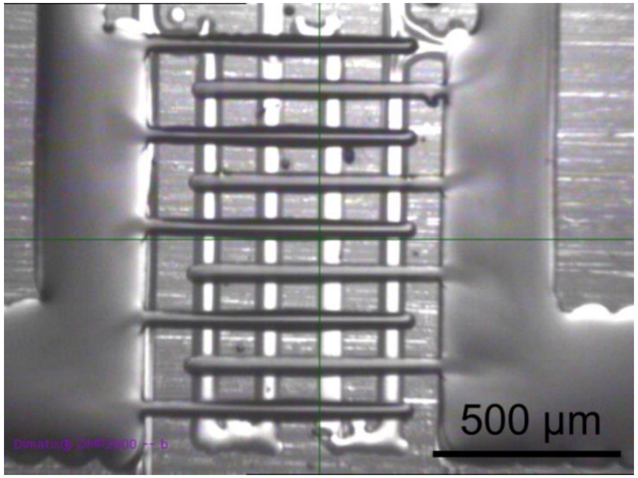
Resistive Gas Sensor





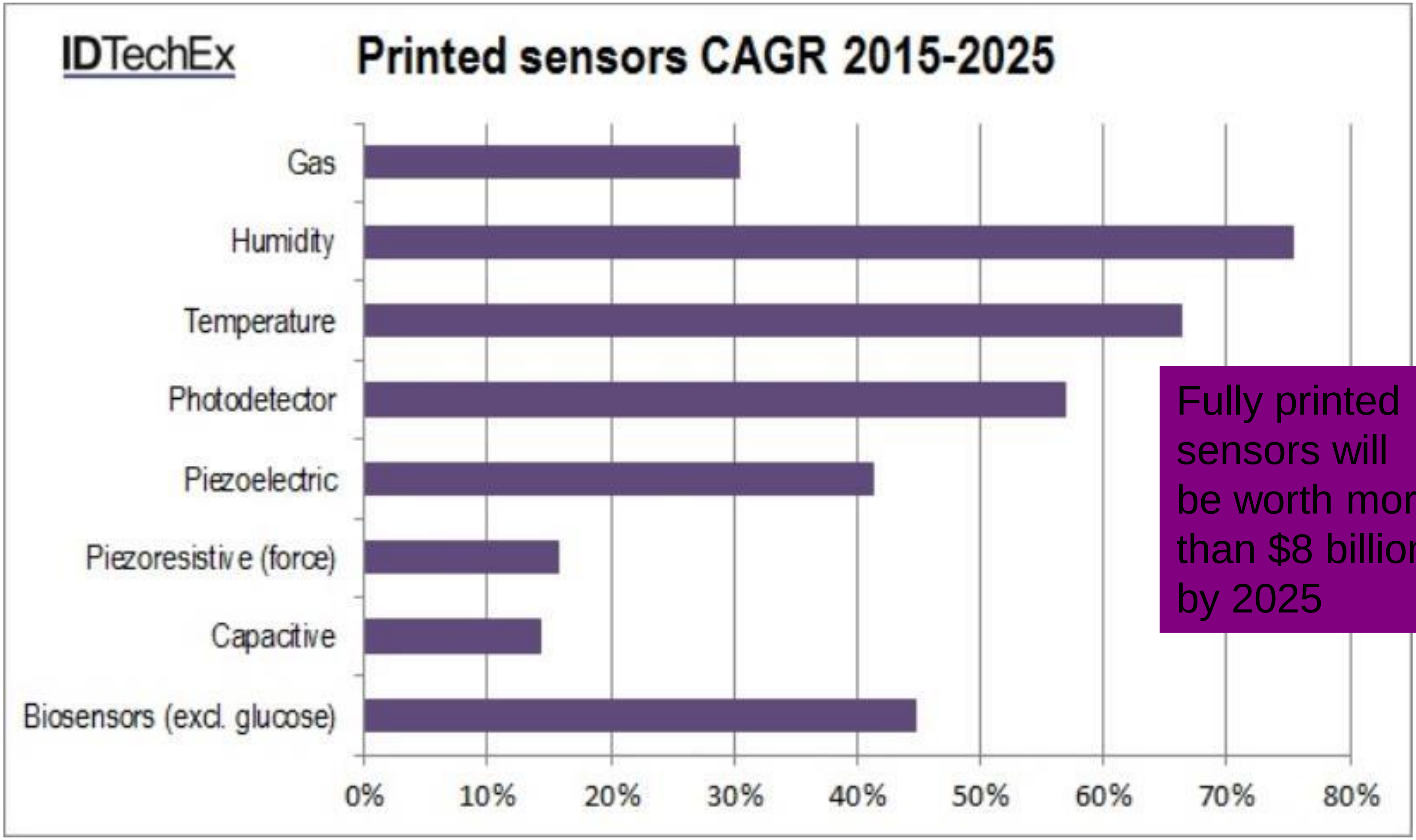
Printed Chemo resistor with heating element





Concept of a printed resistive gas sensor with an integrated heater element

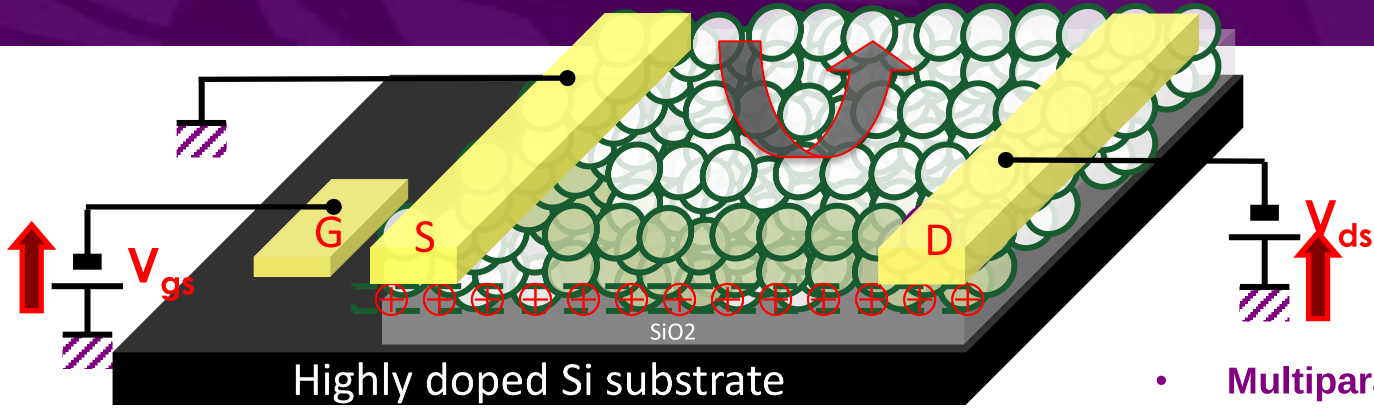
Predicted Growth of Printed Sensors

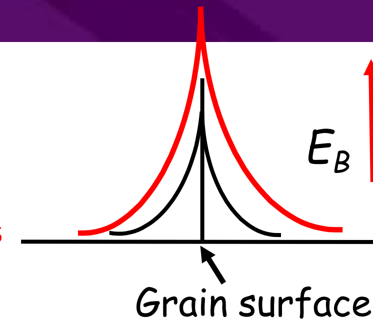


Fully printed sensors will be worth more than $8 billion by 2025

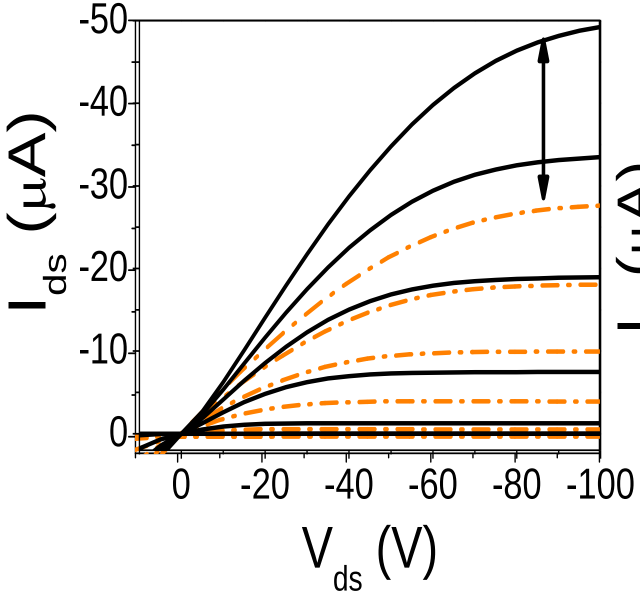
Dr Guillaume Chansin http://www.idtechex.com/research/reports/printed-and-flexible-sensors-2015-2025-technologies-players-forecasts-000428.asp

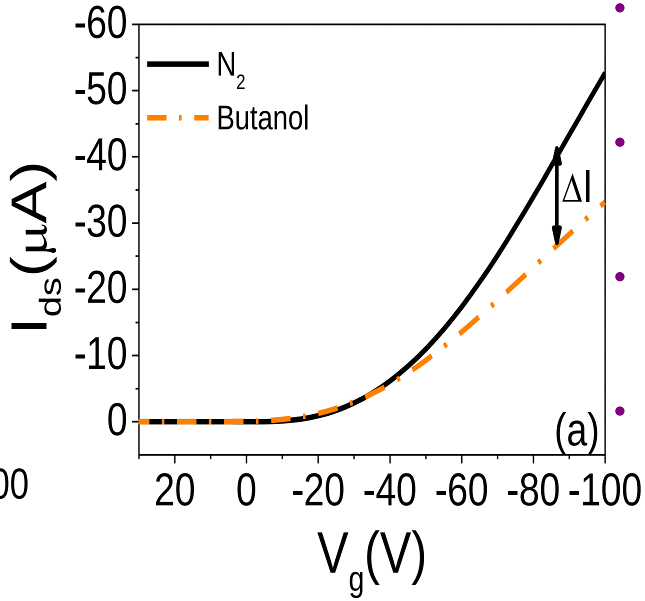
State of the art: Organic Field-Effect Transistor Gas Sensors





NOTE HIGH OPERATING VOLTAGES





- **Multiparametric response (Vt, μ, I_{on}, I_{off})**
- **Fast and repeatable responses**
- **Gate voltage (Vg) induced sensitivity**
- **Recovery of response with reversal of Gate Bias.**
- **Selectivity through tailoring the side groups in active layers.**

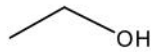
Torsi Group, Italy

What does biological chemoreception do?

- Detection
- Recognition
- Discrimination of complex mixtures of chemicals
- Quantitation of intensity

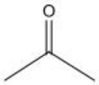
➢ The receptor cells and the receptor proteins they express generally respond to more than one compound. Ensembles of these neurons encode the detailed information about the chemical environment on which animals base their olfactory behaviours.

