Chapter 5

NON-OPTICAL-BASED SENSORS FOR ENVIRONMENTAL MONITORING

Reference textbooks*:*

- L.M.L. Nollet, *"Chromatographic Analysis of the Environment"*, Taylor & Francis, 2005
- D. Harvey, *"Modern analytical chemistry",* McGrawHill, 2000
- L.M. Moretto, K. Kalcher, *"Environmental Analysis by Electrochemical sensors and Biosensors, Vol. I",* Springer, 2015
- H. Hallil, H. Heidari, "*Smart Sensors for Environmental and Medical Applications"*, IEEE Press, 2020

5.1 GAS CHROMATOGRAPHY

Chromatography

Chromatography was firstly developed in 1903 by Mikhail Semyonovich Tswett, a Russian botanist working at the University of Warsaw, Poland. Tswett managed to separate plant pigments extracted from leaves by depositing them on top of a column packed with solid adsorbents and percolating various solvents through the column. In the process, the initially uniform band of pigment was separated into several bands of different colors. **This activity of separating colors formed the basis of the name "chromatography."**

The technique as described by Tswett was largely ignored for nearly 30 years and it was rediscovered in 1931 by Edgar Lederer. The rise of chromatography to one of the most important methods of chemical analysis started in the late thirties and early forties with the introduction of liquid – liquid chromatography by Martin and Synge, for which the researchers were awarded the Nobel Prize in 1952. In the same year, together with A.T. James, Martin introduced the technique of gas liquid chromatography.

Today, chromatographic techniques are some of the most important tools in many areas, including environmental analysis.

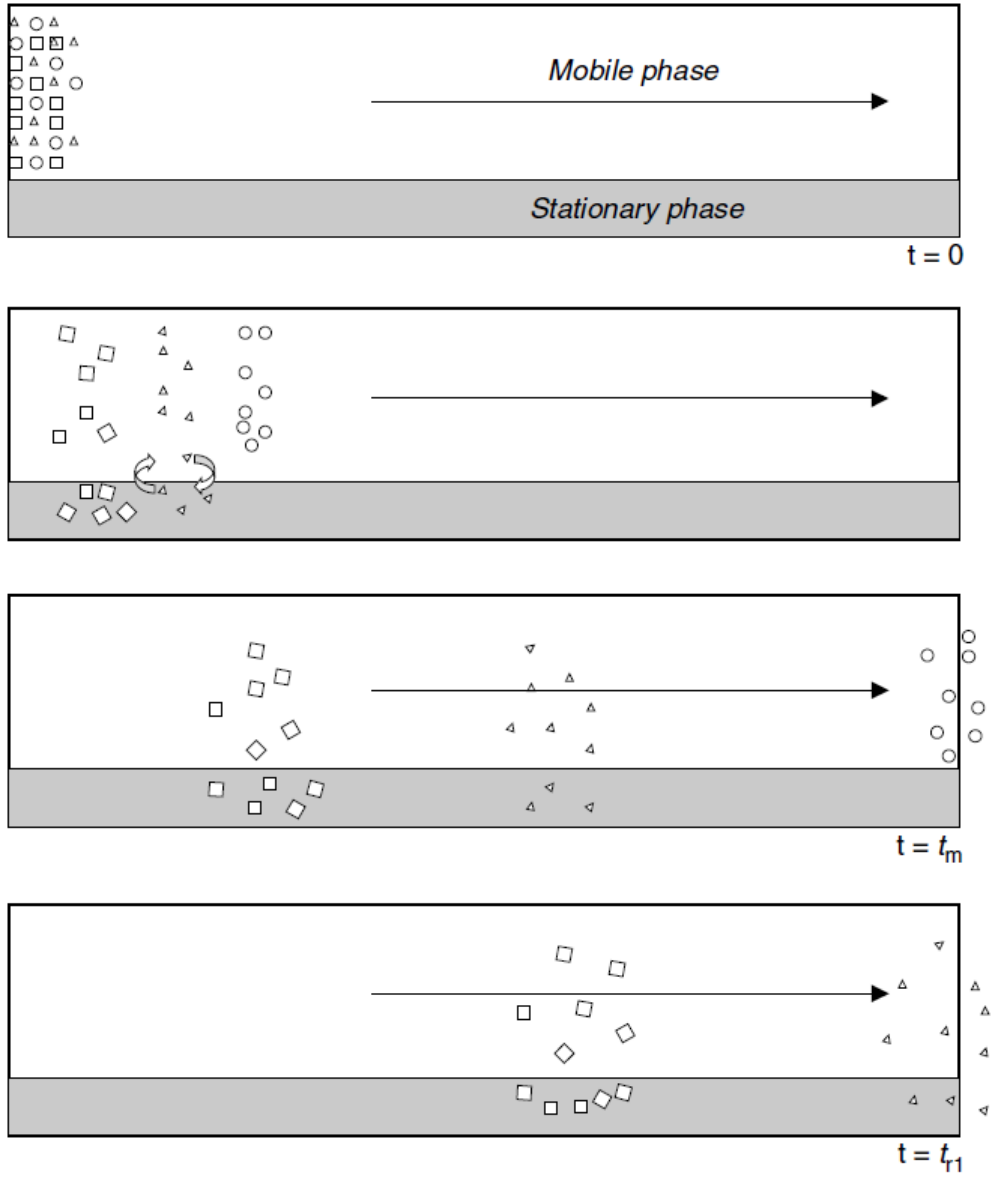
5.1 GAS CHROMATOGRAPHY

Chromatography

Chromatography is a physical method of separation, in which the components to be separated are carried by a **mobile phase** along or through a layer of a **stationary phase**.

In the process, the **components move continuously between the two phases**. Components momentarily associated with the stationary phase do not migrate, while all of the components momentarily present in the mobile phase migrate at the same speed. Thus, **the separation does not occur in either of the two phases, but it is the result of the continuous movement of molecules between them**.

The **components become separated** when one of them spends a **different length of time in the stationary phase than the rest**. The time spent in the stationary phase by any of the components depends on its affinity to the stationary phase under given conditions.



5.1 GAS CHROMATOGRAPHY

Chromatography

Chromatographic methods can be **classified according to the type of the mobile phase used** in the separation process. In essence, any type of fluid can be used as the mobile phase.

- Historically, liquids were the first to be used, giving rise to a broad range of methods classified as liquid chromatography (LC). Gases can be used as the mobile phase whenever the components to be separated have appreciable vapor pressures. Methods based on this principle are classified as **gas chromatography (GC).**

Chromatographic methods can be also classified according to the type of **interaction between the solute and the stationary phase**.

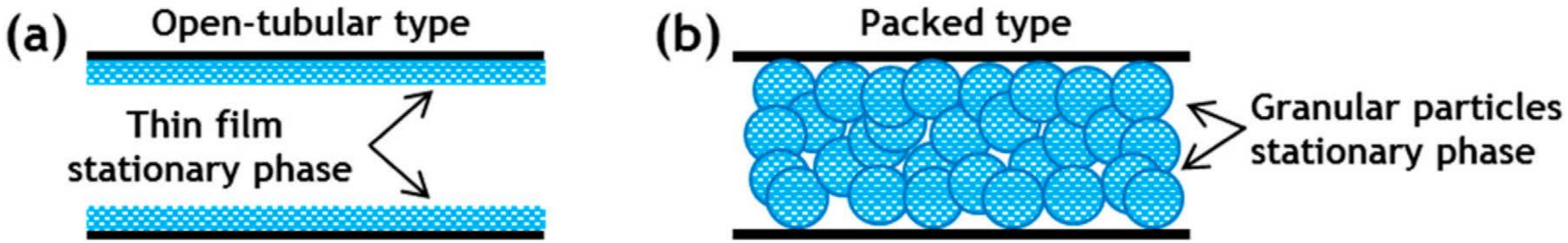
- Sorption is by far the most common interaction. Whenever the solute is confined to the surface of the stationary phase, we call the process adsorption, and the method is called **adsorption chromatography**. Whenever the solute penetrates the stationary phase and enters the bulk of it absorption occurs; however, chromatographic methods based on this principle are usually called **partition chromatography**. Ion exchange makes it possible to separate ions by liquid chromatography. Methods based on this principle are referred to as **ion chromatography.**

5.1 GAS CHROMATOGRAPHY

Chromatography

Another classification of chromatographic methods is based on the **physical form of the stationary phase used**.

- In the vast majority of chromatographic separations, the stationary phase is confined within a tube through which the mobile phase is fed. The tube is called a chromatographic column. The stationary phase in column chromatography can have the form of a compact bed of small, usually porous particles packed inside the column, or can be spread on the walls of the column. Columns of the first type are called **packed columns**, while columns of the second type are called **open tubular columns**.

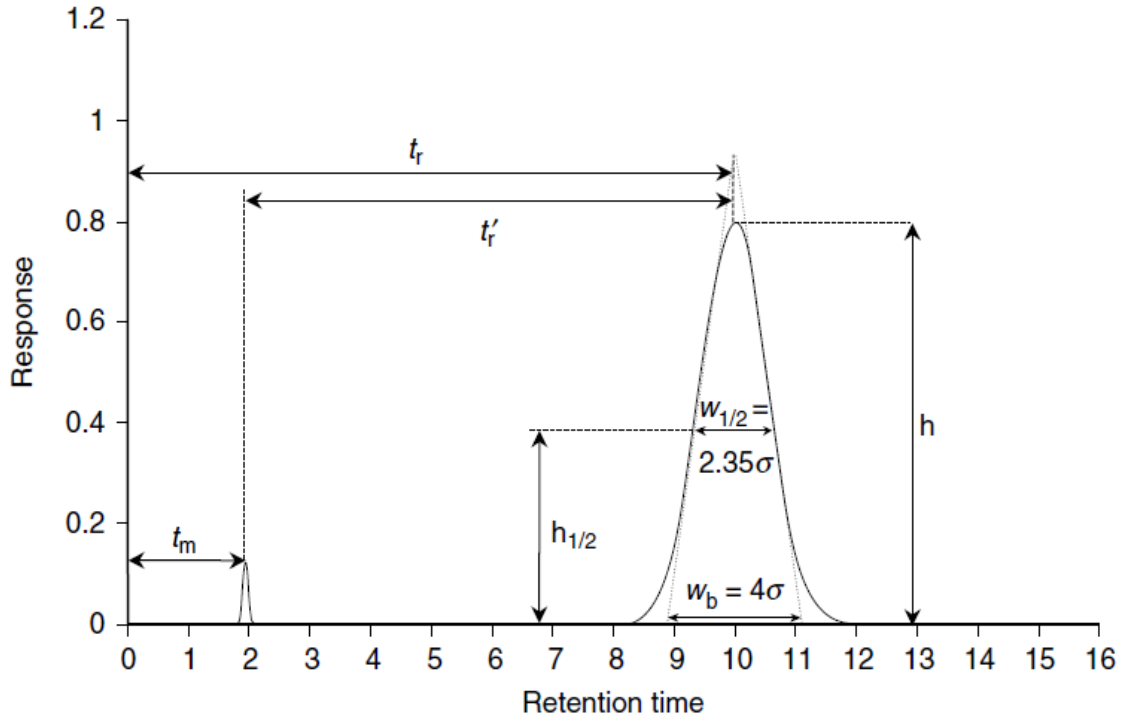


5.1 GAS CHROMATOGRAPHY

Chromatography – fundamental relationships

The result of chromatographic separation is usually presented in the form of a **chromatogram**, i.e., a plot of the concentration or mass of the sample components recorded as a function of the amount of mobile phase passed through the system.

In column chromatography, instead of measuring the amount of mobile phase, one usually **measures the time from the moment the sample was introduced to the column and plots the chromatogram as a function of time.**

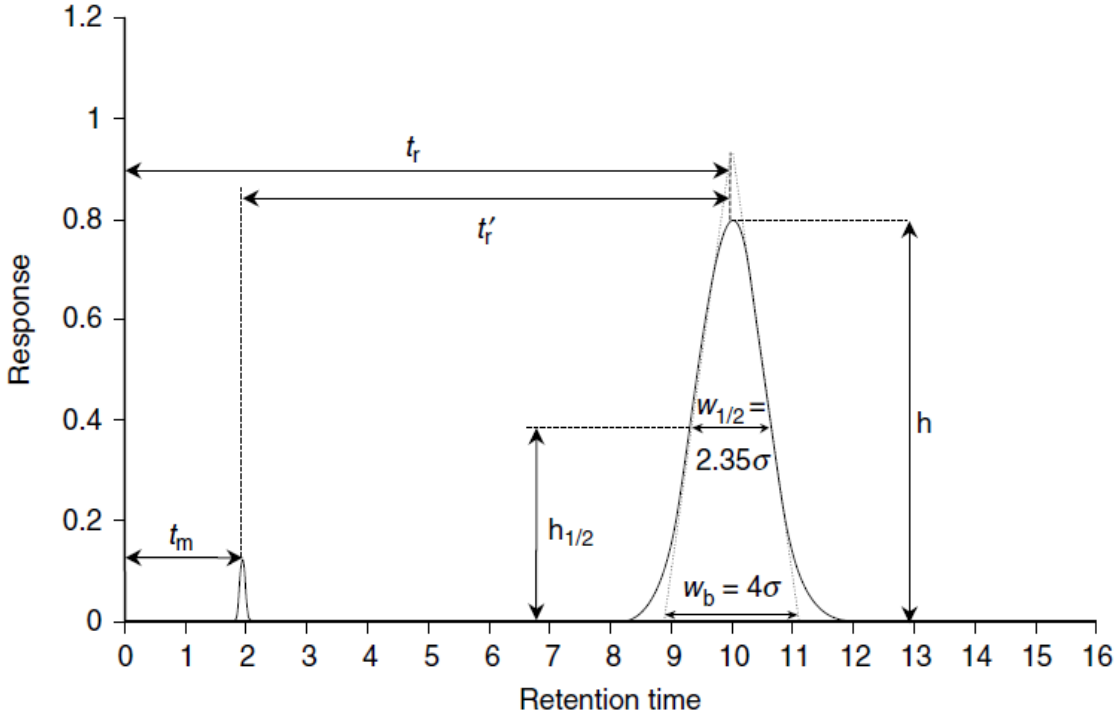


5.1 GAS CHROMATOGRAPHY

Chromatography – fundamental relationships

Solute bands elute from the column in the form of peaks, whose profiles ideally are Gaussian. An unretained solute elutes from the column in time t_m **called dead time or hold-up time**.

A solute which interacts with the stationary phase elutes from the column in time t_r **called retention time**. It is important to understand that if a retained solute molecule enters the mobile phase, it travels with it at the same speed as the unretained solute.



Consequently, each solute spends exactly the same amount of time in the mobile phase before it reaches the detector, and this time is represented by t_m . The **adjusted retention time** is given by the **difference between t_m and t_r, namely t'_r.**

5.1 GAS CHROMATOGRAPHY

Chromatography – fundamental relationships

The adjusted retention time t'_r represents the additional time required for the solute to travel the length of the column. It therefore corresponds to the time spent by the solute in the stationary phase.

The ratio of the time spent by the solute in the stationary phase to that spent in the mobile phase is called the **solute capacity factor k**:

$$k = \frac{t'_r}{t_m} = \frac{t_r - t_m}{t_m} \tag{5.1}$$

The capacity factor plays an important role in optimization of chromatographic separations, as it is related to the **partition coefficient of the solute between the mobile phase and stationary phase K**:

$$k = K \cdot \frac{V_s}{V_m} \tag{5.2}$$

where $K = C_s/C_m$; C_s is the concentration of the solute in the stationary phase, C_m is its concentration in the mobile phase, V_s is the volume of the stationary phase and V_m is the volume of the mobile phase.

5.1 GAS CHROMATOGRAPHY

Chromatography – fundamental relationships

Therefore, separation of two chromatographic peaks can be described in the first approximation by their **relative retention α**:

$$\alpha = \frac{t'_{r2}}{t'_{r1}} = \frac{K_2}{K_1} \tag{5.3}$$

Relative retention is constant for a given set of analytical conditions (stationary phase, temperature, etc.) and is independent of the column dimensions. However, it is not the best measure of peak separation, because **it takes into account only the separation of peak maxima while ignoring the fact that bands traveling along the column (or the stationary phase in general) become progressively broader**. Consequently, two bands characterized by the same relative retention may either be completely separated if they are narrow or may be effectively not separated at all if they are very broad. To account for this phenomenon, the degree of separation of two chromatographic peaks is usually described by their **resolution R_s** :

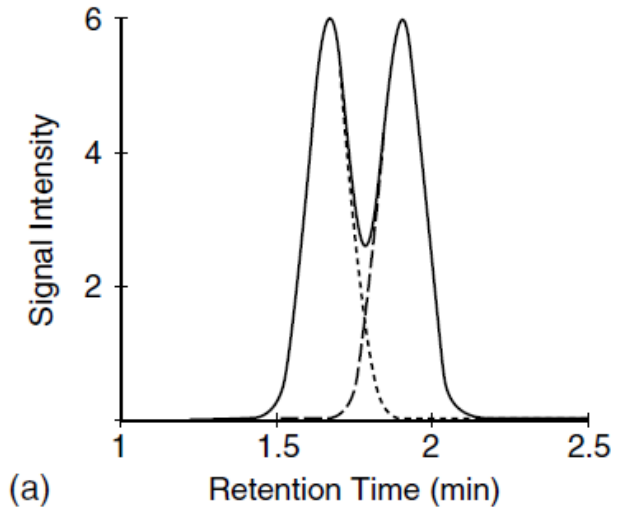
$$R_s = \frac{t_{r2} - t_{r1}}{(w_{b2} - w_{b1})/2} \tag{5.4}$$

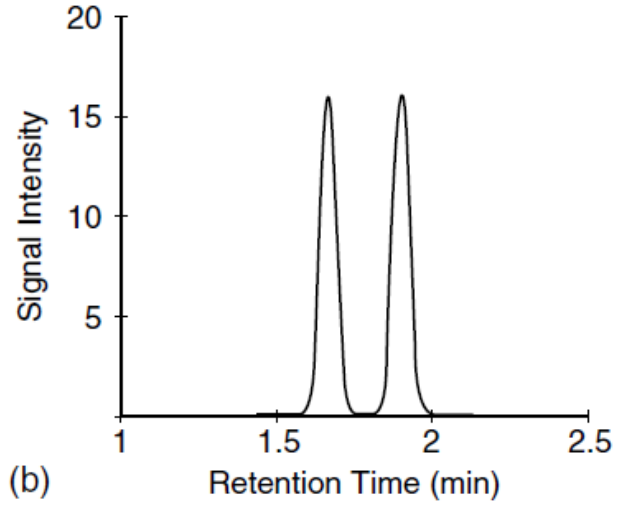
5.1 GAS CHROMATOGRAPHY

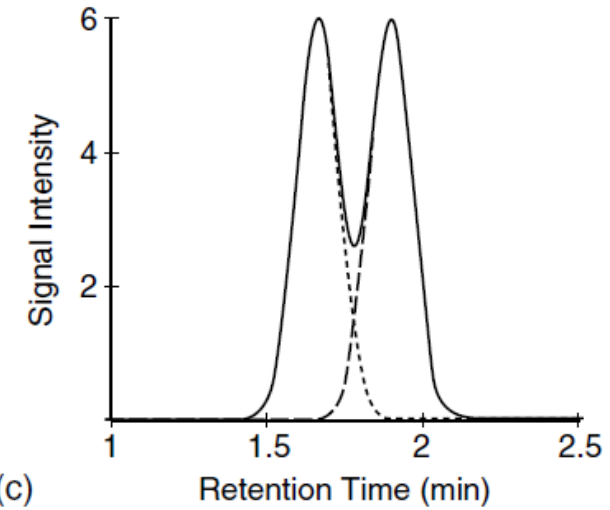
Chromatography – fundamental relationships

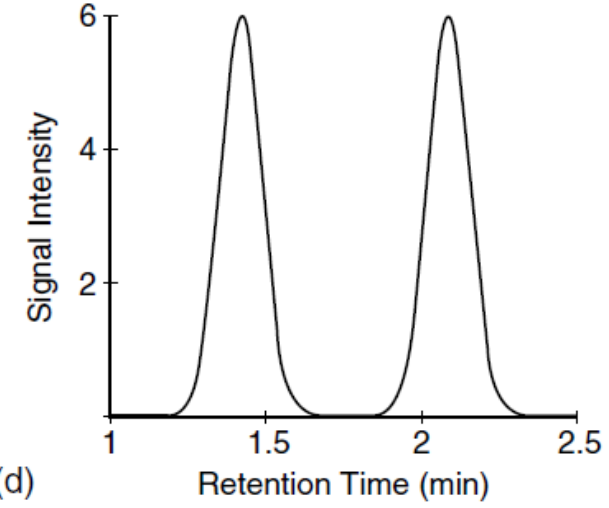
Partially separated peaks

Same relative retention
Narrower peaks









Partially separated peaks

Larger relative retention
Same peak widths

5.1 GAS CHROMATOGRAPHY

Chromatography – fundamental relationships

The width of the band eluting from the chromatographic system depends on the distance it has traveled. The proportionality factor between the two, termed "**height equivalent to theoretical plate**" (HETP), or **plate height** in short:

$$H = \frac{\sigma^2}{x} \tag{5.5}$$

Where σ^2 is the variance of the band and x is the distance traveled by the band. The smaller the plate height, the narrower the band eluting from the column. H depends on a number of parameters, the most prominent of which is the **linear flow rate of the mobile phase u** . The relationship between H and u is described by the **van Deemter equation**:

$$H = A + \frac{B}{u} + (C_s + C_m) \cdot u \tag{5.6}$$

Where A is a term representing the contribution from eddy diffusion, B is the contribution from longitudinal diffusion, and $C_s + C_m$ represent contributions from the mass transfer in the stationary and the mobile phases, respectively, to the total column plate height.

5.1 GAS CHROMATOGRAPHY

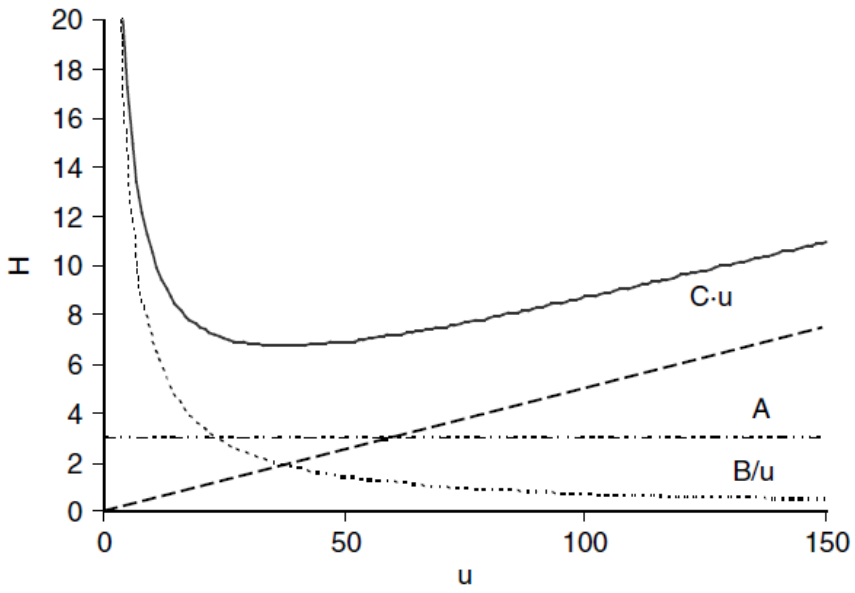
Chromatography – fundamental relationships

Eddy diffusion occurs only in packed columns due to multiple paths which exist between the packing particles. Thus, the value of term A in open tubular columns is zero. The contribution of longitudinal diffusion to plate height is important in gas chromatography, but often negligibly small in LC due to small molecular diffusion coefficients of the solutes dissolved in the liquid phase.

Since the B/u term decreases as the linear flow rate of the mobile phase increases, while the other term $C \cdot u$ increases, **there must be a minimum in the plate height**.

The linear **flow rate** at which the **minimum** occurs is considered **optimal in chromatographic separations**, as it corresponds to the least band broadening during separation.

However, when optimizing the separation, one should also take into account the separation time. Minimum plate height often occurs at relatively low mobile phase flow rates, which translates into long separation times. **In many cases, adequate resolution can be achieved at flow rates higher than optimal, resulting in faster separations.**



5.1 GAS CHROMATOGRAPHY

Chromatography – fundamental relationships

For a column of length L, the **number of theoretical plates** can be calculated by dividing the length of the column by the plate height:

$$N = \frac{L}{H} = \frac{L^2}{\sigma^2} \tag{5.7}$$

If both the length of the column and peak variance are expressed in units of time the number of theoretical plates can be easily determined from a chromatogram using the following relationships:

$$N = \frac{t_r^2}{\sigma^2} = \frac{16t_r^2}{w_b^2} \tag{5.8}$$

For two peaks eluting close together on a reasonably efficient column, N is related to resolution as:

$$R_s = \frac{\sqrt{N}}{4}\left(\frac{\alpha-1}{\alpha}\right)\left(\frac{k_2}{1+k_2}\right) \tag{5.9}$$

where k_2 is the capacity factor of the later eluting peak.

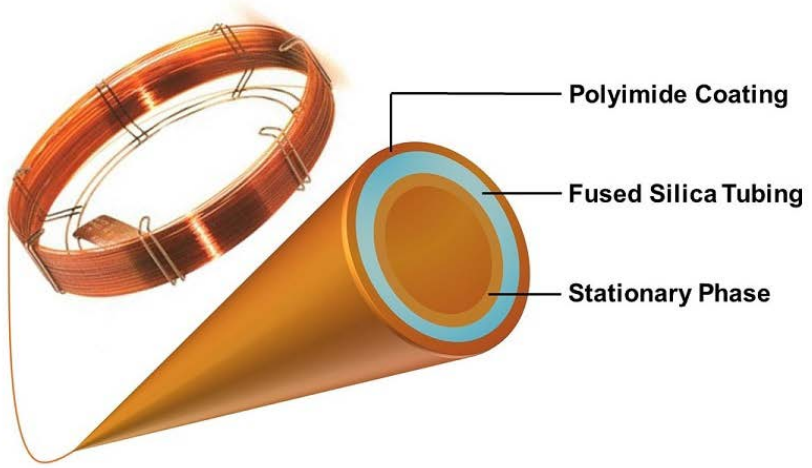
5.1 GAS CHROMATOGRAPHY

Chromatography – fundamental relationships

Equation 5.9 indicates that **to double the resolution** between two peaks, **the number of theoretical plates has to be quadrupled**.

This could be accomplished for example by using a **four times longer column**; however, that would result in a concomitant **increase in the separation time** and pressure required to drive the mobile phase.

Thus, increasing the length of the column is not a very efficient way of improving the resolution. Much **better results can be achieved by changing the relative retention of the two peaks** α.



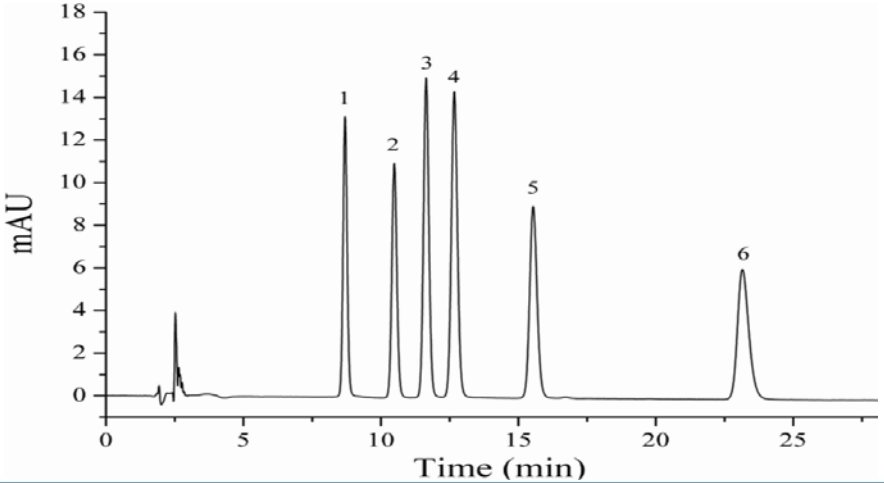
5.1 GAS CHROMATOGRAPHY

Gas chromatography

GC is one of the most widely used **separation tool in environmental analysis**.

For a sample to be suitable for gas chromatographic separation, its components should be **thermally stable** and have appreciable **vapor pressures in the temperature range typical for GC**, typically up to 320°C.

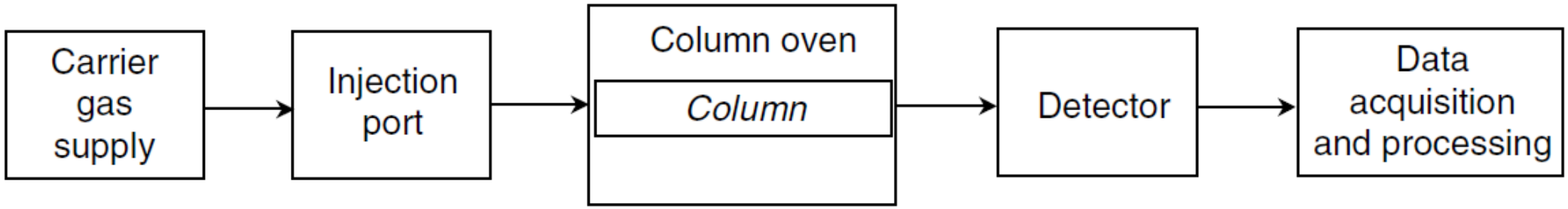
A **molecular weight of about 1000 is considered the practical limit** of gas chromatography. According to various estimates, this means only about 10% of all organic compounds known are amenable to gas chromatography. However, considering that a large number of environmentally relevant chemicals fall within this range, this is not a significant limitation.



5.1 GAS CHROMATOGRAPHY

Gas chromatography

The main components of a GC instrument include **injector**, **chromatographic column**, **column oven**, **detector** and **data acquisition system**.



Separations in GC are achieved through analyte distribution between the **gaseous mobile phase and the stationary phase**.

Most of GC separations are carried out using **liquid stationary phases**, into which the sample components can partition via **absorption** (gas-liquid chromatography, GLC). In certain applications (e.g., analysis of light hydrocarbons or permanent gases) better results can be achieved with solid stationary phases, which interact with the analytes via **adsorption** (gas-solid chromatography, GSC).

5.1 GAS CHROMATOGRAPHY

Gas chromatography - column

Historically, GC was first performed using **packed columns.** These columns consisted of tubes with 1 to 5 m length and internal diameter of few millimeters, packed with small particles coated with nonvolatile liquid stationary phases.

- Packed columns were characterized by **poor efficiencies** related to multiple flow paths among the packing particles (“*A*” term in the van Deemter equation), as well as uneven distribution of the liquid phase within the particles and at the contact points between the particles. The **number of theoretical plates in packed columns was ~1000 at the most.**

Today, packed columns are replaced by **open tubular columns** containing no packing particles, usually called **capillary columns**.

- Open tubular columns are characterized by **superior efficiencies compared to packed columns**. Their efficiencies are governed solely by longitudinal diffusion and resistance to mass transfer (the *B* and *C* terms in the van Deemter equation). The number of theoretical plates depends on the column diameter and the stationary phase film thickness, but a **capillary column** can easily reach **100,000 theoretical plates**.