Ethanol



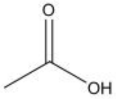
Sweet smelling

Acetone



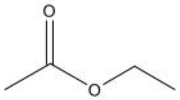
Pungent

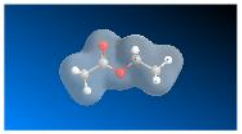
Acetic acid



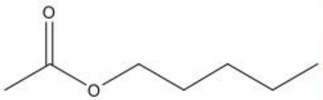
Vinegar

Ethyl acetate





Fruity, brandy, ethereal

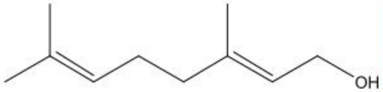


Amyl acetate

Fruity, banana, ethereal

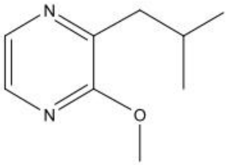
Butyl mercaptan

Putrid, skunk



Geraniol

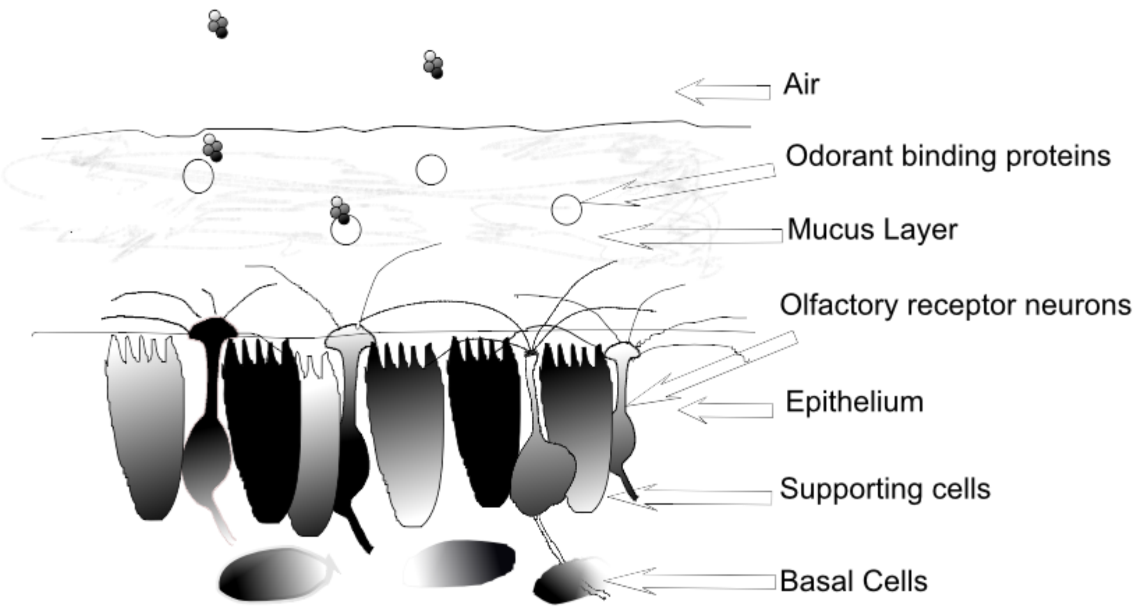
Sweet, floral



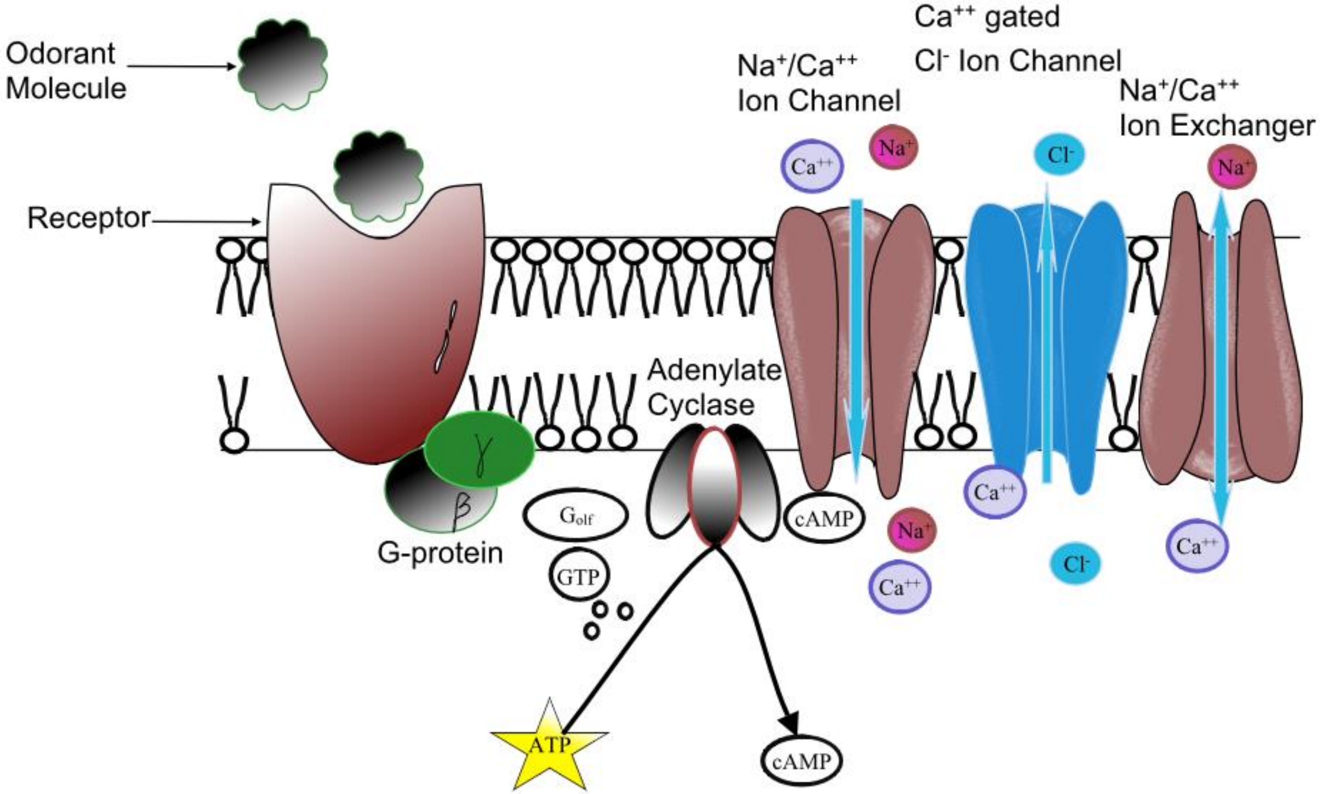
2-isobutyl-3-methoxypyrazine

Green, bell peppers

Olfactory Sensing System



Olfactory Transduction



Sensor Arrays-The Electronic Nose

Olfactory systems operate on the principle that a relatively small number of non-selective receptors allow the discrimination of thousands of different odours.

- The electronic nose consists of an array of chemical sensors (usually gas sensors) and a pattern-recognition algorithm.
- The sensor array "sniffs" the vapours from a sample and provides a set of measurements; the pattern-recogniser compares the pattern of the measurements to stored patterns for known materials.
- Gas sensors tend to have very broad selectivity, which in the electronic nose, it is a definite advantage. Thus, although every sensor in an array may respond to a given chemical, these responses will usually be different.

Digital smells!

An example of the electronic nose is given below, where an array of 8 sensors output different patterns for each gas. If the array is "trained" properly it can recognise the individual gases in mixtures (chemometrics).

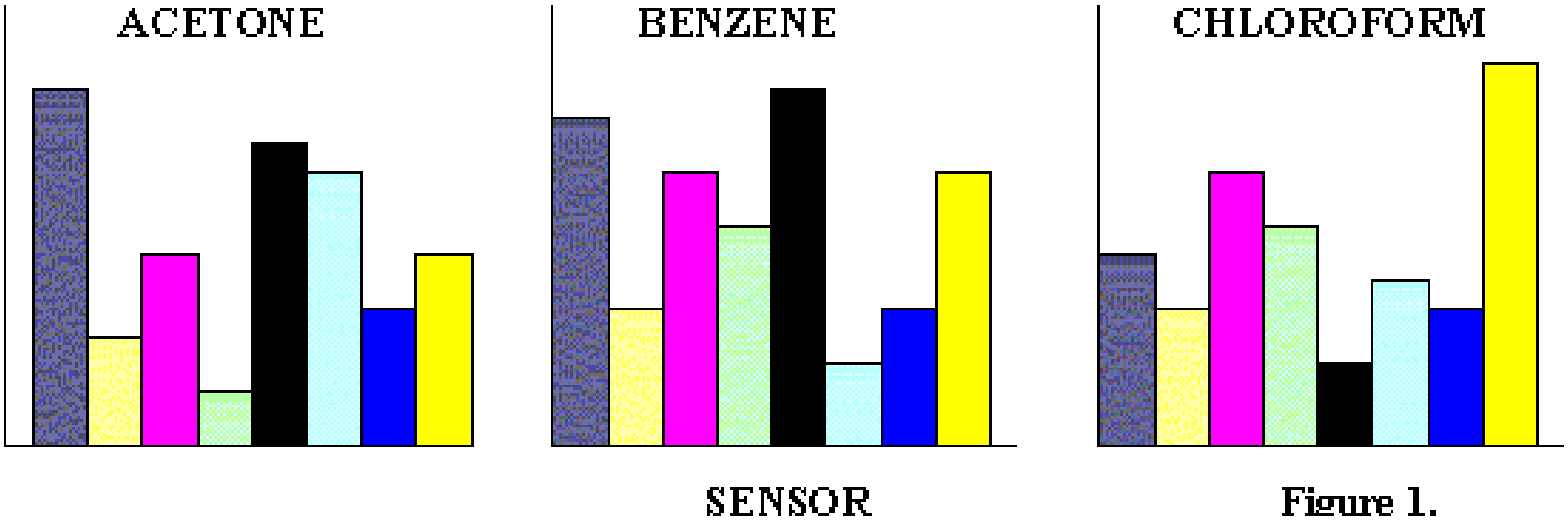
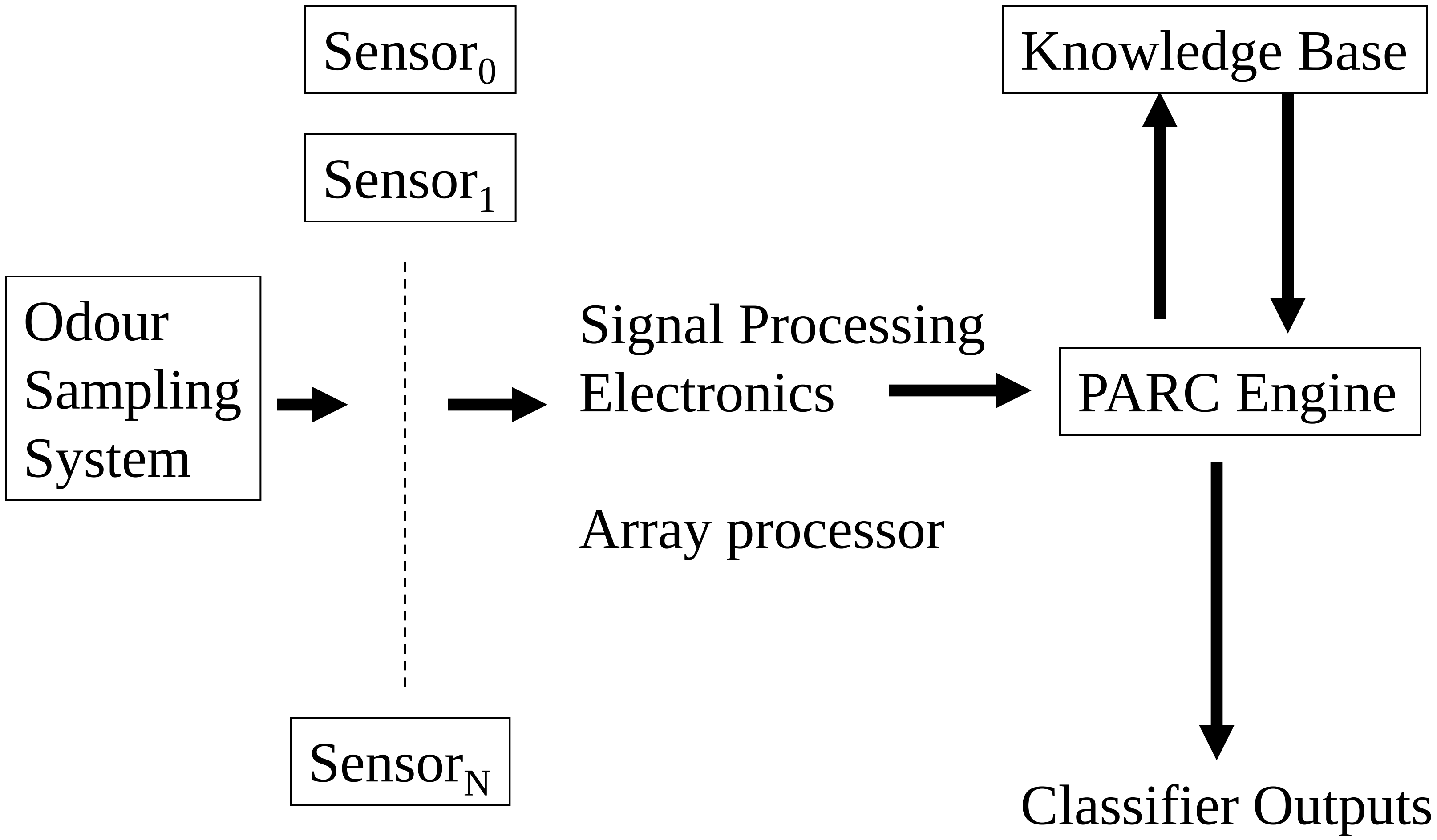
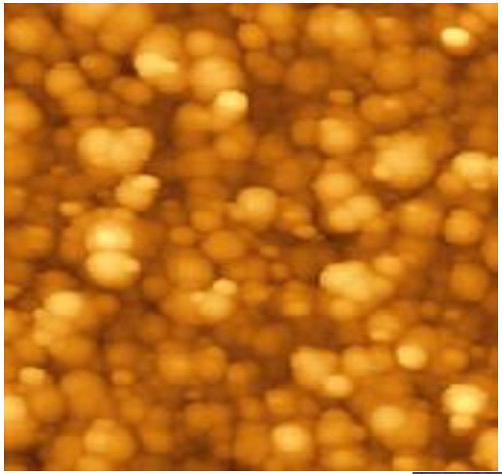