5.1 GAS CHROMATOGRAPHY

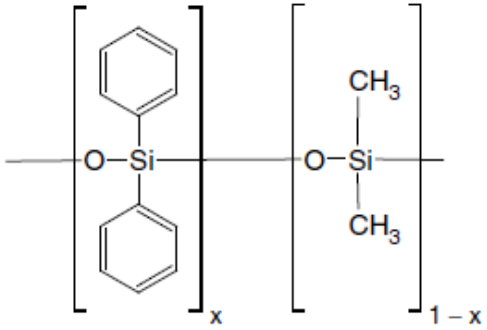
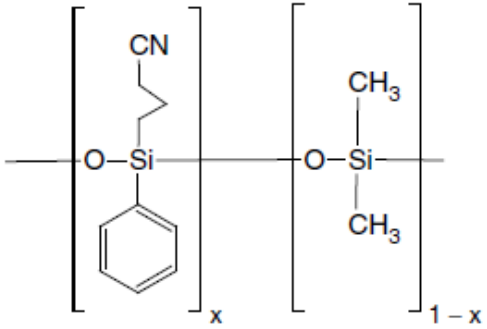
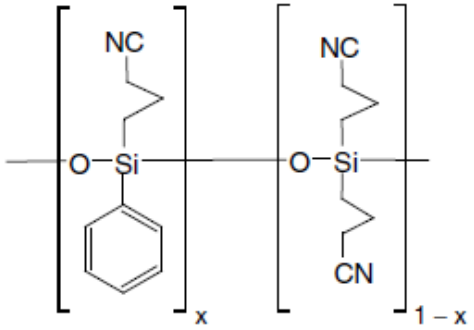
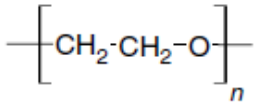
Gas chromatography - column

In the most popular type of open tubular column in use today, the stationary phase has the form of a thin film of a viscous liquid coated on the walls of the capillary tube. Such columns are called **wall-coated open tubular, or WCOT, and the separation is achieved through gas – liquid chromatography.** Because of the superior efficiency of capillary columns, the selection of stationary phases does not have to be as extensive as for packed columns. In fact, most separations can be accomplished using just a handful of stationary phases.

Capillary columns usually have diameters ranging from 0.1 to 0.53 mm and length between 10 and 60 m. In general, columns with **smaller diameters** are characterized by **better efficiencies** (larger number of theoretical plates).

However, very **narrow bore columns** (0.1 mm and below) **require high pressures** to operate, and the **amount of a sample** which can be introduced to such columns without the risk of stationary phase overloading **is very limited**. Columns with diameters greater than 0.53 mm are characterized by efficiencies similar to those of packed columns, therefore they offer no real advantages and are seldom used.

5.1 GAS CHROMATOGRAPHY

Structure	Polarity	Temperature Range (°C)	Trade Names (Examples)
	$x = 0$ Nonpolar	−60 to 360	DB-1, Rtx-1, SPB-1
	$x = 0.05$ Nonpolar	−60 to 360	DB-5, Rtx-5, SPB-5
	$x = 0.35$ Intermediate	−20 to 340	DB-35, Rtx-35, SPB-35
	$x = 0.50$ Intermediate	0 to 340	DB-17, Rtx-50, SPB-50
	$x = 0.65$ Intermediate	50 to 340	Rtx-65
	$x = 0.06$ Intermediate	−20 to 280	DB-1301, Rtx-1301, SPB-1301, DB-624, Rtx-624
	$x = 0.14$ Intermediate	−20 to 280	DB-1701, Rtx-1701, SPB-1701
	$x = 0.1$ Polar	0 to 275	Rtx-2330, SP-2330, SP-2560, BPX-70
	$x = 0$ Polar	0 to 275	Rt-2340, SP-2340
	Polar	40 to 260	Carbowax, Stabilwax, Supelcowax, DB-Wax

5.1 GAS CHROMATOGRAPHY

Gas chromatography - oven

Column ovens in typical laboratory gas chromatographs are forced circulation air thermostats, capable of maintaining constant temperature (within ± 0.1°C). The **geometry of column ovens is such that the temperature distribution inside the oven is as uniform as possible**. Most analyses in GC are performed under temperature-programmed conditions, the ovens must have the capabilities to raise the temperature at a controlled rate.

Typical GC ovens can be operated at temperatures between 350 and 400°C. Higher temperatures are not usually required as very few columns could withstand them. The heating rates of typical GC ovens can range from a fraction of a degree per minute to as much as 50°C/min with high-power heating elements.

Field portable GC instruments most often do not have the capability of temperature programming because of the limited amount of power available. In such instruments the separation is typically carried out under isothermal conditions, which vastly simplifies the design of the instrument. **Column assemblies in such systems are usually attached directly to heating blocks**, the thermal mass and conductivity of which assure uniform temperature distribution in the column.

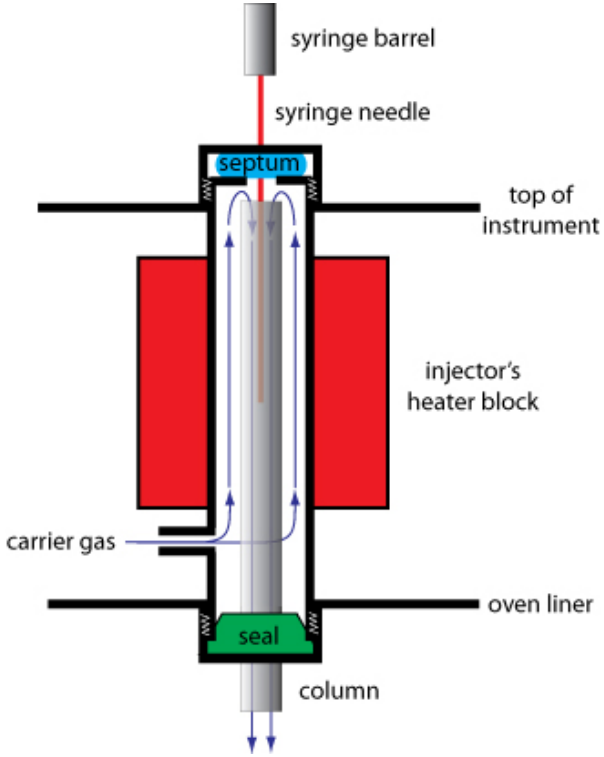
5.1 GAS CHROMATOGRAPHY

Gas chromatography - injectors

Samples analyzed by GC are typically liquid or gaseous. Thus, a **GC inlet (injector) must be able to volatilize the sample components and mix them with the carrier gas** before the GC analysis can commence.

The task is relatively easy to accomplish when using **packed columns** because of the **high carrier gas flow rates** used in this technique, and the injector has the form of a **heated tube equipped with a septum on one end and connected to the column on the other end**. The solvent and the sample components quickly evaporate at the elevated temperature of the injector and are swept rapidly into the column by the carrier gas flowing at a high flow rate.

Sample injection into an **open tubular column** cannot be performed in the same way because of the much **lower carrier gas flow rates and limited sample capacity** of such columns.



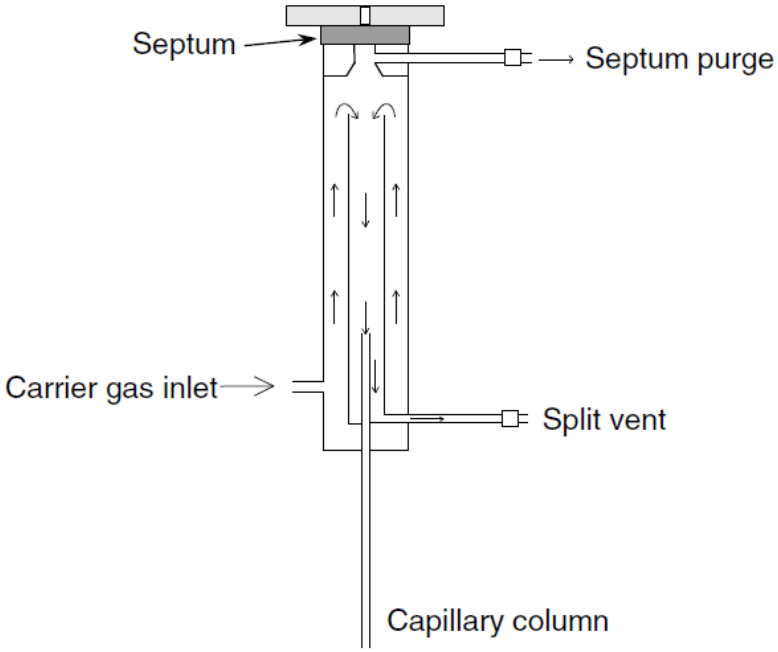
5.1 GAS CHROMATOGRAPHY

Gas chromatography - injectors

For open tubular column, the first employed approach was based on **split injection**. In this injector, the carrier **gas is split at a controlled ratio between the column and the split vent**. The flow rate through the liner is high enough to quickly transfer sample vapors from the injector to the column.

However, only a **small fraction of the sample is introduced to the column**, which adversely affects the sensitivity of the method. Consequently, **split injection is rarely used in environmental analysis**, where ultimate sensitivity is often required.

The goal can be achieved by using the same injector in the **splitless mode**. In this case, the injection is carried out with the split vent closed. The sample evaporates, and the vapors are transferred slowly to the column by the carrier gas. The use of a suitable initial column temperature ensures **condensation and re-concentration of the sample takes place in the column**.



5.1 GAS CHROMATOGRAPHY

Gas chromatography - injectors

Two re-concentration mechanisms can be distinguished:

- **Cold trapping**. Re-concentration of **high boiling components** takes place by a cold trapping mechanism. In the first centimeters of the column there is a **negative temperature gradient**, where the temperature drops from the injection temperature (± 250°C) to the oven temperature (e.g. 40°C). Due to this temperature drop the **mobility of the heavy components reduces to virtually zero**. The components remain in a small band and will only start to migrate when the oven temperature has risen sufficiently during a temperature program. Optimal re-concentration takes place if the initial oven temperature is about 150°C or more, below the boiling point of the components.

- **Solvent effect**. Re-concentration of **low boiling components** takes place by the so-called solvent effect. When the starting temperature of the column is about 20°C below the boiling point of the chosen solvent, then the **lighter components will condense in the column together with the solvent**. The liquid film formed will start to evaporate from the back and the **sample components will concentrate in a continuously shortening liquid film**. This results in a very small band of re-concentrated sample components.

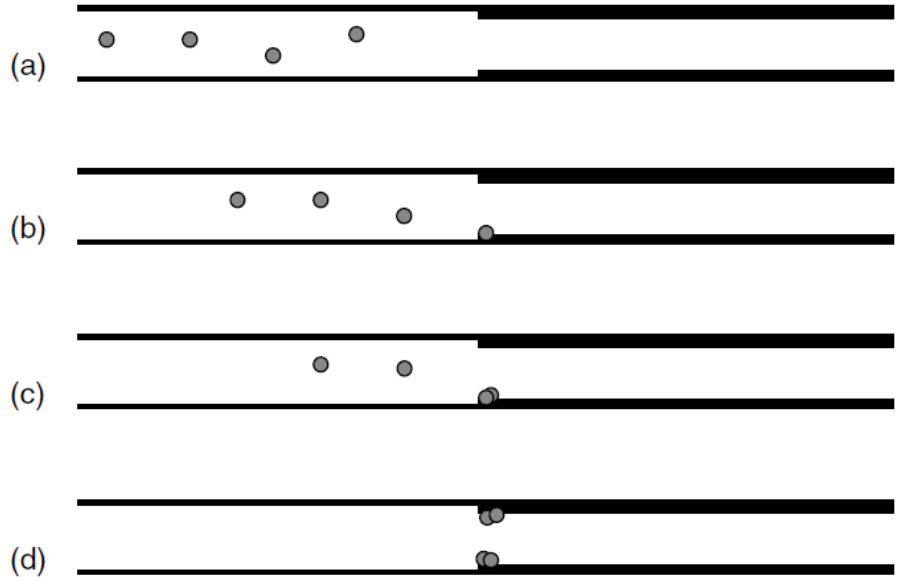
5.1 GAS CHROMATOGRAPHY

Gas chromatography - injectors

The two main re-concentration mechanisms are **cold trapping,** for re-concentration of **high boiling components**, and **solvent effect** for re-concentration of **low boiling components.**

However, when the sample is injected into a open tubular column it undergoes the so-called **retention gap effect.** When solute molecules encounter the stationary phase of the column, their migration rate decreases significantly. This allows solute molecules from the tail end of the band to catch up with its front, narrowing the band considerably.

- When injected, non-retained molecules travel as a broad band.
- Then, the front of the band encounters the stationary phase in the column and partitions into it.
- Consequently, molecules from the tail end of the band catch up with the molecules in the stationary phase.
- As a final result, the initially broad band is focused into a narrow band.



5.1 GAS CHROMATOGRAPHY

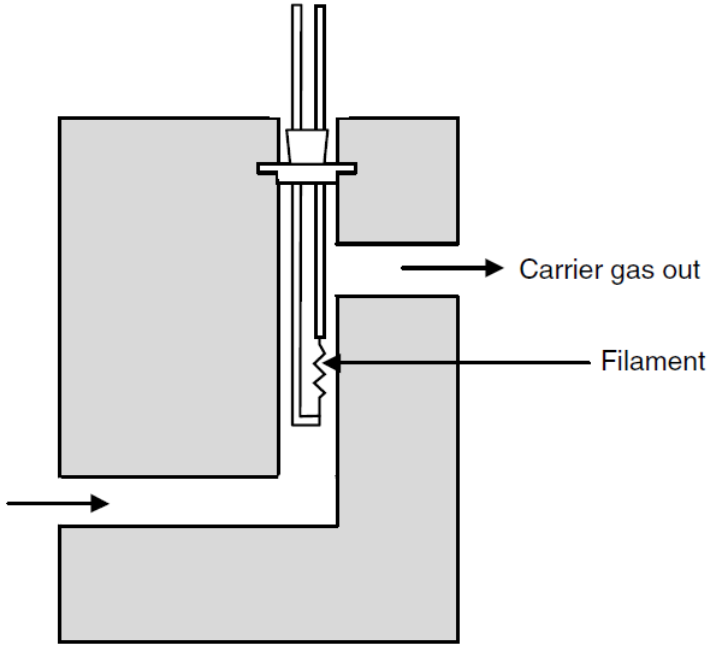
Gas chromatography - detectors

Several detectors have been employed in GC apparatuses.

Historically, one of the first detectors used in GC was the **thermal conductivity detector (TCD)**. TCD measures the **difference in thermal conductivities** between pure carrier gas and carrier gas containing sample components, therefore **its response is universal and nonselective**.

A **typical TCD contains two heated filaments** placed in a thermostated cavity. One filament is swept by the carrier gas from the chromatographic column, while the other is swept by pure carrier gas delivered under identical conditions through a reference column.

Components of the sample eluting from the GC column change the thermal conductivity of the gas in the sensing arm, which causes a change in the temperature of the sensing filament. This, in turn, alters the resistance of the sensing filament compared to the reference filament, and this change is recorded as the detector signal.



The nonselectivity of the TCD and its poor sensitivity limit its applications to permanent gases, light hydrocarbons and other compounds which respond poorly to other detectors.

5.1 GAS CHROMATOGRAPHY

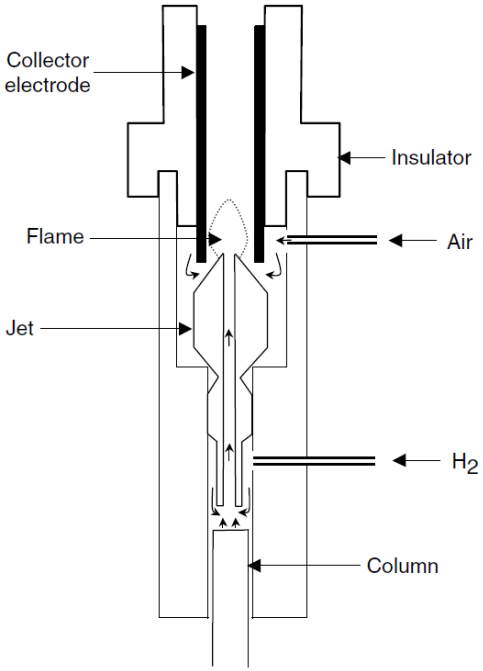
Gas chromatography - detectors

Nowadays, one of the most popular detector in GC is the **flame ionization detector (FID).**

In the FID, the effluent from the column is introduced to a hydrogen – air flame, where the organic **analytes undergo combustion and generate ions**. A collector electrode is placed above the flame jet, and a potential difference of several hundred volts is applied between them. **The ions and electrons generated during the combustion process give rise to a small electric current** between the collector electrode and the jet.

The response of the FID is generally proportional to the **number of carbon atoms delivered to the detector** in unit time. Therefore, the response factors for many different compounds are similar when using this detector.

The universal response of the FID to organic compounds limits its usefulness in environmental analysis, especially when trace analytes have to be detected in complex matrices.



5.1 GAS CHROMATOGRAPHY

Gas chromatography - detectors

Alternatives to FID with similar designs, are the **thermionic ionization detector** (TID) and the **photoionization detector** (PID).

- In **TID**, an electrically heated glass or ceramic bead containing rubidium salts is placed a few millimeters above the flame jet. Hydrogen and air supplied to the detector create plasma next to the bead's surface. The bead is kept at a negative potential to suppress the FID signal. Under such conditions, **nitrogen- and phosphorus-containing compounds undergo selective ionization** in the bead region. TID is very sensitive and has a relatively broad linear range of four- to five- orders of magnitude. **It is commonly used in environmental analysis for the determination of N- and P-containing pesticides.**

- In **PID**, analytes are **ionized after absorbing a photon of light of high energy**. The ionization energy for organic compounds usually ranges from 5 to 20 eV, in the UV range. **PID is nondestructive**, which means that the sample leaving the detector has essentially the same composition as the sample entering the detector. **In environmental analysis**, PID is used most often when selectivity towards **aromatic compounds** is required. It is also often found in **field portable gas chromatographs** and detectors, as it does not require any additional gases for operation

5.1 GAS CHROMATOGRAPHY

Gas chromatography – hyphenated techniques

Analyte identification based only on the retention time of a component is suspect even for simple mixtures. **Selective detectors reduce the uncertainty** by detecting only the components sharing a certain characteristic, **but these do not eliminate the chance of false identification.**

On the other hand, **spectroscopic techniques provide qualitative information** about the analyte which is **often specific enough to make the identification of a component certain**. Therefore, several attempts to couple GC with various spectroscopic techniques were undertaken from the early days of GC. Today, combined instruments, often referred to as "**hyphenated**" systems.

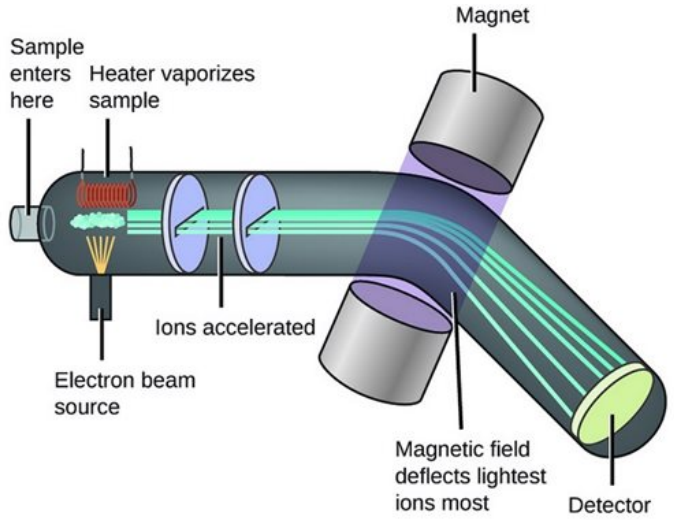
By far, **the most important hyphenated technique is combination of GC with mass spectrometry (GC/MS)**. Mass spectrometry is a technique which allows determination of the masses of molecules or molecule fragments. Molecules which enter the mass spectrometer are ionized (and most often fragmented), and the **ions are separated according to their mass to charge ratio (m/z).**

The plot of detector response vs. the m/z ratio is called a **mass spectrum**. Under given conditions, the mass spectrum of a given compound is characteristic for it and can be used to confirm its identity.

5.1 GAS CHROMATOGRAPHY

Gas chromatography – mass spectroscopy

In mass spectrometers, the sample analysis occurs in 4 phases:



- First, **the sample is ionized** by knocking one or more electrons off to give positive ions by bombardment with a stream of electrons, by means of electron ionization, chemical ionization, or desorption techniques.
- Then, **the generated ions are accelerated** so that they all have the same kinetic energy.
- Once accelerated, **the ions are deflected using a magnetic field**. The motion of a charged particle inside a magnetic field is ruled by the Lorentz force law and by Newton's second law of motion:

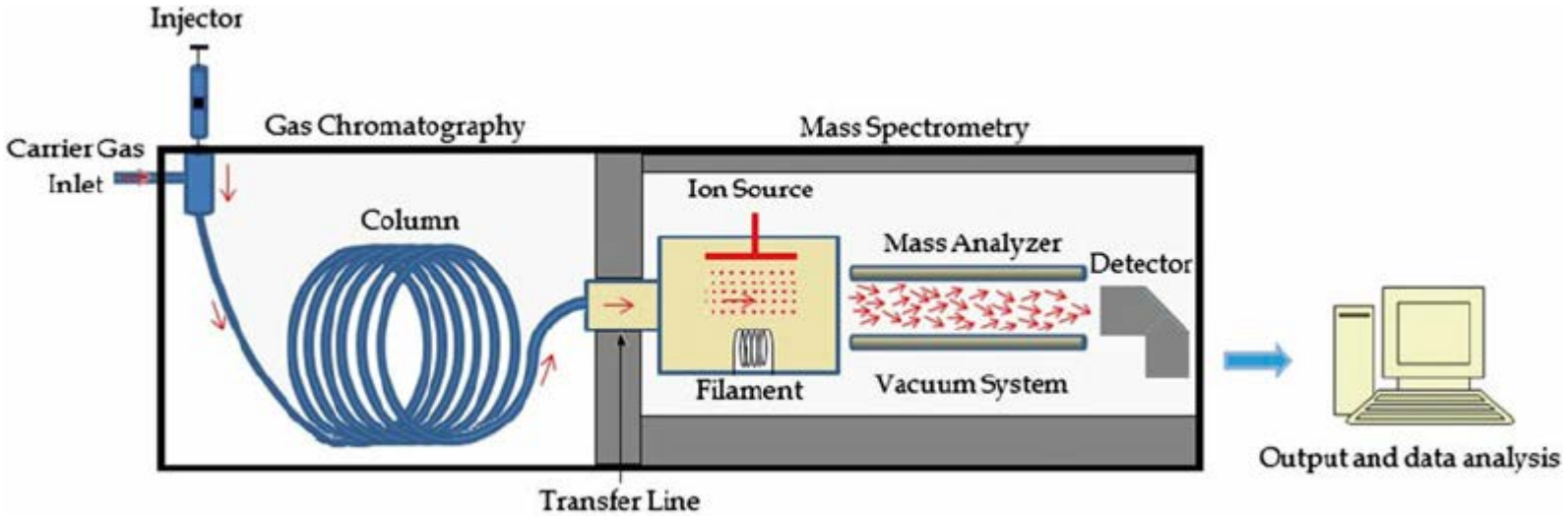
$$\overrightarrow{F} = z \cdot e \left(\vec{E} + \overrightarrow{v} \times \overrightarrow{B}\right) = m\overrightarrow{a} \qquad (5.10)$$

As a result, the deflection angle depends on the ratio between the mass and the charge of the ion.

5.1 GAS CHROMATOGRAPHY

Gas chromatography – mass spectroscopy

- The deflected **ions are then detected after passing through a mass filter**. Different type of filters are currently available, including magnetic sector mass filters; double focusing filters; quadrupole mass filter; Time of Flight (TOF) spectrometers; ion trap spectrometers; ion cyclotron spectrometers.



5.1 GAS CHROMATOGRAPHY

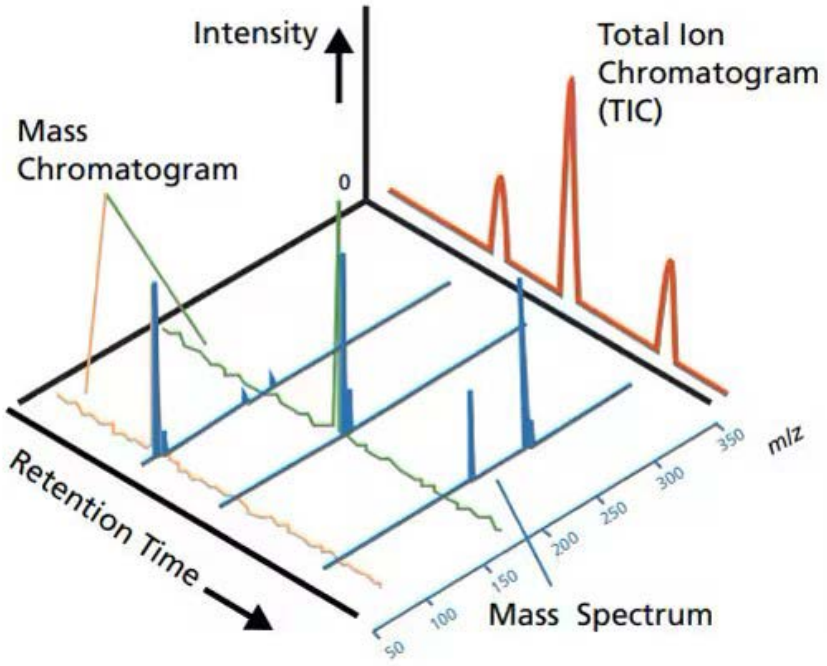
Gas chromatography – mass spectroscopy

The combination of GC and MS provide several benefits compared to the use of other detectors as well as to the use of MS alone, as **allows the accurate identification of the molecules in the sample.**

GC/MS separates and quantifies multi-component samples and complex matrices, as well as have the **capability to identify unknown compounds**.

Both FID and MS detectors can quantitate using the peak intensity or peak area and identify compounds using the retention time from the chromatograms. However, the unknown peak detected by both techniques, can only be further determined and identified easily using GC/MS.

Data such as the ret**ention time, molecular weight and mass spectra** obtained from GC/MS can be retrieved and **compared to those present in several databases**.



5.1 GAS CHROMATOGRAPHY

Example: GC-MS for environmental monitoring

https://doi.org/10.1016/j.chemosphere.2018.04.168

- **Gas chromatography-tandem mass spectrometry (GC-MS/MS)** detection for determination of 31 **pesticides**.
- **Sample type**: river water (RW), river sediment (RS), pond water (PW) and tubewell water (TW) samples.

Contents lists available at ScienceDirect

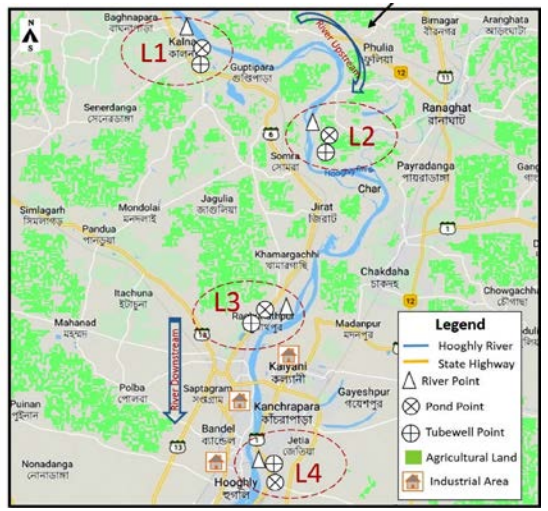
Chemosphere

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

GC-MS/MS determination and ecological risk assessment of pesticides in aquatic system: A case study in Hooghly River basin in West Bengal, India

Rahul Mondal [a], Ayan Mukherjee [b], Subrata Biswas [c], Ramen Kumar Kole [a, *]

- **Sampling location:** Samples were collected from four locations (L1-L4) which encompass a 50 Km stretch of Hooghly River basin in West Bengal. First two locations i.e. L1 and L2 were selected on river upstream whereas second two locations i.e. L3 and L4 on river downstream receiving untreated sewage water or agricultural/industrial effluent water



5.1 GAS CHROMATOGRAPHY

Example: GC-MS for environmental monitoring

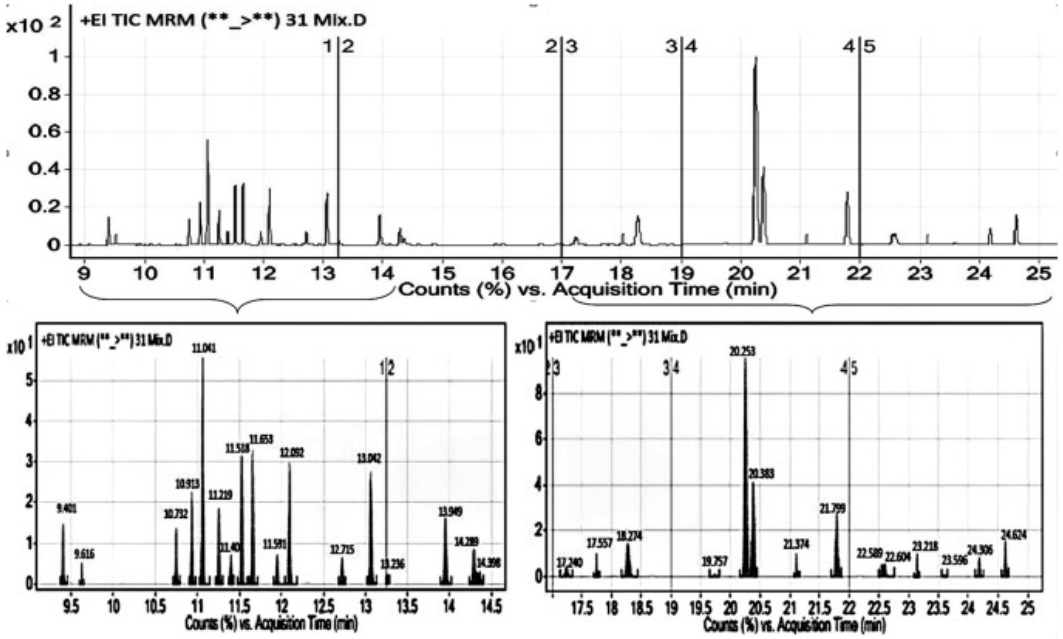
- **Sample collection, transportation and storage:** Amber coloured high quality glass (1 L capacity) container with stopper cap was used for collection of water samples. The container was cleaned by washing with acid, detergent, tap water, distilled water, acetone (AR grade) and finally with the working organic solvent. Nansen Type water sampler was used for collection of river and pond water (1 L of water with three replicates) from a depth of 1 ft from the surface. After collection of samples in glass container chloroform (AR grade, 10 mL L−1) was added to water to protect from microbial degradation and kept in ice box at 4 °C. The upper 10 cm of river bottom sediments (approx. 500 g) were collected using a grab sampler (0.5 L capacity) and transferred in packets of aluminium foil sheets. In the laboratory, collected water samples were filtered through Whatman glass fibre filter (GF/F, 0.45 µm) to remove suspended particle material and wet sediment samples were air dried and sieved (20 mesh) before performing extraction. The samples were analyzed immediately but, in some cases, they were stored at −18 °C for a maximum period of 48 h.

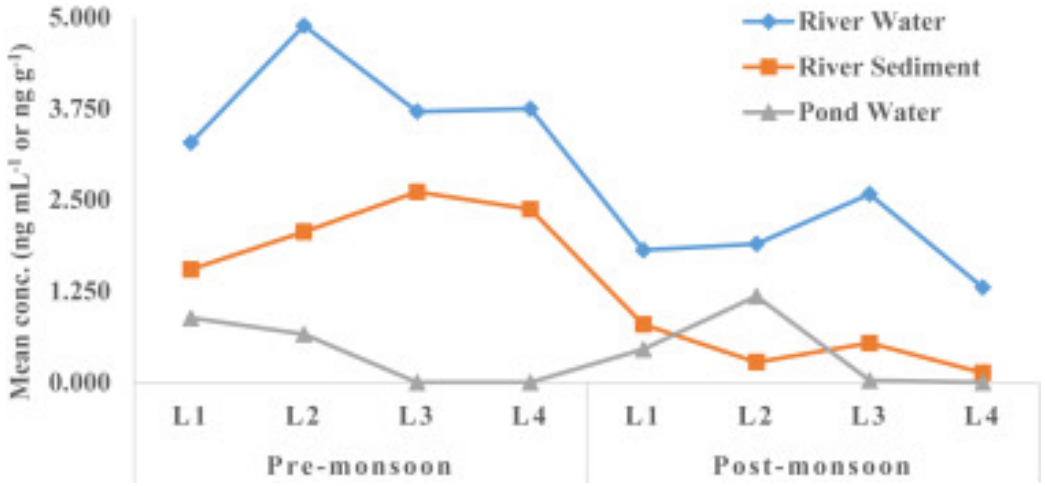
- **Pesticide standards:** The Certified Reference Materials (CRMs) of the 31 selected pesticides were procured from Sigma-Aldrich. Stock solutions of the individual pesticide standards (100 µg mL−1) were prepared in 50 mL ethyl acetate (EA).