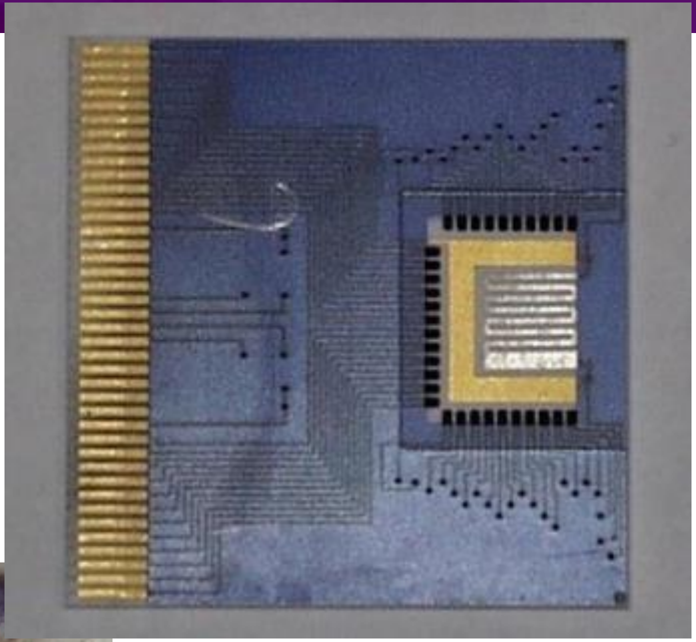
Figure 1.

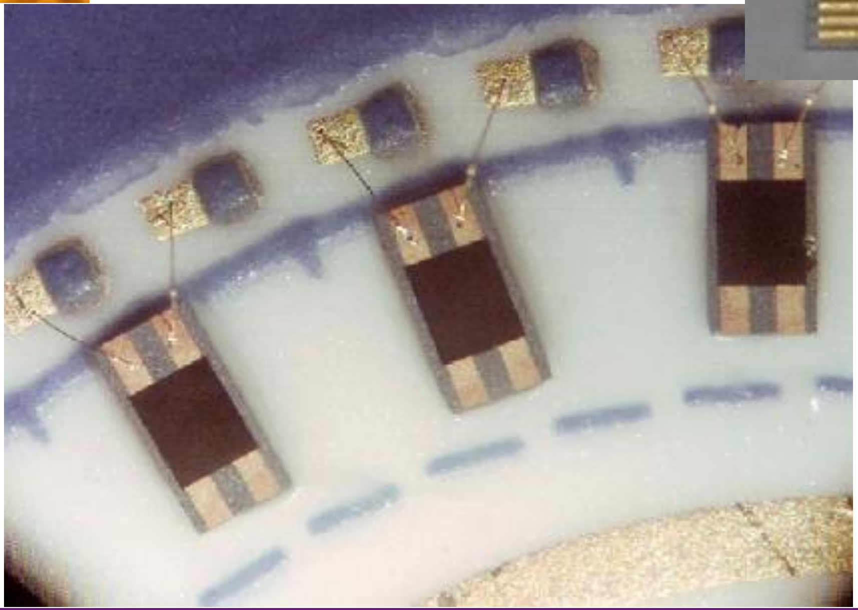
Approach for an Artificial Chemosensory system



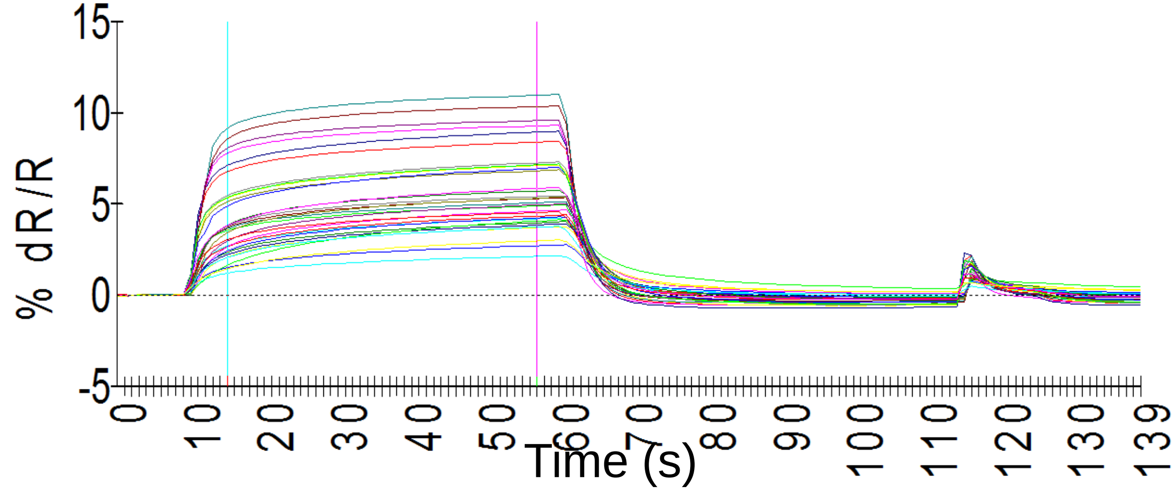
Conducting Polymer Sensor Arrays

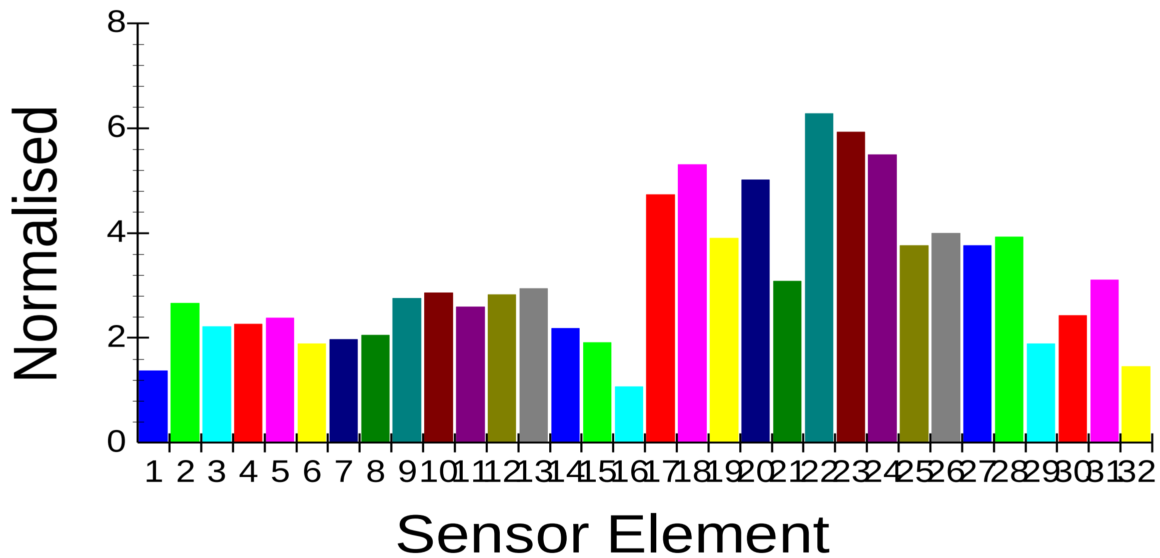






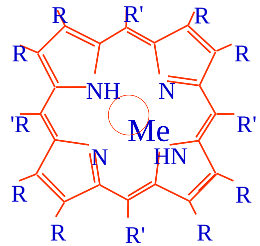
Sensor Array Response to a Vapour Pulse

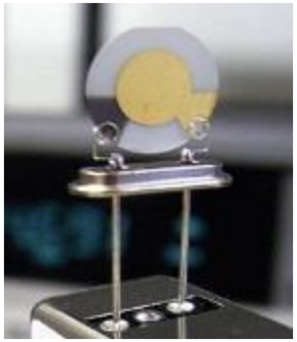




32 element conducting polymer sensor array

Electronic nose Piezoelectric sensors





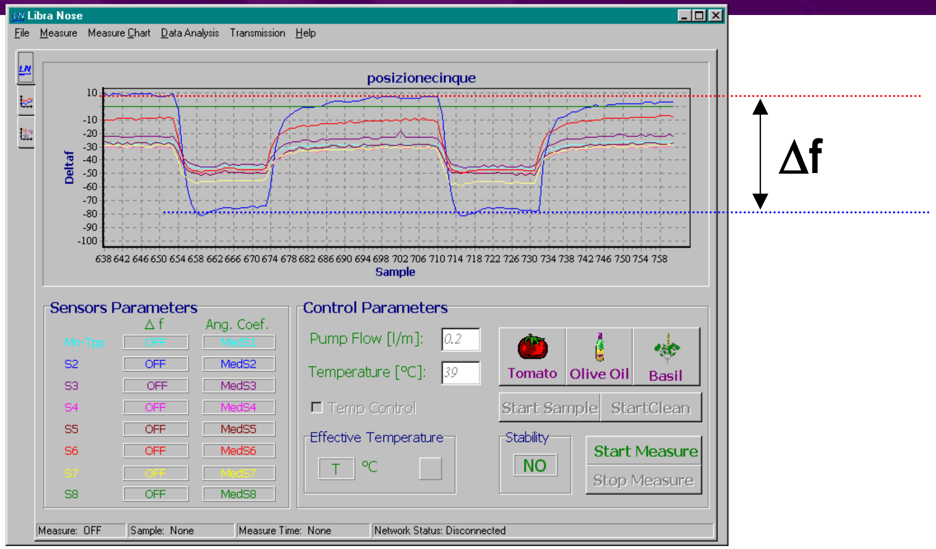
- Eight QCM
- Sensitive coating: eight different kinds of metalloporphyrins
- eight Pierce oscillators

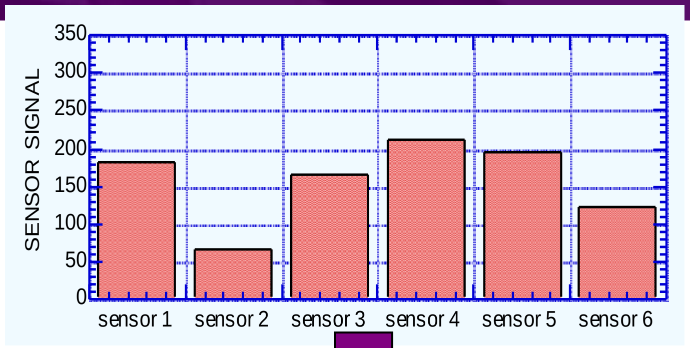
Adsorption of molecules causes a variation of the oscillating mass which induces a variation of the oscillation frequency.

Sauerbrey equation:

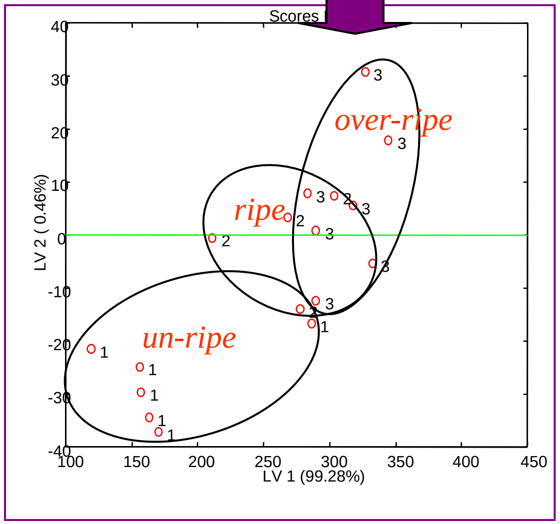
$$\Delta f = -\frac{C_f f_o^2}{A} \Delta m$$

Electronic nose





Pattern Recognition

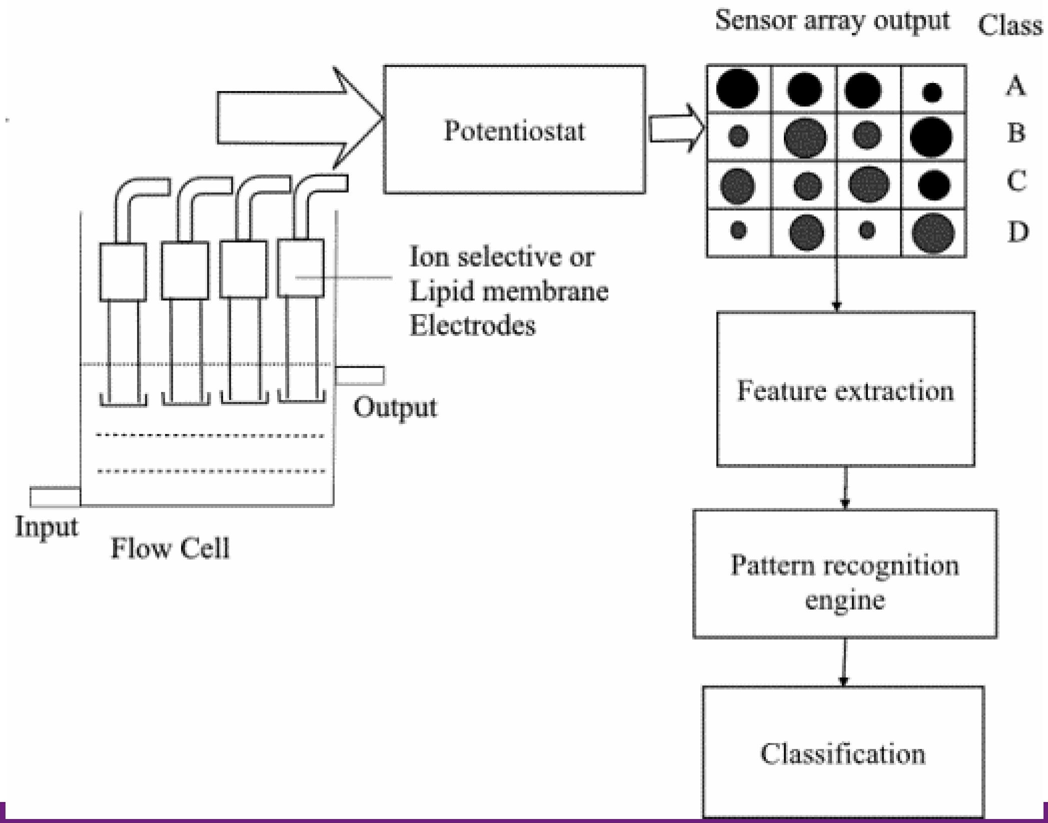


- Sensors array responses are vectors in multidimensional space: each sample corresponds to a vector
- Suitable data analysis techniques allow classification of different odours
- Classify different samples according to some macroscopic features

AirSense PEN E-Nose – metal oxide sensor array

Digital Tastes-the electronic tongue

This is generally the solution analogue of the electronic nose. That is, sensors that can monitor classes of chemicals in solution are placed in an array to output a pattern that is indicative of a event of interest.



Applications

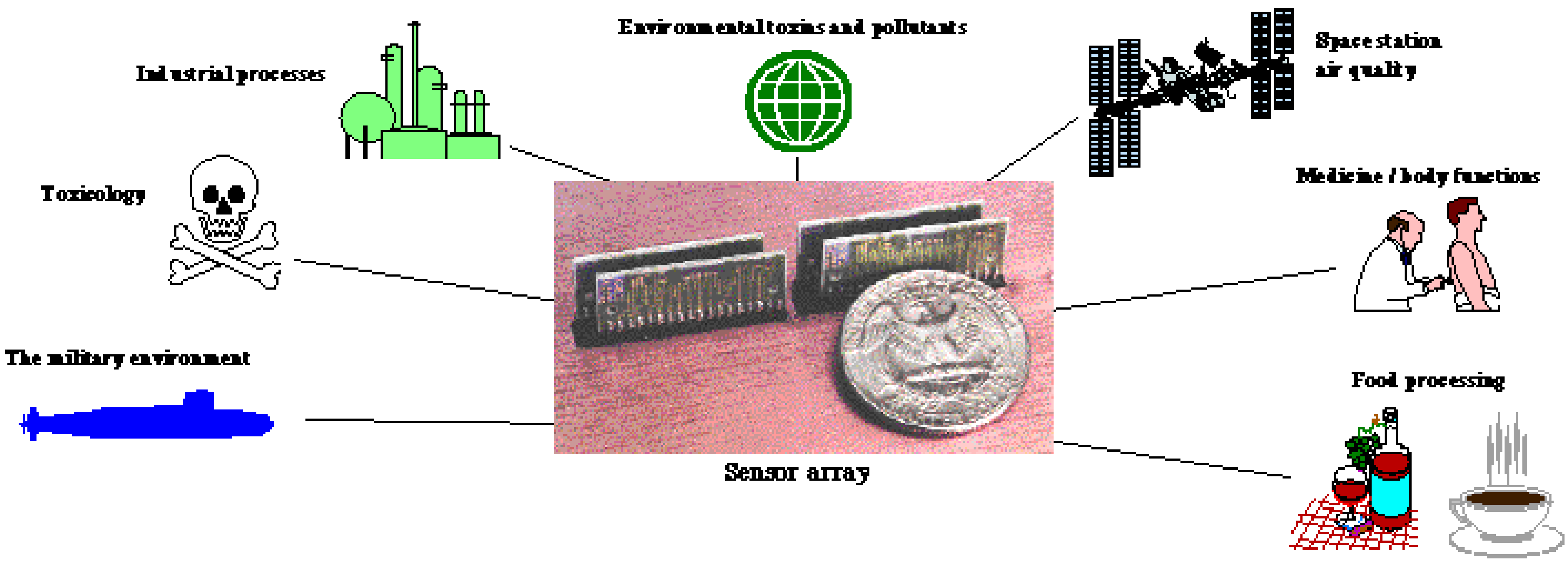
- Best for matching complex samples with subjective endpoints such as odour or flavour.
- For example, when has milk turned sour? Or, when is a batch of coffee beans optimally roasted? When is a water sample toxic?
- The array can be trained to match a set of sensor responses to a calibration set produced by the human taste panel or olfactory panel routinely used in food science.
- Although these arrays are effective for pure chemicals, conventional methods are often more practical.