5.1 GAS CHROMATOGRAPHY

Example: GC-MS for environmental monitoring

- **Instrumentation:** the extracts were analyzed using Gas Chromatograph (Agilent Technologies 7890A) coupled with Mass Spectrometric system (Model 7000 triple quadrupole, TQD) equipped with 7693A autosampler. Agilent Mass Hunter software (Version B.50.00) was used for instrument control and data analysis. Individual chromatographic behavior was used to determine and prepare the composition of the mixed standard solution for analysis of multiple pesticides. In this context, tandem mass analysis using the triple quad provided good selectivity and improved the signal to noise (S/N) ratio of the target analyte.



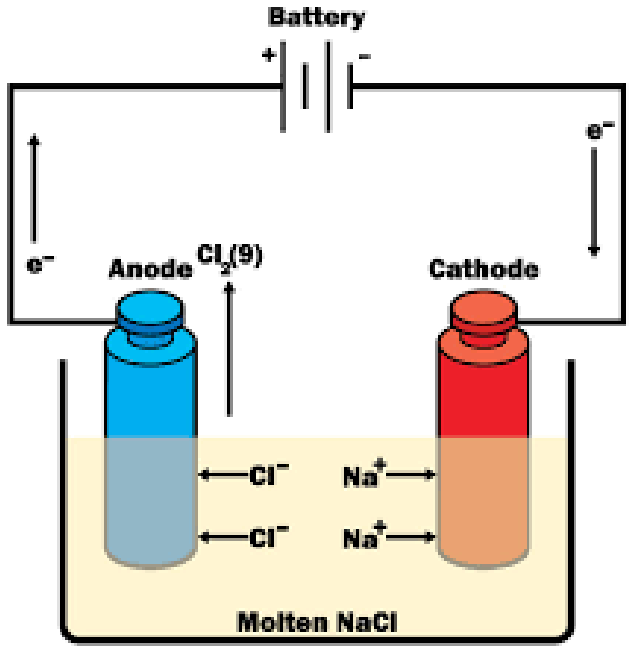


5.2 ELECTROCHEMICAL SENSORS

Electroanalysis

For lengthy decades, electroanalysis represents the largest area of applied electrochemistry, involving **measurements of the electric signals associated with the behaviour and/or transformations of charged species in the solution**.

From traditional point of view, electroanalysis can be classified as a special area of electrochemistry which is primarily focused on the **determination (quantification) of chemical substance(s) in a sample**, but also on qualitative characterization, i.e., **identification**.



5.2 ELECTROCHEMICAL SENSORS

Electroanalysis - advantages

- Long tradition and highly elaborated theoretical background.
- Relatively simple and inexpensive instrumentation (mass fabrication).
- Wide flexibility in practical analysis, versatile for different target analytes.
- Very good performance in trace analysis.
- High compactness.
- Adaptability for field monitoring and similar outdoor employment.

5.2 ELECTROCHEMICAL SENSORS

Electroanalysis - disadvantages

- Relatively high knowledge required to understand principles and techniques, as well as to interpret data.
- Low reproducibility (hysteresis), and high susceptibility to matrix influences.
- Limited stability of detection/sensing units, requiring frequent (re)calibration (short lifetime).
- Discontinuity of measurement if low detection limits are required (pre-concentration).
- Limited application to multicomponent analyses.
- Frequent use of toxic and harmful materials or reagents.
- Particular need for well-trained operators/users.

5.2 ELECTROCHEMICAL SENSORS

Electroanalysis – main targets

Electroanalysis, thus electrochemical sensors find a large application in environmental monitoring due to the well-known capabilities in identification, quantification, and monitoring of various chemical species. Some of the most important are:

- **Toxic heavy metals** (mainly Cd, Pb, Cu, and Hg);
- **Metals of strategic importance** (Co, Ni, V, Mn, Cr, Mo, U)
- **Organometallic compounds** containing Hg, Pb, Sn, and Bi; all occurring as both naturally and industrially released species.
- **Metalloids** (As and Se); often as the subjects of interest in speciation analysis
- **Toxic and harmful anions**, such as **nitrogen-based** ions, **sulphur** anions, **phosphates**, all being applied as fertilizers, industrial explosives, food additives, conserving or water-treatment agents.
- **Gases in air and dissolved in aquatic systems** (O_2, CO_2, NH_3, NO_X, SO_2, Cl_2, HCHO, etc.).
- Organic pollutants; namely: polyaromatic hydrocarbons (PAHs), herbicides and pesticides.

5.2 ELECTROCHEMICAL SENSORS

Electrochemical sensors

From the basic researches of the electrochemistry parents, Volta, Galvani, Sir Humphry Davy, and Faraday, a long period of silence followed in this interdisciplinary field that ends only at the beginning of the twentieth century with the invention of the **glass electrode by M. Cremer** and the discovery of **polarography by J. Heyrovsky**. That was the moment when modern electrochemistry was born.

The research boom, which leads to the elaboration of the most well-known electrochemical methods and main types of electrodes, continues even today. **Electrochemical methods (potentiometry, voltamperometry, and conductimetry)** experienced a huge development due to their multiple advantages that they offer.

At the same time the major disadvantage of the electrochemical methods became obvious: **lack of selectivity.** Practically, all the electroactive species can be reduced or oxidized from a sample or from a matrix and **the simultaneous detection in the same sample is possible only in the case when two species possess redox potentials sufficiently separated in the investigated domain of potential.**

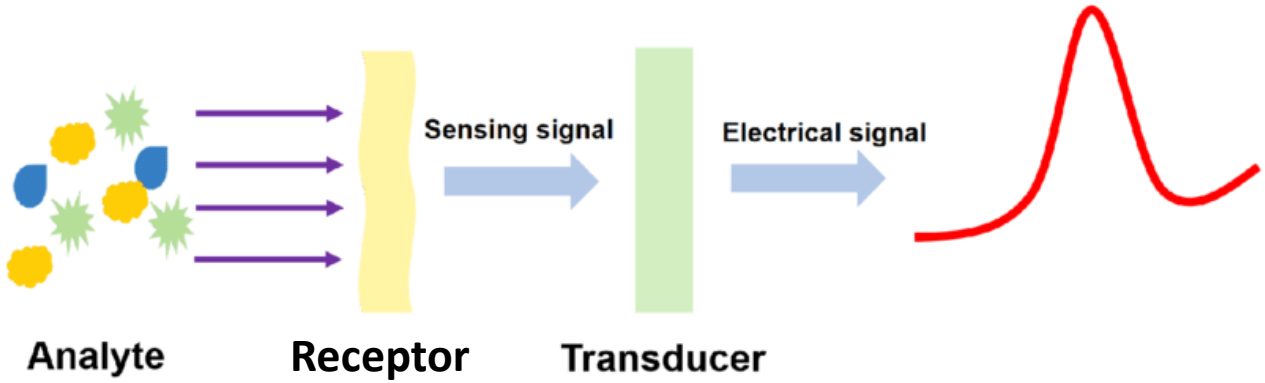
The reduced selectivity was the main issue that pointed the researchers' attention towards the electrode surface, where essential phenomena take place and trigger the race that still continues today having the goal of increasing the selectivity.

5.2 ELECTROCHEMICAL SENSORS

Electrochemical sensors

According to IUPAC a chemical sensor is "**a device that transforms chemical information, originating from a chemical reaction of the analyte or from a physical property of the investigated system**, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal."

Generally, chemical sensors contain two basic functional units connected in series: a chemical (molecular) recognition system, named **receptor**, which transforms the chemical information into a measurable form of energy, and a **transducer** capable of transforming the energy carrying the chemical information about the sample into a useful analytical signal.



5.2 ELECTROCHEMICAL SENSORS

Electrochemical sensors

The main function of the **receptor** is to provide the sensor with a **high degree of selectivity for the analyte to be measured**. While most chemical sensors are more or less selective (specific) for a particular analyte, some are, by design and construction, only class specific.

The second part of a sensor, the **transducer**, serves to transfer the signal from the output domain of the recognition system into an output signal (usually electric) which is then amplified by the electronics and converted into useful data. The transducer part is **responsible for the sensitivity of the device.**

Electrochemical devices transform the effect of the **electrochemical interaction which takes place between the analyte and the electrode into an exploitable electric signal (current or potential)**. Such effects may be stimulated electrically or may result in a spontaneous interaction at zero-current conditions.

5.2 ELECTROCHEMICAL SENSORS

Electrochemical sensors

In the field of electrochemical sensors, two main subgroups may be distinguished:

- **Voltammetric sensors**, including amperometric devices, in which a current is measured in direct or alternating current mode. This subgroup may include sensors based on chemically inert electrodes, chemically active electrodes, and modified electrodes. In this group are included also sensors with and without (galvanic sensors) external current source.

- **Potentiometric sensors**, in which the potential of the indicator electrode (ion-selective electrode, redox electrode, metal/metal oxide electrode) is measured against a reference electrode.

The systematic strategy for designing sensors should consider five features: (1) the detected or measured parameter, (2) the working principle of the transducer, (3) the physical and chemical/biochemical model, (4) the practical application, and (5) the available technology and materials for sensor fabrication.

5.2 ELECTROCHEMICAL SENSORS

Electrochemical sensors

The selection of materials and fabrication techniques is crucial for an adequate sensor function and the performance of a sensor often ultimately depends upon these factors. Consequently, future developments in sensor design will inevitably focus upon the technology of new materials.

Materials used in electrochemical sensors are classified as

- **materials for the electrode and supporting substrate** (metals: platinum, gold, silver, and stainless steel; carbon-based materials: graphite, carbon black, and carbon fibre; new mixed materials; or organic electroconductive polymers or salts)
- **materials for improved sensitivity and selectivity** (especially nano-sized materials: nanoparticles and carbon nanotubes)
- **materials for the immobilization of biological recognition elements** (multifunctional agents or alternatively non-conductive polymers).

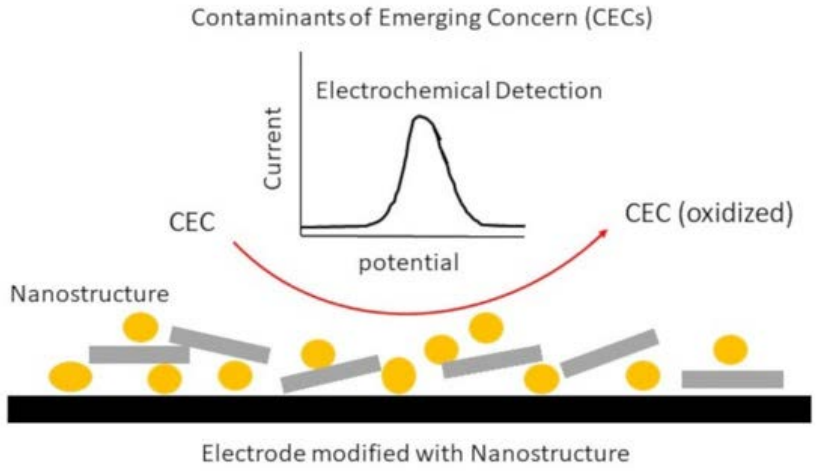
5.2 ELECTROCHEMICAL SENSORS

Electrochemical sensors

Nanomaterials are acquiring a big impact on the development of electrochemical sensors as they bring new possibilities for **developing novel electrochemical assays**. Nanoscale materials for **electrode construction or modification** offer the advantages of better sensitivity and selectivity and shorter response time.

Nanoparticles are very stable (compared to enzyme labels) and offer high sensitivity (thousands of atoms can be released from one nanoparticle) and a wide variety of them are available on the market.

In **environmental analysis** modified electrodes could be useful due to the acceleration of the electron transfer reaction, accumulation of pollutants at the surface of the electrodes, permselective transport.



5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors

A **potentiometric analysis measure the potential of an electrochemical cell under static conditions**.

Because no current, or only a negligible current, flows through the electrochemical cell, its composition remains unchanged. For this reason, potentiometry is a useful quantitative method of analysis.

A potentiometer is used to determine the difference between the potential of two electrodes.

The potential of one electrode (the **working or indicator electrode**) responds to the analyte's activity and the other electrode (the **counter or reference electrode**) has a known, fixed potential.

In **environmental analysis**, potentiometry is important for the detection of redox potential and as an analytical tool for the measurement of a variety of ionic and ionizable species.

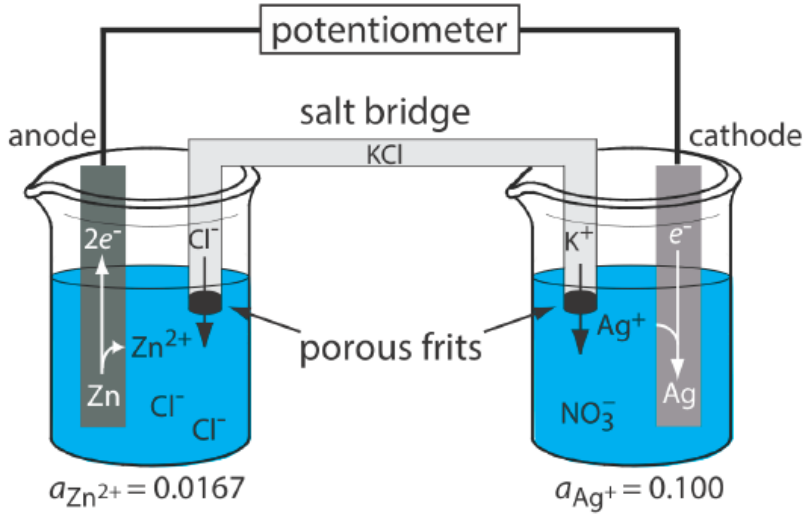
5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors

In a potentiometric sensor, the electrochemical cell consists of **two half-cells**, each of which contains an electrode immersed in a solution of ions whose activities determine the electrode's potential.

A **salt bridge** that contains an inert electrolyte, such as KCl, connects the two half-cells. The ends of the salt bridge are fixed with porous frits, which allow the electrolyte's ions to move freely between the half-cells and the salt bridge. This movement of ions in the salt bridge completes the electrical circuit.

One of the electrode acts as the **anode** (oxidation), while the other acts as the **cathode** (reduction). The anode is employed as **reference electrode** while the cathode is employed as **indicator electrode**.



5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors

The potential of a potentiometric electrochemical cell is:

$$E_{cell} = E_{cathode} - E_{anode} \tag{5.11}$$

where $E_{cathode}$ and E_{anode} are reduction potentials for the redox reactions at the cathode and the anode, respectively. Each reduction potential is given by the **Nernst equation**:

$$E = E^{\circ} - \frac{RT}{zF} \ln Q = E^{\circ} - \frac{RT}{zF} \ln \frac{c_{prod}}{c_{reag}} \tag{5.12}$$

where E° is the standard-state reduction potential, R is the gas constant, T is the temperature in Kelvins, z is the number of electrons in the redox reaction, F is Faraday's constant ($96487\ C \cdot mol^{-1}$), and Q is the reaction quotient.

At a temperature of 298 K (25°C) the Nernst equation can be approximated as:

$$E = E^{\circ} - \frac{0.05916}{z} \log Q \tag{5.13}$$

5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors

Nernst equation provides an easy determination of the analytes in the sample, however there are **several issues with this approach**.

- First, the **standard-state potentials are temperature-dependent** and the values in reference tables usually are for a temperature of 25°C. This issue can be overcome operating the electrochemical cell at 25°C or by measuring the standard-state potential at the desired temperature.