Areas of application

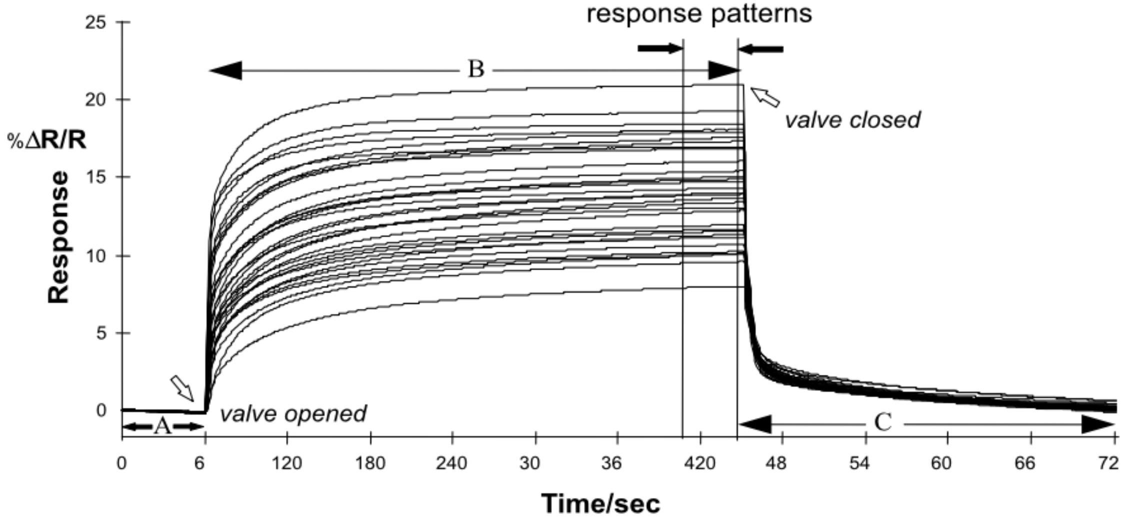
Identification of spilled chemicals. Air quality monitoring

Quality of foods and drinks. Water and wastewater analysis.

Detection and diagnosis of infections.



Data Analysis



Response Patterns

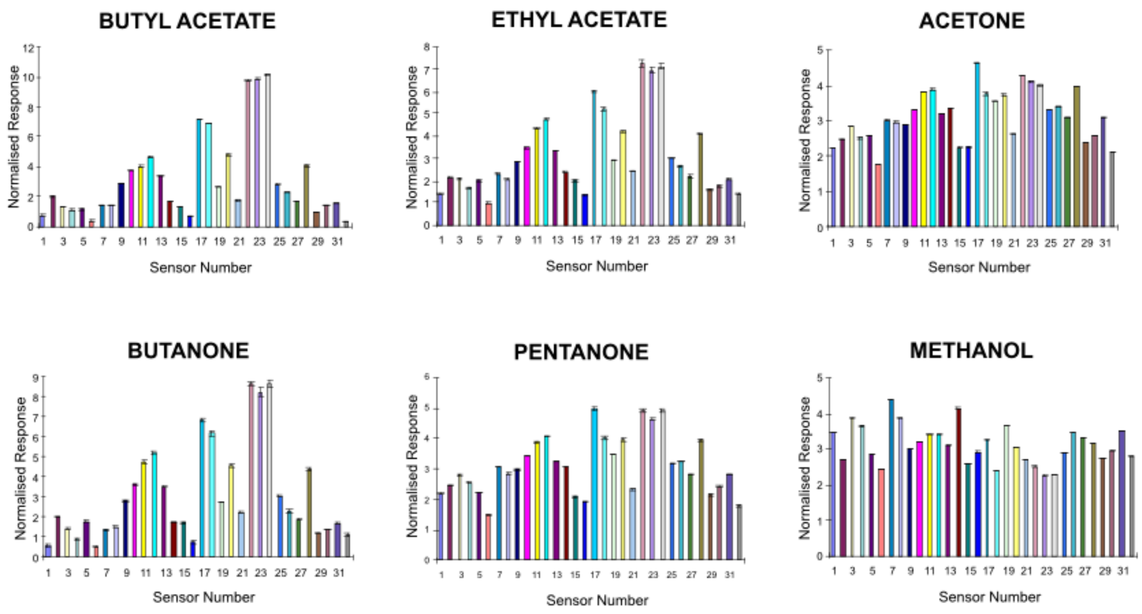


Figure 1.14

- Multivariate Analysis
  - Chemometrics Multivariate statistics
    - Linear methods
      - Multiple linear regression
      - Partial least squares
      - Principal components analysis
      - Discriminant function analysis
    - Other methods
      - Support vector machines
      - Independent component analysis
      - Cluster analysis
  - Biologicaly Inspired
    - Artificial Neural networks
      - Self organising maps
      - Multilayer perceptrons
      - Probabilistic neural networks
      - Radial basis function networks
      - Learning vector quantisation
    - Fuzzy methods
      - Fuzzy neural networks
      - Fuzzy inference systems
    - Other methods
      - Genetic algorithms
      - Wavelet neural network
      - Neuro fuzzy systems
      - Neuromorphic methods

Figure 1.13

iSOCS Short Course 2016

25-26 June, Otranto

Biosensors

Krishna Persaud

Krishna Persaud, SCEAS, The University of Manchester, UK

International Society for Olfaction and Chemical Sensing

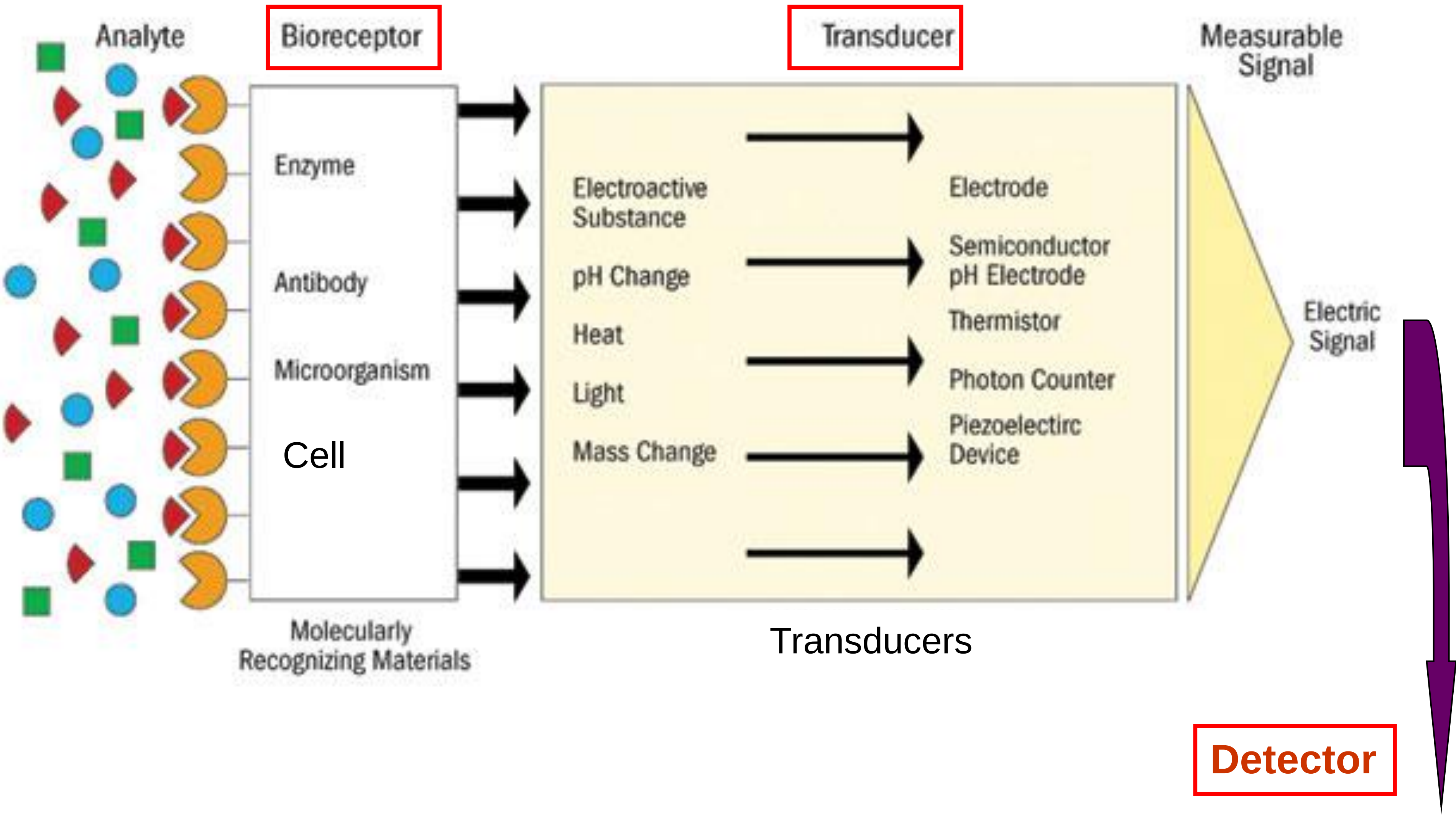
Pit Viper

Thermoreceptors

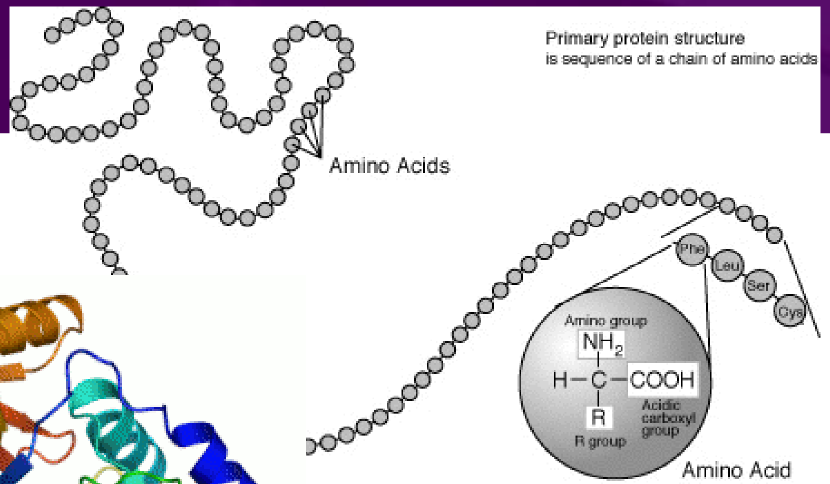
Father of the Biosensor

Professor Leland C Clark Jnr
1918–2005

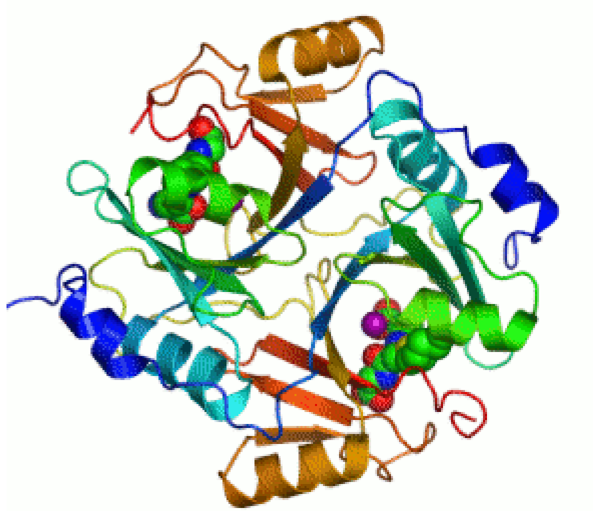
Components of a Biosensor

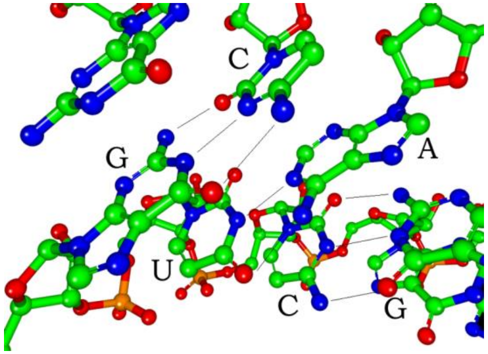


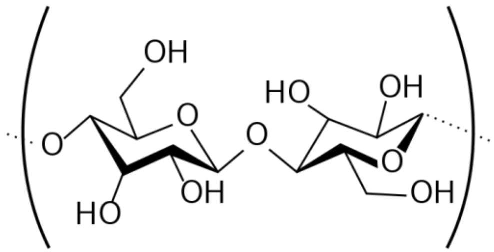
Biomolecules



- Peptides, polypeptides (chain of amino acids)
- Proteins
  - E.g. enzymes, antibodies
- Nucleic acids
  - E.g. ribonucleic acid (uracil not thymine), deoxyribonucleic acid
- Polysaccharides
  - E.g. cellulose
- Lignin (plant cells)
- …