- Moreover, the **standard-state reduction potential is significantly affected by the matrix**. For example, the standard-state reduction potential for the Fe^{3+}/Fe^{2+} redox couple is +0.735 V in 1 M $HClO_4$, +0.70 V in 1 M HCl, and +0.53 V in 10 M HCl.

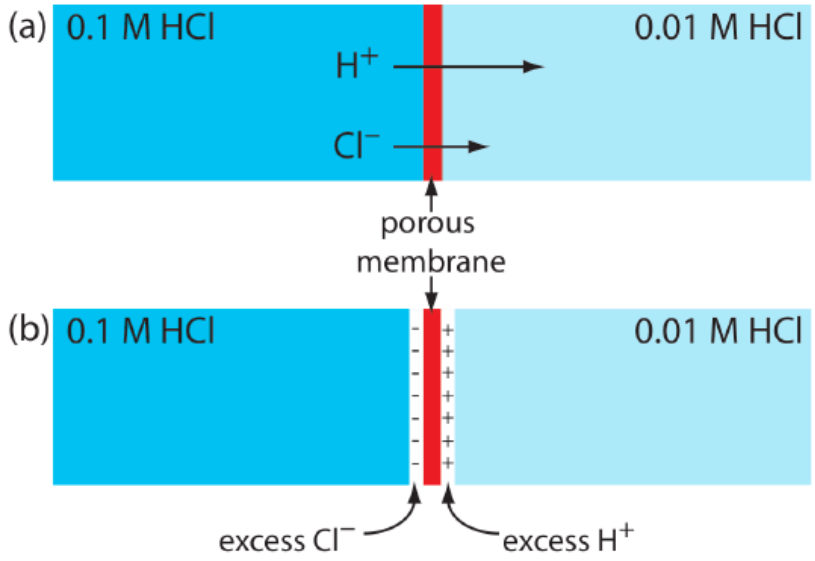
- Finally, **additional potentials in the electrochemical cell not included in Eq. (5.11) are observed**. In particular, a potential exists at the interface between each end of the salt bridge and the solution in which it is immersed. This is known as **junction potential**.

5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – junction potential

A junction potential develops at the interface between two ionic solution if there is a difference in the **concentration and mobility** of the ions.

Indeed, the ions will diffuse from the solution with higher concentration toward the solution with lower concentration. However, due to the difference in mobility, an **accumulation of positive and negative charges will occur at the junction barrier**, determining a potential difference. The latter is named junction potential (E_j).



5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – junction potential

The magnitude of the **junction potential depends upon the difference in the concentration of ions on the two sides of the interface**, and may be as large as 30–40 mV.

A salt bridge's junction potential is minimized by using a salt, such as KCl, for which the **mobilities of the cation and anion are approximately equal.**

Nevertheless, a small junction potential, generally of unknown magnitude, is always present.

When we measure the potential of an electrochemical cell, the **junction potential also contributes to E_{cell}.** Therefore, (Eq. 5.11) can be rewritten as:

$$E_{cell} = E_{cathode} - E_{anode} + E_j \qquad (5.14)$$

This potential can be estimated by means of standardization methods (external standards, the method of standard additions, or internal standards).

5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – reference electrode

In potentiometric sensor, the anode electrode acts as reference electrode.

The ideal reference electrode provides a stable, known potential so that we can attribute any change in E_{cell} to the analyte's effect on the indicator electrode's potential. In addition, it should be easy to make and to use the reference electrode.

The most used reference electrodes are:

- **Standard Hydrogen electrode (SHE)**, consisting of a Pt electrode immersed in a solution in which the activity of hydrogen ion is 1.00 and in which the fugacity of $H_2(g)$ is 1.00
- **Calomel electrodes (SCE)**, based on the redox reaction between Hg_2Cl_2 and Hg (calomel is the common name for Hg_2Cl_2)
- **Silver/Silver Chloride electrodes**, based on the reduction of AgCl to Ag

5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – indicator electrode

In potentiometry, the potential of the **indicator electrode** is proportional to the analyte's activity. Two classes of indicator electrodes are used to make potentiometric measurements:

- **Metallic electrodes**.
- **Membrane electrodes or ion-selective electrodes.**

Membrane electrodes were discovered in 1906, observing that a thin glass membrane develops a potential, called a membrane potential, when opposite sides of the membrane are in contact with solutions of different pH led to the eventual development of a whole new class of indicator electrodes called ion-selective electrodes (ISEs). Following the discovery of the glass pH electrode, **ion-selective electrodes have been developed for a wide range of ions.**

Membrane electrodes have been also developed to respond to the concentration of molecular analytes by using a chemical reaction to generate an ion that can be monitored with an ion-selective electrode.

5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – ion-selective electrode

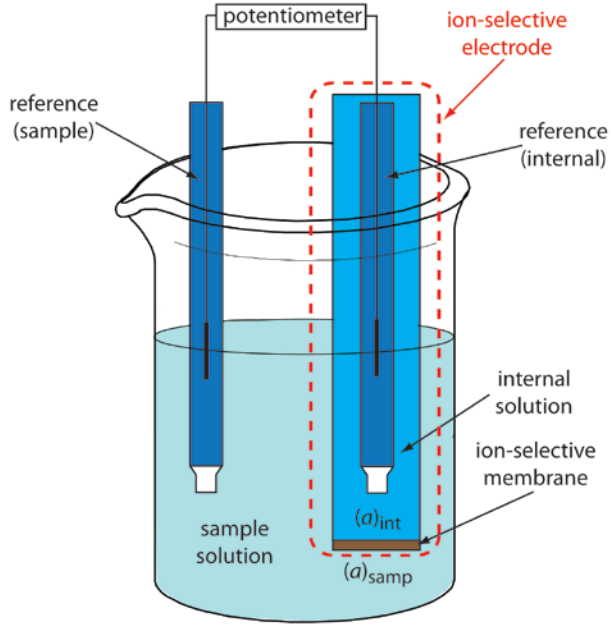
Two reference electrodes are used: one positioned within the internal solution, and one in the sample solution. The cell potential can be thus written as:

$$E_{cell} = E_{Ref(int)} - E_{Ref(samp)} + E_{mem} + E_j \qquad (5.15)$$

where E_{mem} is the potential across the membrane. Since the liquid junction potential and reference electrode potentials are constant, any change in the cell's potential is attributed to the membrane potential.

The analyte's interaction with the membrane generates a membrane potential if there is a difference in its activity on the membrane's two sides.

Current is carried through the membrane by the movement of either the analyte or an ion already present in the membrane's matrix.



5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – ion-selective electrode

The membrane potential is given by the following Nernst-like equation

$$E_{mem} = E_{asym} - \frac{RT}{zF} \ln \frac{(a_A)_{int}}{(a_A)_{samp}} \tag{5.16}$$

where $(a_A)_{samp}$ is the analyte's activity in the sample, $(a_A)_{int}$ is the analyte's activity in the ion-selective electrode's internal solution. Ideally, E_{mem} is zero when $(a_A)_{int} = (a_A)_{samp}$. The term E_{asym}, which is an **asymmetry potential**, accounts for the fact that E_{mem} usually is not zero under these conditions.

Combining Eq. (5.15) and (5.16), results:

$$E = K + \frac{0.05916}{z} \log(a_A)_{samp} \tag{5.17}$$

where *K* is a constant that includes the potentials of the two reference electrodes, the junction potentials, the asymmetry potential, and the analyte's activity in the internal solution. **Under ideal conditions, the potential change at the ISE membrane is proportional to the change in the logarithmic ion activity.**

5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – gas-sensing electrode

Several membrane electrodes have been developed to respond to the concentration of dissolved gases. The basic design of these electrodes consists of a thin membrane separating the sample from an inner solution containing an ion-selective electrode.

The membrane is permeable to the gaseous analyte, but is not permeable to nonvolatile components in the sample matrix. Once the gaseous analyte passes through the membrane, it reacts in the inner solution, producing a species whose concentration can be monitored by an appropriate ion-selective electrode. **The composition of the inner solution changes with use, and both it and the membrane must be replaced periodically**. Gas-sensing electrodes are stored in a solution similar to the internal solution to minimize their exposure to atmospheric gases.

Table 11.4 Characteristics of Gas-Sensing Membrane Electrodes

Analyte	Reaction in Inner Solution	Inner Solution	Ion-Selective Electrode
CO_2	$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+$	0.01 M $NaHCO_3$, 0.01 M NaCl	glass pH electrode
HCN	$HCN + H_2O \rightleftharpoons CN^- + H_3O^+$	0.01 M $KAg(CN)_2$	Ag_2S membrane electrode
HF	$HF + H_2O \rightleftharpoons F^- + H_3O^+$	1 M H_3O^+	F^- electrode
H_2S	$H_2S + H_2O \rightleftharpoons HS^- + H_3O^+$	pH 5 citrate buffer	Ag_2S membrane electrode
NH_3	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	0.01 M NH_4Cl, 0.1 M KNO_3	glass pH electrode
NO_2	$2NO_2 + 3H_2O \rightleftharpoons NO_3^- + NO_2^- + 2H_3O^+$	0.02 M $NaNO_2$, 0.1 M KNO_3	glass pH electrode
SO_2	$SO_2 + 2H_2O \rightleftharpoons HSO_3^- + H_3O^+$	0.001 M $NaHSO_3$, pH 5	glass pH electrode

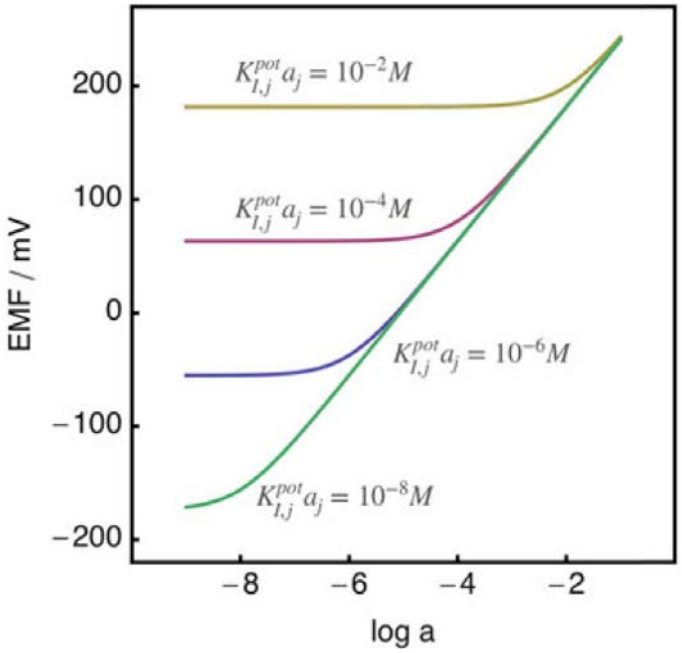
5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – selectivity

If a sample contains other ions of the same charge sign of the primary ion (analyte ion), they may displace the primary ion from the ion-selective membrane. If this occurs, a **deviation from the Nernst equation is observed**. For interfering ions of the same charge as the primary ion, an expanded Nernst equation may be used to describe this behavior:

$$E = K_I + \frac{0.05916}{z_I}\log(a_I + \sum_{J \neq I} K_{I,J}^{pot}\, a_J) \qquad (5.18)$$

where $K_{I,J}^{pot}$ is the **selectivity coefficient**. This equation is known as the Nicolsky equation. The selectivity coefficient $K_{I,J}^{pot}$ is effectively a weighting factor for any interfering ion activity, a_J. **Smaller selectivity coefficients** and more dilute interfering ions give lower levels of interference and hence **lower detection limits**.



5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – detection limits

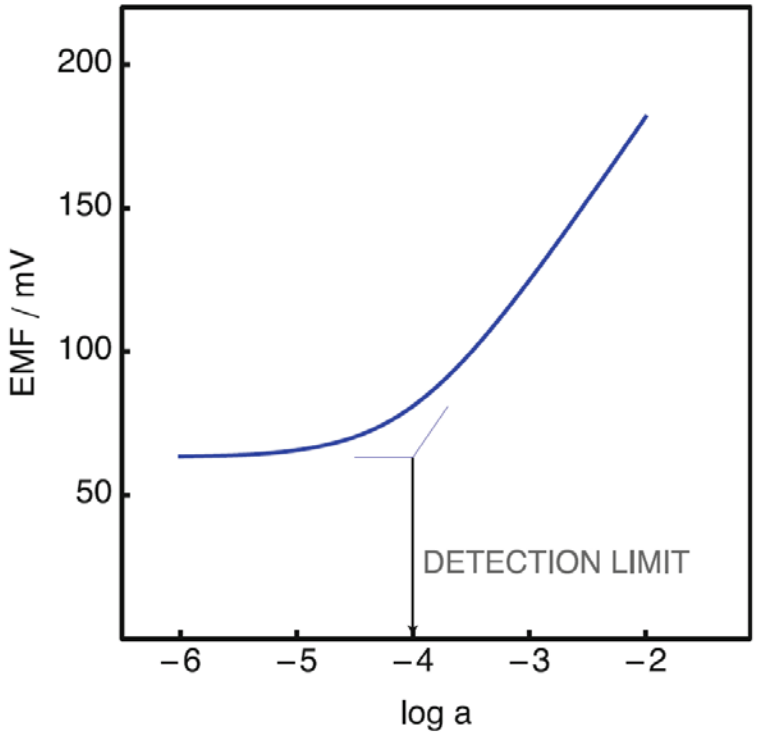
In potentiometry, the **lower detection limit is defined as the intersection of the two extrapolated linear portions of the calibration curve.**

The lower detection limit may be understood as the point in the calibration curve where a substantial deviation from the Nernst slope is observed.

For a well conditioned membrane electrode with an optimized inner solution composition or a suitable solid contact material the following relationship may be used to estimate the kinetic detection limit.

$$c_{I,min} = \sqrt{q \cdot c_R^m \sum_{I \neq J} K_{I,J}^{pot} a_J} \qquad (5.19)$$

where c_R^m is the molar ion-exchanger concentration in the membrane and the permeability ratio q (typically ~ 10^{-3})



5.2 ELECTROCHEMICAL SENSORS

Potentiometric sensors – response time

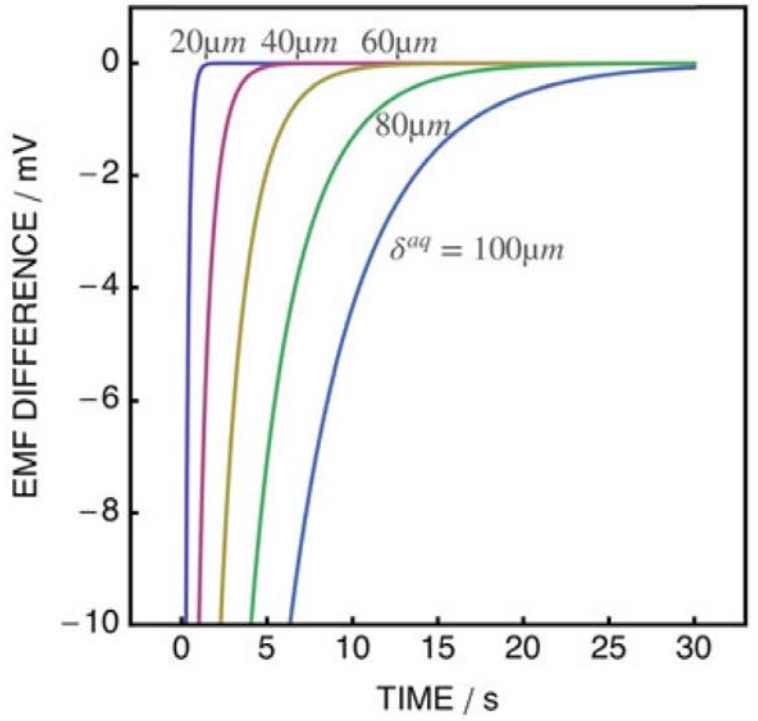
Ideally, for planar ion-selective electrode responding to analyte concentration changes in the sample, the composition of the membrane phase remains unchanged. **The response time for such membranes depends solely on the time required for the boundary concentrations in the diffusion layer to equilibrate with the sample bulk**. An approximate solution from diffusion equations can be used conveniently for practical use:

$$E(t) = E(\infty) + \frac{RT}{zF}\ln\left(1 - \left(1 - \frac{a_I^{aq}(t=0)}{a_j^{aq,bulk}}\right)\frac{4}{\pi}e^{-\frac{t}{\tau}}\right) \qquad (5.21)$$

Where the time constant τ is given by:

$$\tau = \frac{(\delta^{aq})^2}{2D_I^{aq}} \qquad (5.22)$$

where D and δ are the diffusion coefficient and diffusion layer thicknesses. As a result, **the response time depends strongly on the diffusion layer thickness and is longer when going from a concentrated to a more dilute sample solution.**



5.2 ELECTROCHEMICAL SENSORS

Electrochemical dynamic techniques

In principle, a potentiometric cell, can be illustrated starting from a galvanic one. In a true galvanic cell spontaneous redox occur. The goal is to transform the free energy change (ΔG) accompanying the conversion of reactants into products in useful (electrical) work (w_u).

The yield of transformation tends to one only if the current flowing (i) tends to zero, i.e., occurs through equilibrium states: a thermodynamically reversible process.

Therefore, potentiometric analysis perform a sort of thermodynamic measurement on a solution, when the system is under equilibrium conditions.

On the other hand, if a **voltage generator** is connected in opposition to the galvanic cell, **it slows down the rate of the cell reaction** as far as the voltage supplied, ΔV, is lower than E_{eq} of the cell; when $\Delta V = E_{eq}$, the process is stopped ($i = 0$). Further increase of $|\Delta V|$ reverses the process: it is forced to a non-spontaneous sense in an electrolytic cell.

5.2 ELECTROCHEMICAL SENSORS

Electrochemical dynamic techniques

In dynamic techniques the current flow is evaluated among the so-called **working electrode (WE)** and the **auxiliary (AE) or counter electrode**:

$$-\Delta V = E_{eq} + \eta + iR_s = E + iR_s \tag{5.24}$$

Where η is the sum of the anodic and the opposite of the cathodic overvoltages necessary to make the current flow, while iR_s accounts for the ohmic drop in solution, R_s, in Ohm, being the resistance of the solution between anode and cathode.

ΔV, i and E_{eq} are known quantities, R_s can be computed independently, or made small enough to make the iR_s term negligible as a first approximation.

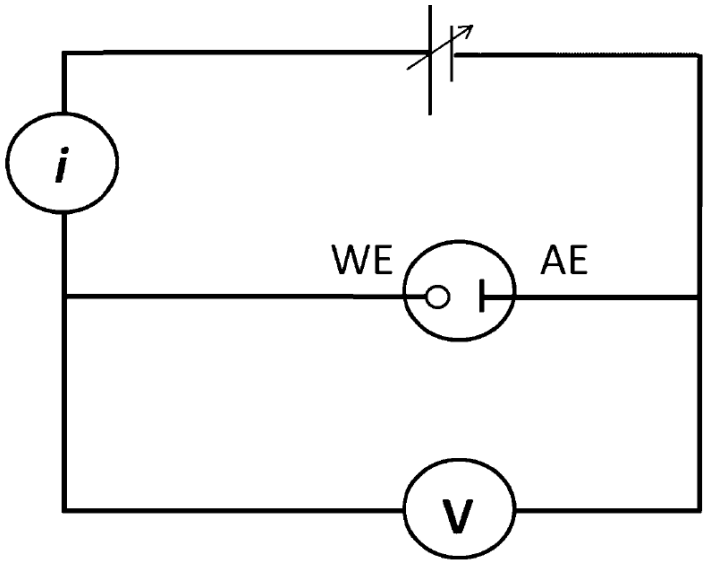
However, since the interest lies in knowing either E_{anode} or $E_{cathode}$, depending on which one is WE, we need knowing $E_{WE} = E_{eq,WE} + \eta_{WE}$; **however, we only know η, i.e., the sum of the over voltages of WE and AE.**

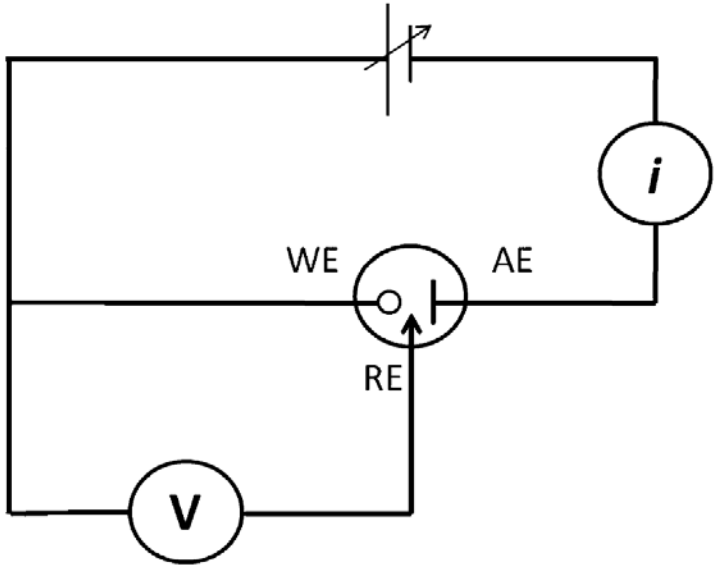
5.2 ELECTROCHEMICAL SENSORS

Electrochemical dynamic techniques

The accurate knowledge of the WE potential requires the use of a three-electrode circuit.

ΔV is applied between WE and AE, and the current flowing is correspondingly measured; however, the potential difference between WE and a suitable **reference electrode (RE)** is measured in an additional circuit, in which current is prevented from flowing by the high impedance voltmeter (V). This voltmeter measures the potential difference between WE and RE corresponding to the current passing in the "primary" circuit.





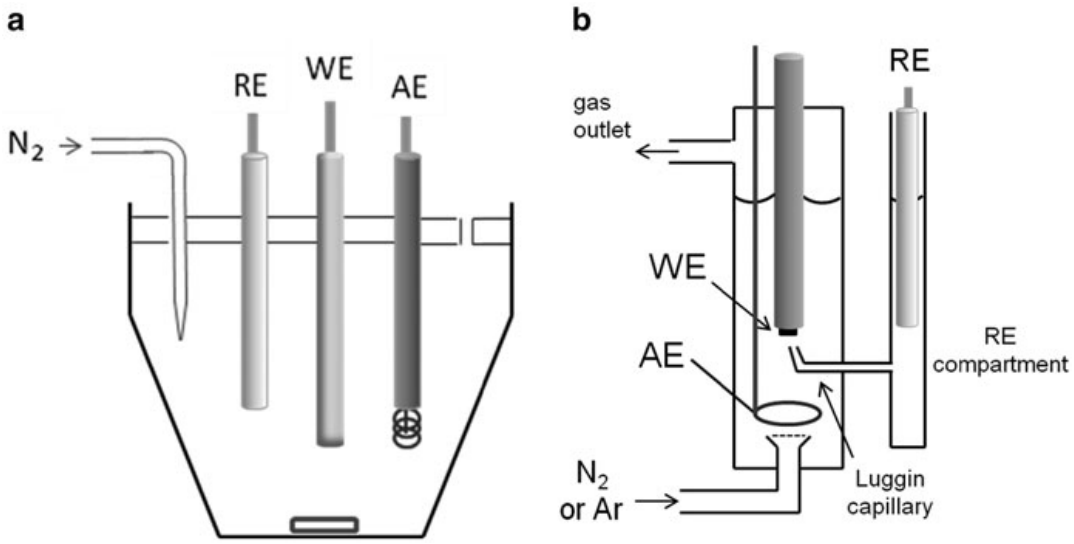
5.2 ELECTROCHEMICAL SENSORS

Electrochemical dynamic techniques

However, **the electric field generated in the solution by the WE-AE system induces different values of Φ, the "inner" or Galvani's potential**, in the different points of the solution. This implies that a potential difference exists between WE and RE ascribable to an ohmic drop in solution: iR_u, the so-called **uncompensated ohmic drop**.

Partial solution to this drawback is achieved by inserting the RE electrode into a compartment containing the solvent with the supporting electrolyte that ends with a capillary (**Luggin capillary**) positioned as close as possible to the WE surface.

No current flows between the end of the capillary and RE inside the relevant compartment and, consequently, no change in Φ arises between the two points: the residual iR_u drop is then between the WE surface and the end of the capillary.



5.2 ELECTROCHEMICAL SENSORS

Electrochemical dynamic techniques

The instrument devoted to manage the experiment employing a three electrode circuit is called “potentiostat.” It fixes the potential between WE and RE at a selected value, either constant or variable with time according to the chosen potential waveform, through the imposition of a suitable voltage between WE and AE.

Dynamic techniques, in which current passes through the electrochemical cell and concentrations change, also are important electrochemical methods of analysis. The main sensors are based on:

- **Coulometric measurements**
- **Voltametric measurements**
- **Amperometric measurements**

5.2 ELECTROCHEMICAL SENSORS

Coulometry

Coulometry is based on an **exhaustive electrolysis of the analyte**. By exhaustive we mean that the analyte is oxidized or reduced completely at the working electrode, or that it reacts completely with a reagent generated at the working electrode. There are two forms of coulometry:

- **controlled-potential coulometry**, where a constant potential is applied to the electrochemical cell
- **controlled-current coulometry**, where a constant current through the electrochemical cell

During an electrolysis, the total charge, Q, in coulombs, that passes through the electrochemical cell is proportional to the absolute amount of analyte by Faraday's law:

$$Q = nFN_a \tag{5.23}$$

where n is the number of electrons per mole of analyte and N_A is the moles of analyte.

5.2 ELECTROCHEMICAL SENSORS

Coulometry

In coulometry, the electric charge can be correlated to an electric current, which can be time dependent, according to the formula:

$$Q = \int_0^{t_e} i(t)dt \tag{5.24}$$

where t_e is the electrolysis time.

In coulometry, current is monitored as a function of time to calculate *Q*. **Knowing the total charge, we the moles of analyte can be determined.**

To obtain an accurate value for NA, **all the current must oxidize or reduce the analyte.** Therefore, coulometry requires 100% current efficiency (i.e., the percentage of current that actually leads to the analyte's oxidation or reduction) or an accurate measurement of the current efficiency using a standard.

Coulometric analysis can be performed in **controlled-potential mode** or **controlled-current mode**.

5.2 ELECTROCHEMICAL SENSORS

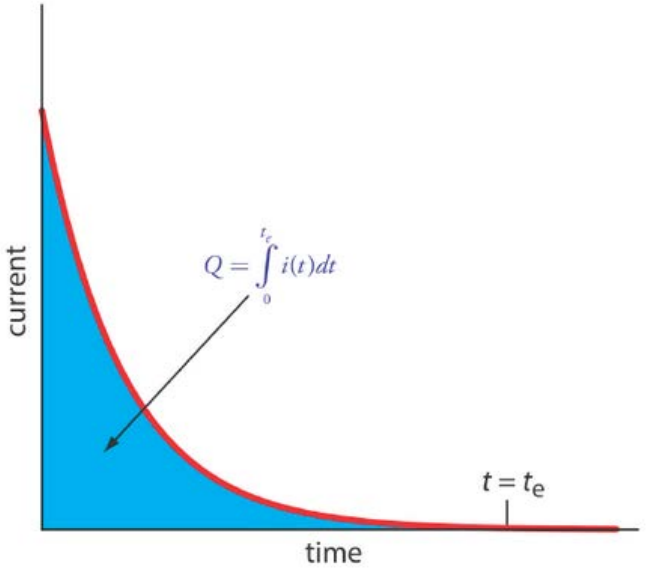
Controlled-Potential Coulometry

In controlled-potential analysis, the **working electrode is kept at a constant potential** where the analyte is oxidized or reduced completely and where no potential interfering species are oxidized or reduced. As electrolysis progresses, the analyte's concentration and the current decrease.

Integrating the area under the curve from $t = 0$ to $t = t_e$ the total charge can be calculated.

During this process, the current decreases over time. As a result, **the rate of electrolysis becomes slower, and an exhaustive electrolysis of the analyte may require a long time**.

Because time is an important consideration when designing an analytical method, we need to consider the factors that affect the analysis time.



5.2 ELECTROCHEMICAL SENSORS

Controlled-Potential Coulometry

The current decrease can be approximated as an **exponential decay**, such as:

$$i(t) = i_0 e^{-kt} \tag{5.25}$$

where i_0 is the current at t = 0 and ***k* is a rate constant that is directly proportional to the area of the working electrode and the rate of** stirring, and that is inversely proportional to the volume of solution.

For an exhaustive electrolysis in which we oxidize or reduce 99.99% of the analyte, the current at the end of the analysis, should be:

$$i(t_e) \leq 0.0001 \cdot i_0 \tag{5.26}$$

Combining Eq. (5.25) and (5.26), the electrolysis time can be referred to the rate constant as:

$$t_e = -\frac{1}{k}\ln(0.0001) = \frac{9.21}{k} \tag{5.27}$$

A quantitative electrolysis typically requires approximately 30–60 min, although shorter or longer times are possible.

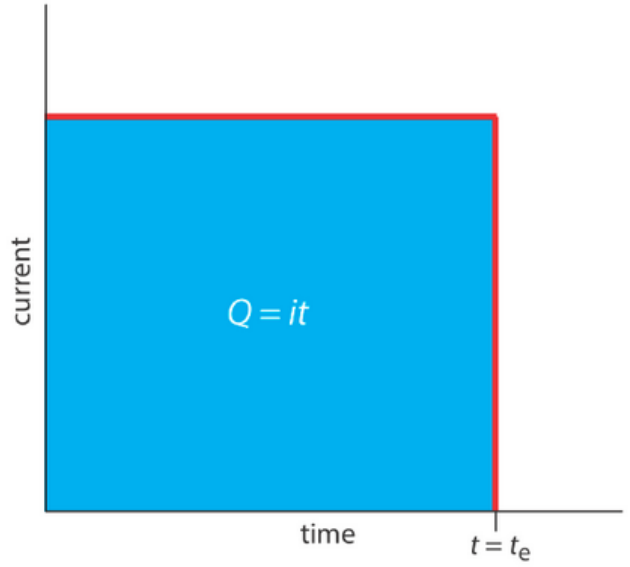
5.2 ELECTROCHEMICAL SENSORS

Controlled-Current Coulometry

A second approach to coulometry employs **constant current in place of a constant potential**. Controlled-current coulometry has two advantages over controlled-potential coulometry.

- First, **the analysis time is shorter** because the current does not decrease over time. A typical analysis time for controlled-current coulometry is **less than 10 min**, compared to approximately 30–60 min for controlled-potential coulometry.

- Second, because the total charge simply is the product of current and time, **there is no need to integrate the current-time curve.**



5.2 ELECTROCHEMICAL SENSORS

Controlled-Current Coulometry

However, the controlled-current method presents two important **experimental issues**.

- First, during electrolysis the analyte's concentration and, therefore, the current resulting from oxidation or reduction, decreases continuously. To maintain a constant current, **we must allow the potential to change** until another oxidation reaction or reduction reaction occurs at the working electrode. Unless we design the system carefully, this secondary reaction results in a **current efficiency that is less than 100%.**

- Second, in a controlled-current coulometric analysis **the current continues to flow even when the analyte's electrolysis is complete**, thus a method to determine when the analyte's electrolysis is complete is required.

The first issue can be solved by means of a "mediator", i.e., adding a species to the solution which has the role to react rapidly and quantitatively with the secondary oxidation process. The second issue is typically solved employing end points for a redox titration to signal the end of a controlled-current coulometric analysis. These can be visual indicators and potentiometric or conductometric measurements.

5.2 ELECTROCHEMICAL SENSORS

Amperometric and voltammetric techniques

The term **amperometry**, i.e., measurement of a current, indicates a technique in which **a current is measured.**

This current is measured as a function of an **independent variable** that, in electroanalysis/electrochemistry is reasonably the corresponding **electrode potential or time**, but in principle, however, all possible experimental variables are plausible. Measuring a current as a function of temperature, or of pressure, or even of the gravity force, constitutes in all cases an amperometric measurement.

Dealing with time as independent variable, the technique is typically referred as **chronoamperometry**.