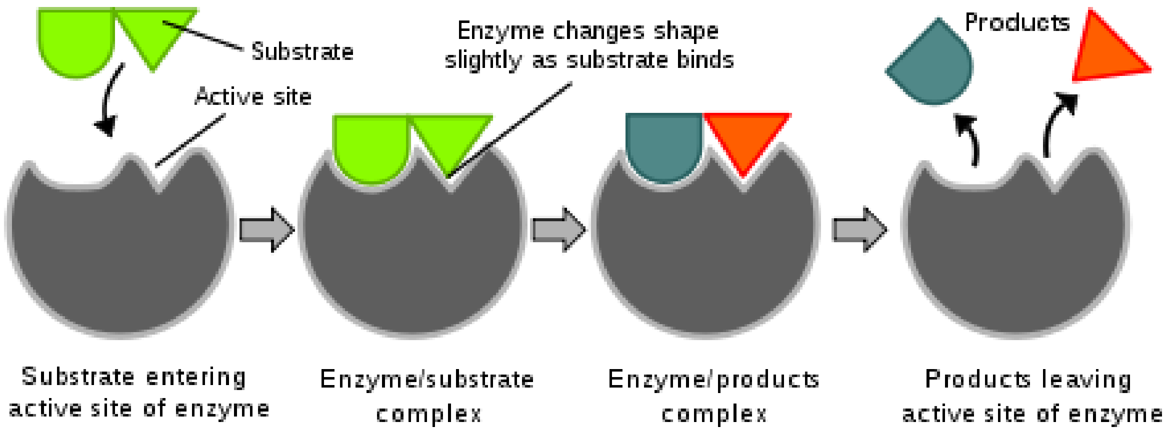


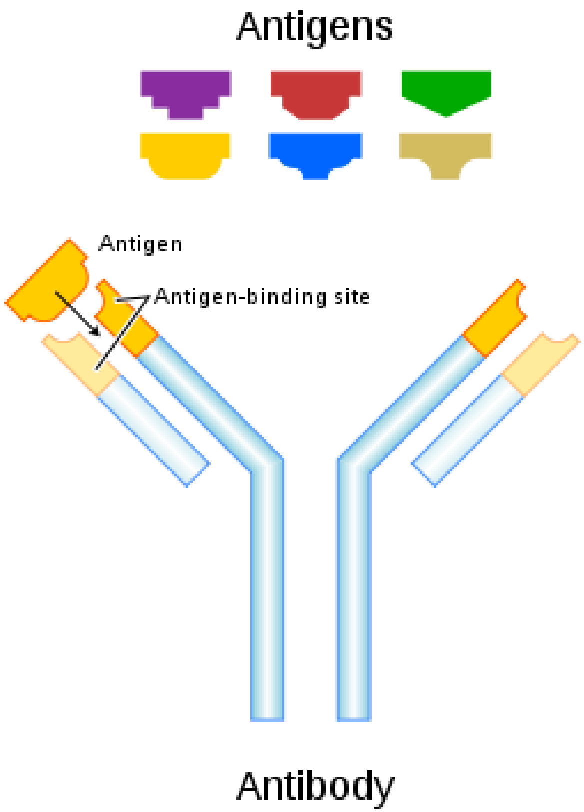




Key-Lock Mechanism – Selectivity

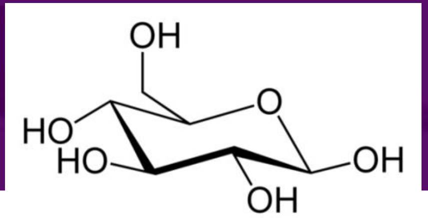
Enzyme to catalyse reaction



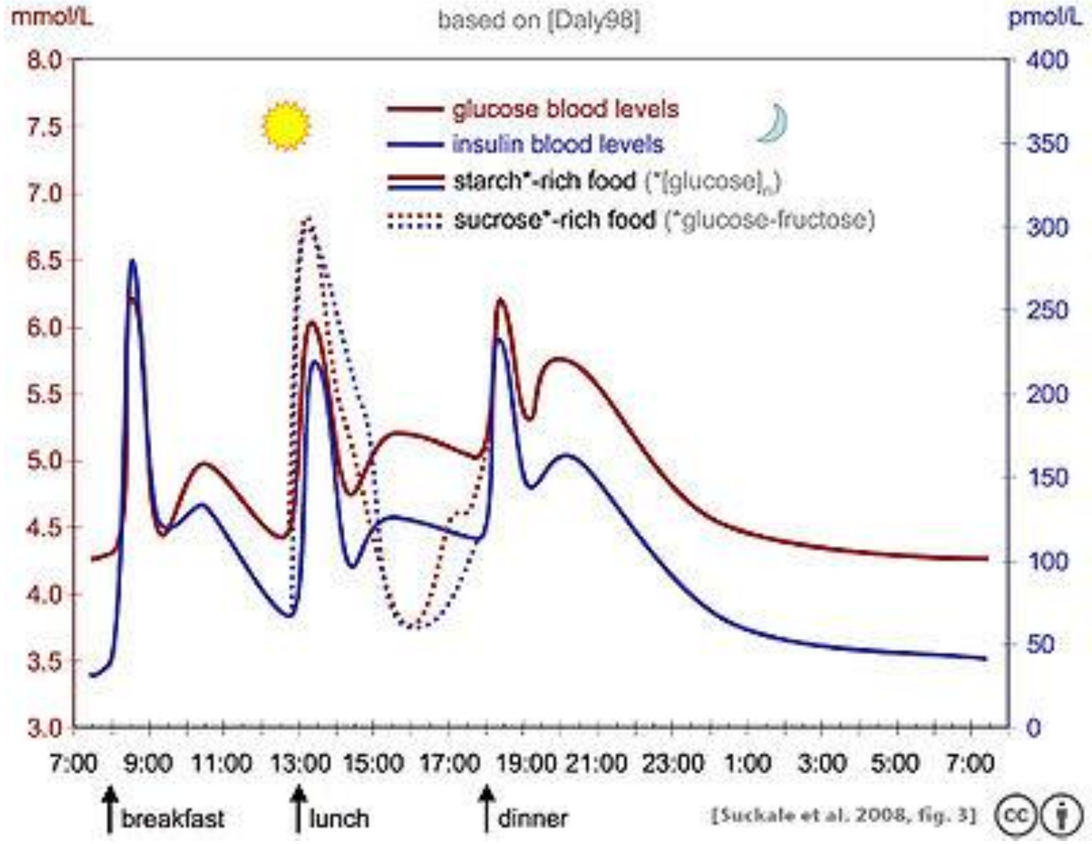


Antibody to neutralise bacteria and virus

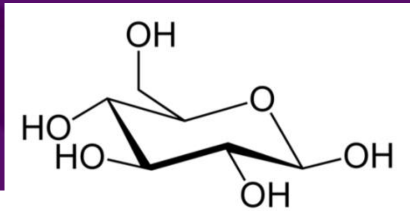
Electrochemical biosensors



- Blood glucose sensor
- Diabetes common in elderly people/obese
- Millions sold since 1993
- Disposable strips
- Sold by Abbott et al.

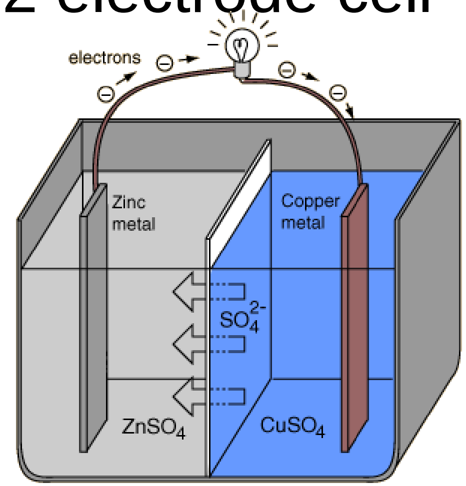


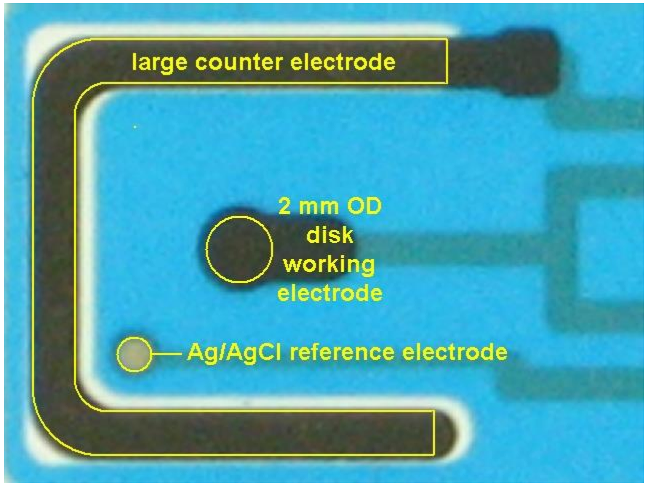
Electrochemical biosensors



- Based on electrochemistry
- Use enzymatic redox reaction
- Plastic strips with polymers and enzyme
- Millions sold since 1993
- 2 electrode cell

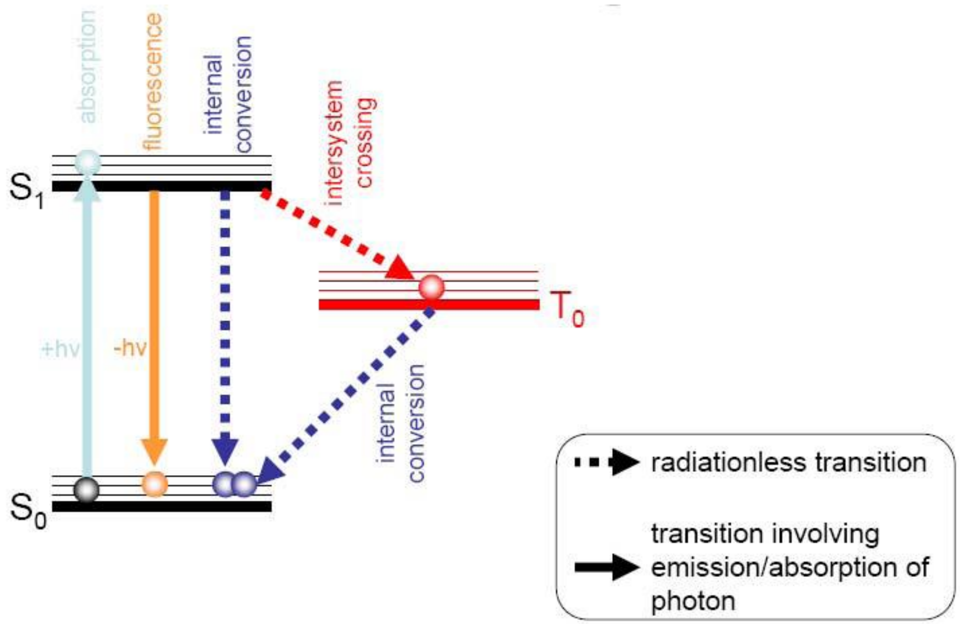
$$\text{Glucose} + O^2 \xrightarrow[\text{Oxidation}]{\text{glucose oxidase}} \text{Cuprous Oxide}$$

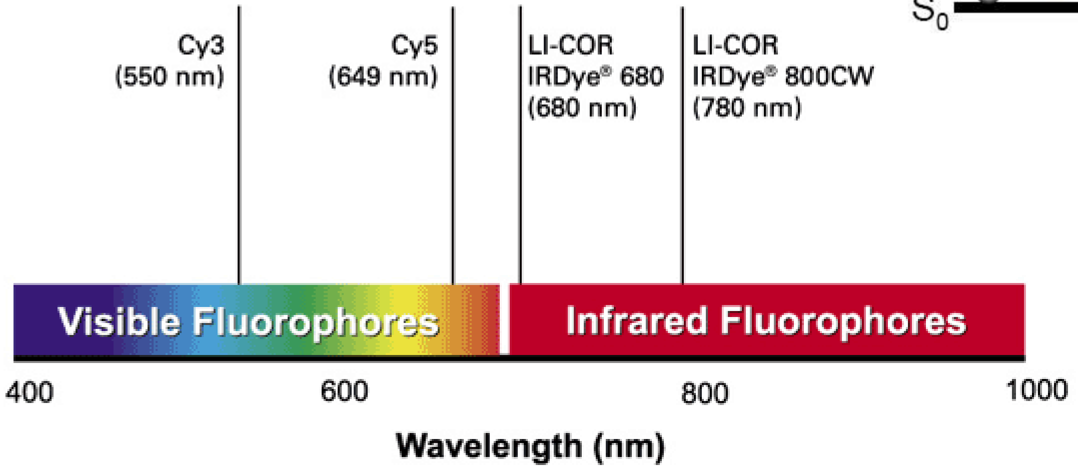




Optical biosensors – I

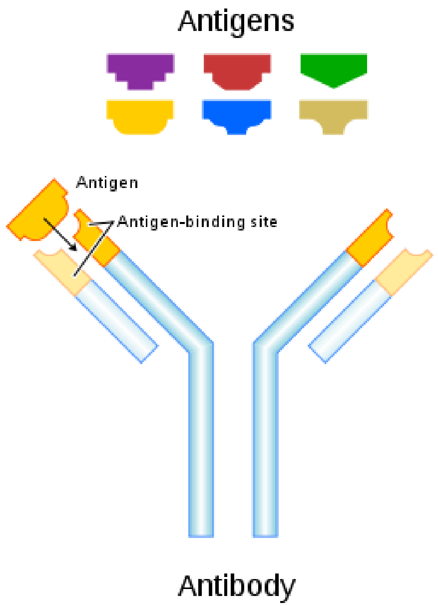
Fluorescent dyes

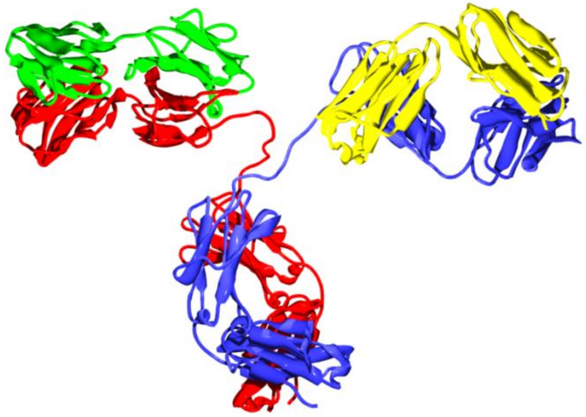




Optical biosensors – Labelled antibodies

- Inject antigen into host (chicken, duck, mouse, rat, goat, horse, sheep ..) and obtain anti-body
- Large molecule 150kDa
- Label anti-body (e.g. anti-goat) with fluorescent dye
- Used for biochemical assays
- Like ELISA

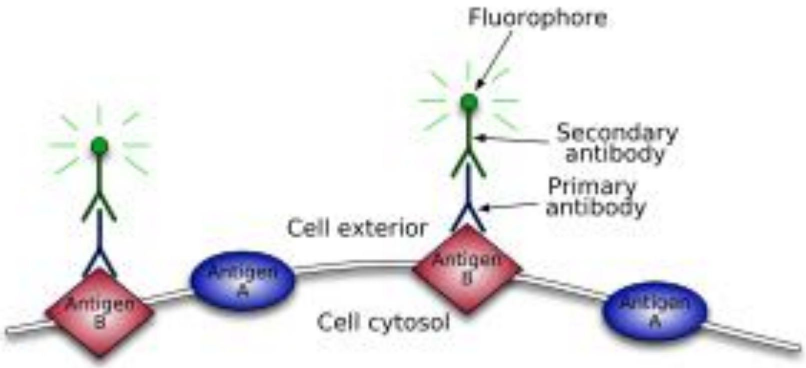


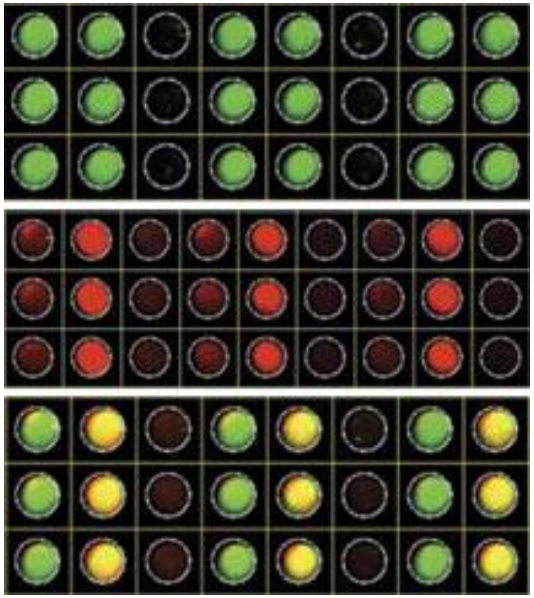


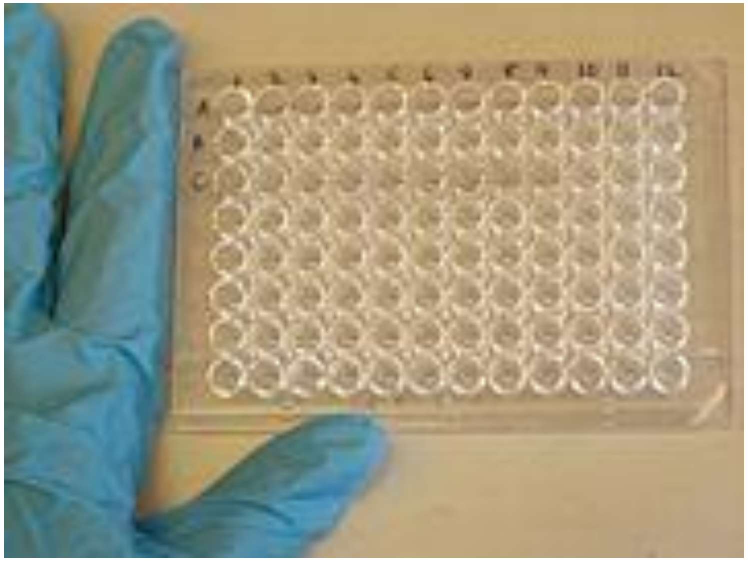
Competitive ELISA

Enzyme-linked immuno sorbent array

Many welled micro-titer plate

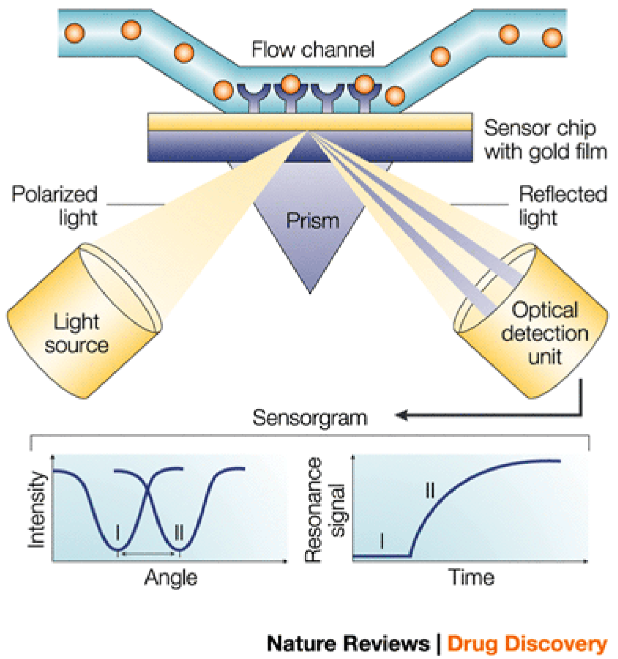


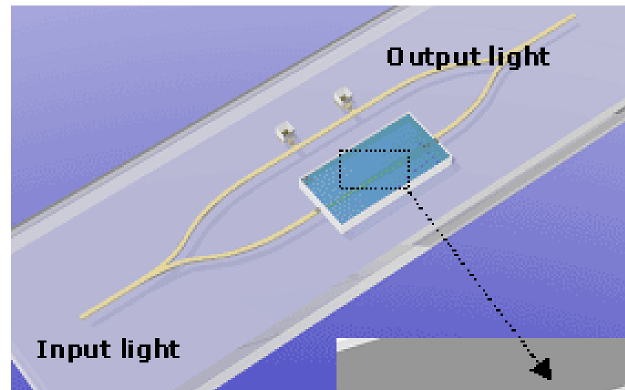




Optical biosensors

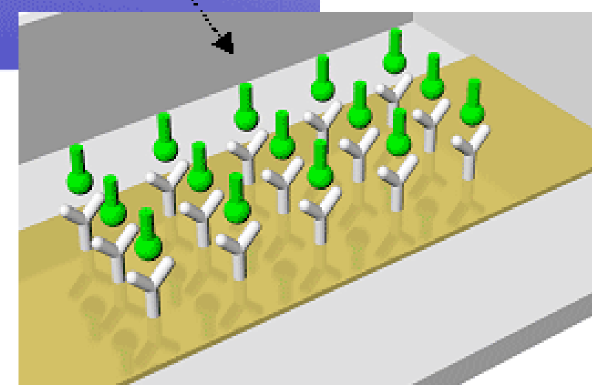
Surface plasmon resonance sensor





STC participates in a project on optical biosensors headed by Bioneer A/S with participation from several companies and research groups. STC has contributed by developing system concepts and by evaluating commercial exploitation.

The sensor is based on surface plasmons guided in metal waveguides. Refractive index changes at the coated metal surface are measured in real-time.

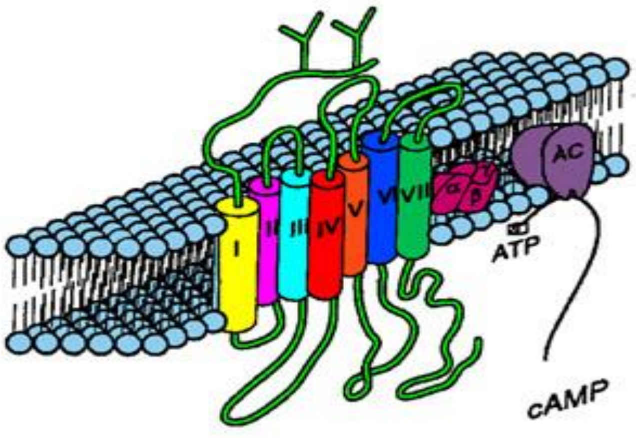


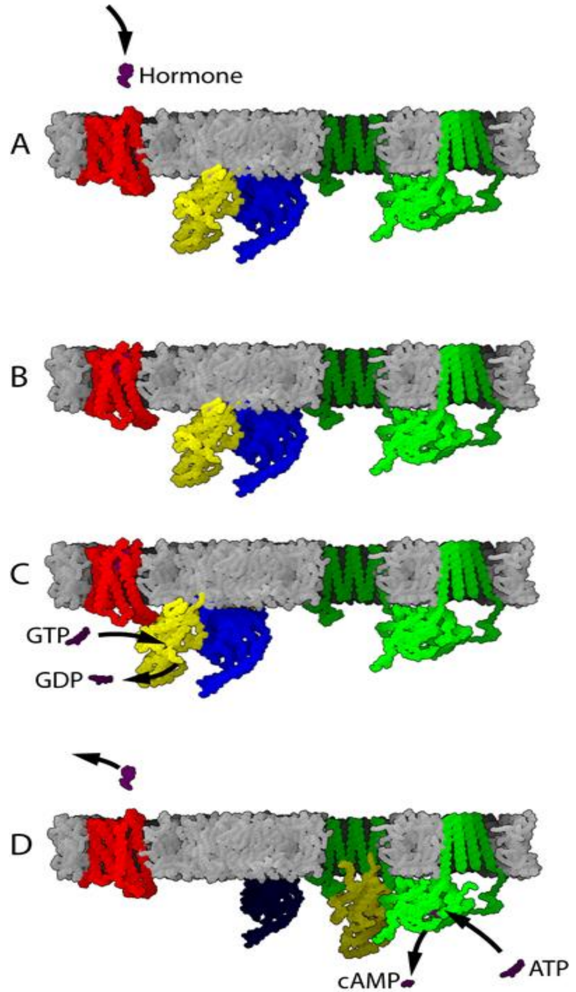
Receptors as biosensors

7TM receptor/GPCR

Target protein

Measure conformal change or cell pathway

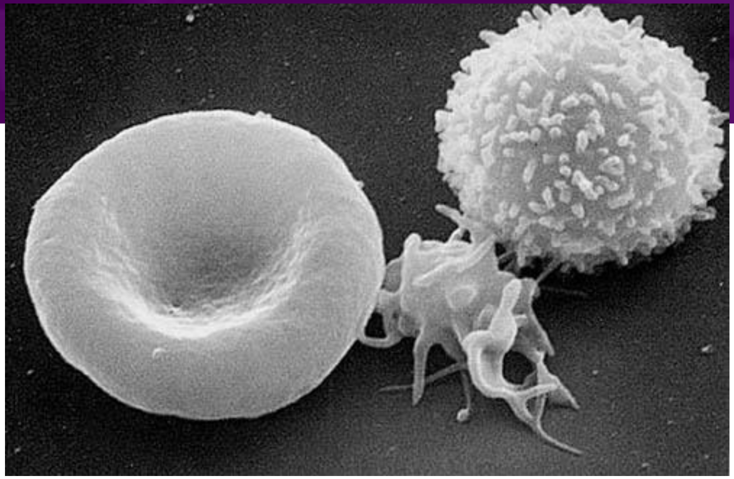




Olfactory receptor biosensor

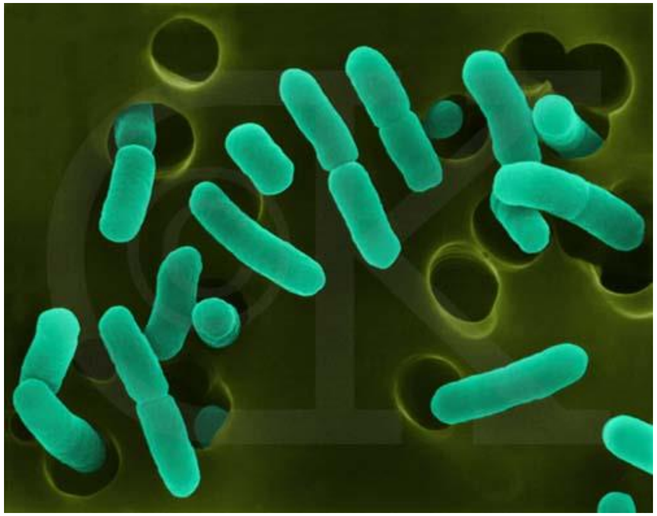
(Olfactory receptor (OR) membrane proteins coupled with carbon nanotubes)

Cell based biosensors



Cytometers for

- Red blood cells
- Platelets
- White blood cells
- Bacteria



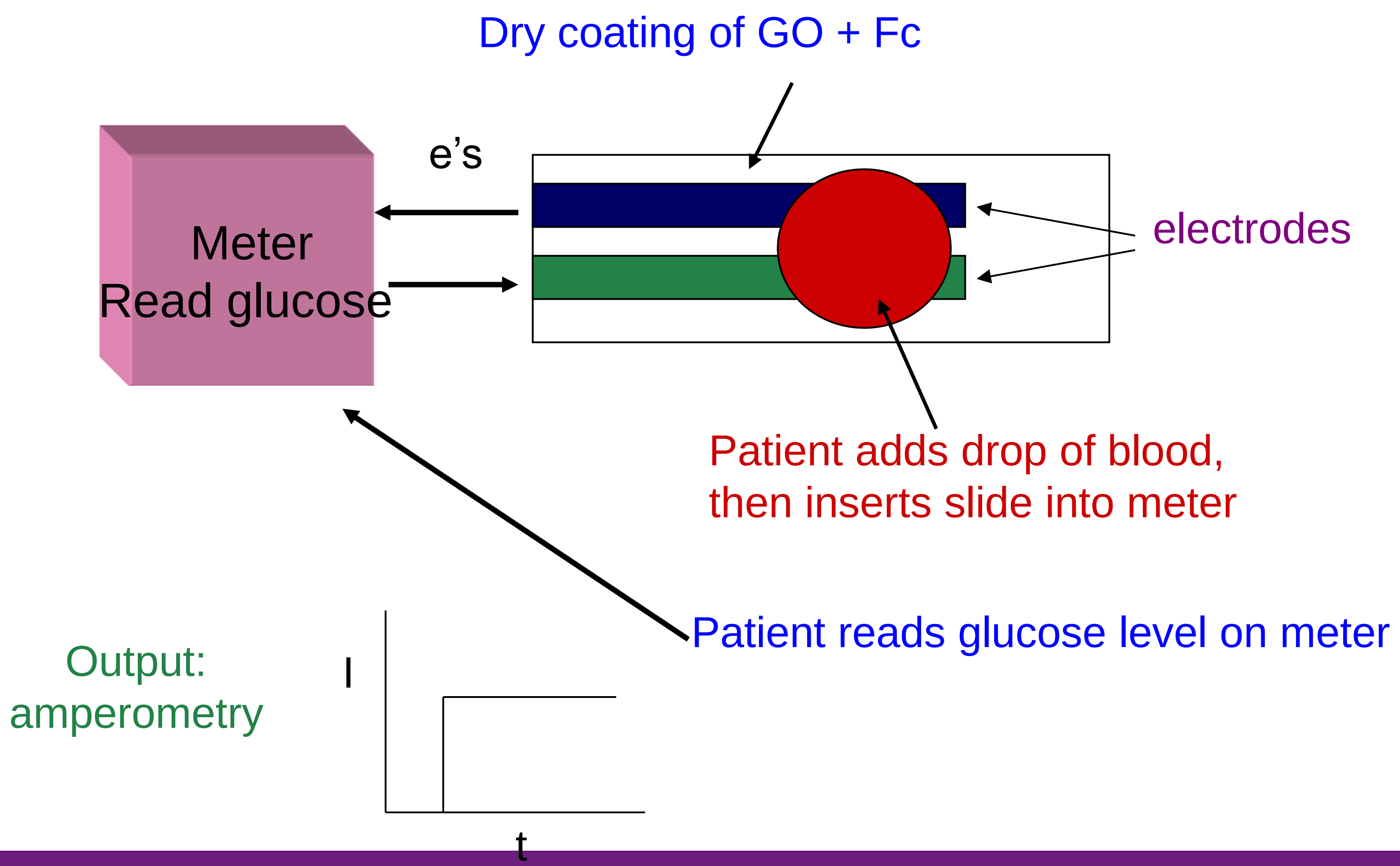
SAW resonators

Cantilever beams

…

1 ul blood = 5M erythrocytes, 500k thrombocytes, 10k leukocytes

Glucose biosensor test strips (~$0.40-0.80 ea.)



Example of biosensors

Pregnancy test

Detects the hCG protein in urine.

Glucose monitoring device (for diabetes patients)

Monitors the glucose level in the blood.

Example of biosensors

Infectious disease biosensor from RBS

Old time coal miners' biosensor

Thank You

- Chemical Sensing – many emerging technologies
- Many Applications
- Multidisciplinary
- Many Career Possibilities