Conversely, when the electrode potential is used as independent variable, we refer to the technique as **voltammetry**. This potential varies with time according to different waveforms, thus univocally defining the voltammetric technique.

In principle, chronoamperometry can be considered as a special case of voltammetry in which a constant potential is applied to the working electrode and the current is measured as a function of time.

5.2 ELECTROCHEMICAL SENSORS

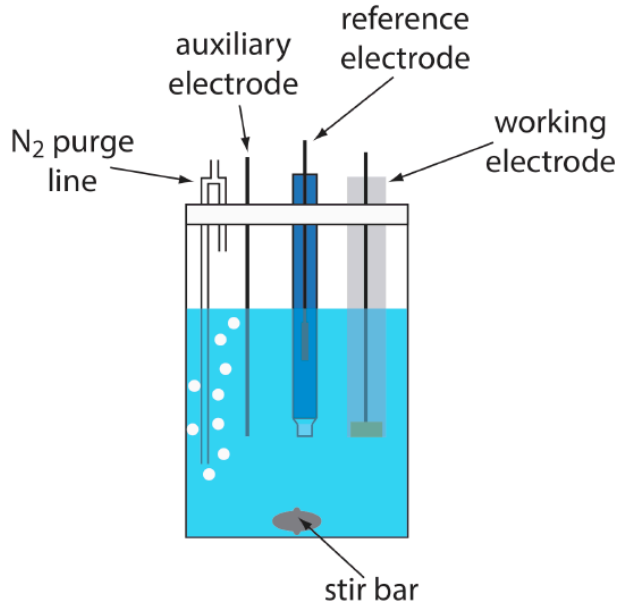
Amperometric and voltammetric techniques

In voltammetry, **time-dependent potential is applied to an electrochemical cell and measure the resulting current as a function of that potential.**

The resulting plot of current versus applied potential is called **voltammogram**, and it is the electrochemical equivalent of a spectrum in spectroscopy, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction.

As for coulometry, **three-electrode potentiostats** are widely employed for voltammetric measurements.

In this case, a **time-dependent potential excitation signal is applied to the working electrode to change its potential relative to the fixed potential of the reference electrode, and to measure the current that flows between the working electrode and the auxiliary electrode.**



5.2 ELECTROCHEMICAL SENSORS

Voltammetry

The **auxiliary electrode** generally is a platinum wire, and the reference electrode usually is a calamel electrode or a Ag/AgCl electrode. Several different materials have been used as **working electrodes**, including mercury, platinum, gold, silver, and carbon.

- **Mercury** provide several advantages, such as the capability of metals to dissolve in it (resulting in the **amalgam** formation), and the ability to renew the surface of the electrode by extruding a new drop. One limitation to mercury as a working electrode is the **ease with which it is oxidized**.

- Conversely, **solid electrodes** are manufactured into a disk and sealed into the end of an inert support with an electrical lead. With respect to mercury, the solid electrode's surface is altered by the adsorption of a solution species or by the formation of an oxide layer. For this reason, a **solid electrode needs frequent reconditioning**, either by applying an appropriate potential or by polishing.

5.2 ELECTROCHEMICAL SENSORS

Voltammetry

When we **oxidize an analyte at the working electrode**, the resulting electrons pass through the potentiostat to the auxiliary electrode, reducing the solvent or some other component of the solution matrix. If we **reduce the analyte at the working electrode**, the current flows from the auxiliary electrode to the cathode.

In either case, the current from the redox reactions at the working electrode and the auxiliary electrodes is called a **faradaic current.**

Because the reaction of interest occurs at the working electrode, we describe the faradaic current using this reaction. A faradaic current due to the analyte's reduction is a **cathodic current, and its sign is positive**. An **anodic current** results from the analyte's oxidation at the working electrode, and its sign is **negative**.

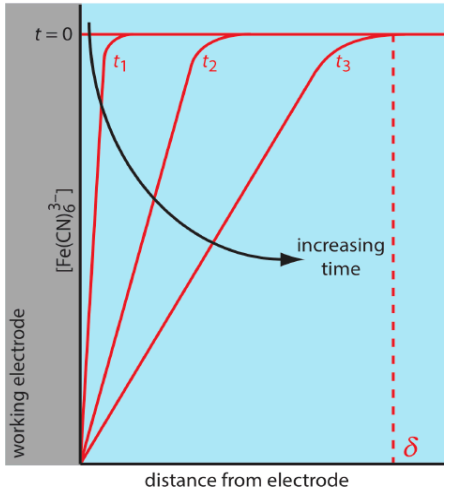
Although the potential at the working electrode determines if a faradaic current flows, **the magnitude of the current is determined by the rate of the resulting oxidation or reduction reaction**. Two factors contribute to the rate of the electrochemical reaction: the rate at which the reactants and products are transported to and from the electrode, **mass transport**, and the rate at which electrons pass between the electrode and the reactants and products in solution.

5.2 ELECTROCHEMICAL SENSORS

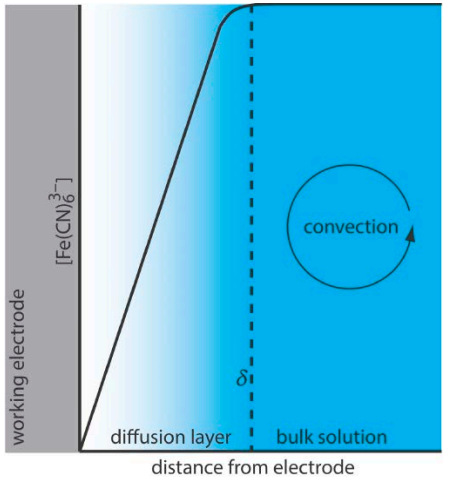
Influence of Mass Transport on the Faradaic Current

Mass transport can affect the rate at which reactants and products move toward or away from the electrode surface in three different modes: **diffusion**, **convection**, and **migration**.

- **Diffusion occurs whenever the concentration of an ion or a molecule at the surface of the electrode is different from that in bulk solution.** If we apply a potential sufficient to completely reduce the analyte at the electrode surface, a concentration gradient is observed. The region of solution over which diffusion occurs is the diffusion layer. In the absence of other modes of mass transport, the width of the diffusion layer, δ, increases with time as the analyte must diffuse from an increasingly greater distance.



- **Convection occurs when we mix the solution, which carries reactants toward the electrode and removes products from the electrode**. The most common form of convection is stirring the solution with a stir bar; other methods include rotating the electrode and incorporating the electrode into a flow-cell.



5.2 ELECTROCHEMICAL SENSORS

Influence of Mass Transport on the Faradaic Current

- **Migration occurs when a charged particle in solution is attracted to or repelled from an electrode that carries a surface charge.** If the electrode carries a positive charge, for example, an anion will move toward the electrode and a cation will move toward the bulk solution. Unlike diffusion and convection, migration affects only the mass transport of charged particles.

The movement of material to and from the electrode surface is a **complex function of all three modes of mass transport**. However, as first-order approximation, we can consider diffusion as the only significant form of mass transport. In this case, the current in a voltammetric cell is equal to:

$$i = \frac{nFAD(C_{bulk} - C_{x=0})}{\delta} \tag{5.28}$$

where *n* the number of electrons in the redox reaction, *F* is Faraday's constant, *A* is the area of the electrode, *D* is the diffusion coefficient for the species reacting at the electrode, C_{bulk} and $C_{x=0}$ are its concentrations in bulk solution and at the electrode surface, and δ is the thickness of the diffusion layer.

5.2 ELECTROCHEMICAL SENSORS

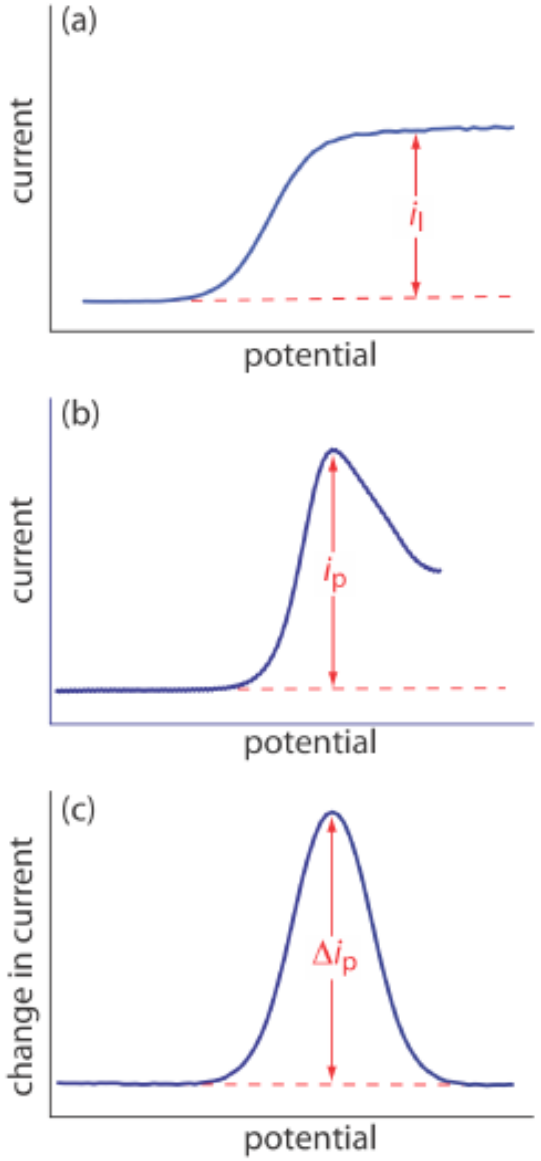
Voltammograms

The shape of a voltammogram is determined by several experimental factors. Despite an abundance of different voltammetric techniques, there are three common shapes for voltammograms.

In the first case, the **current increases from a background residual current to a limiting current, i_l**. Because the faradaic current is inversely proportional to δ, a limiting current occurs only if the thickness of the diffusion layer remains constant because we are stirring the solution, i.e., if convection occurs.

In the **absence of convection**, the diffusion layer increases with time and the resulting **voltammogram shows a peak current** instead of a limiting current.

The **change in collected current, Δi,** can be also monitored following a change in potential. Also in this case, the resulting voltammogram points out a **peak current**.



5.2 ELECTROCHEMICAL SENSORS

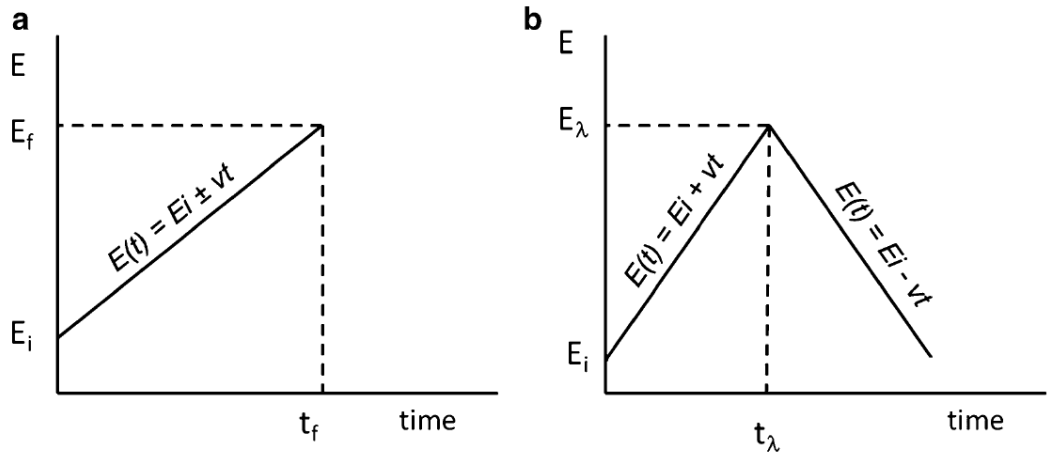
Voltammetric techniques

In voltammetry there are **three important experimental parameters under our control**: i) how we change the potential applied to the working electrode; ii) when we choose to measure the current, and iii) if we choose to stir the solution.

As a result, there are many different voltammetric techniques, such as: polarography, rotating disk electrode voltammetry, linear sweep and cyclic voltammetry, stripping voltammetry. From an historical perspective, polarography was the first developed method, based on the Hg drops working electrodes. However, nowadays this approach is rarely employed.

Linear sweep voltammetry (LSV), with the corresponding "reversal technique," **cyclic voltammetry** (CV), are the most frequently used voltammetric techniques.

In the first case, the potential in varied in one direction, either to more positive potentials or to more negative potentials. In cyclic voltammetry we complete a scan in both directions.



5.2 ELECTROCHEMICAL SENSORS

Voltammetric techniques

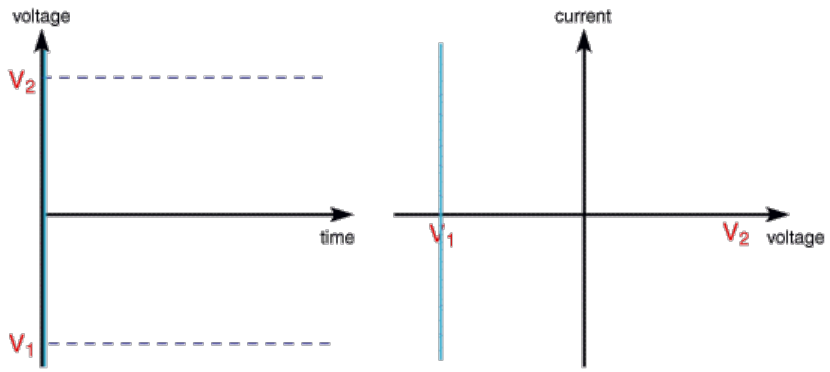
The typical voltammogram curve for LSV consists of a **peak-shaped curve**. Such a trend of the current may be accounted for the occurrence of **diffusion and convection effects**.

The increase of the applied potential causes an increase of the concentration gradient due to the decrease of electroactive species concentration at the electrode, till the zero-value is reached. On the other hand, at increasing time, expansion of the diffusion layer occurs that leads to a decrease of the gradient. The former effect prevails till a given potential **(E_p),** while the latter effect prevails beyond that point.

The peak current can be correlated to the target analyte concentration by means of the Randles–Sevcik equation for LSV:

$$i_p = (2.69 \times 10^5)\, n^{3/2} A \sqrt{Dv}\, C_{bulk} \qquad (5.29)$$

Where *v* is the potential sweep rate. **A linear dependence of the peak current on the bulk concentration is observed.**



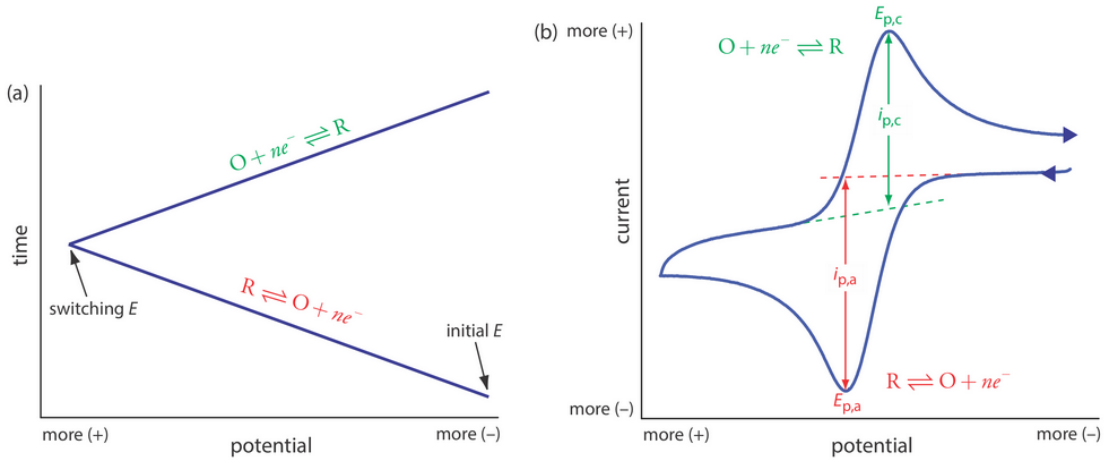
5.2 ELECTROCHEMICAL SENSORS

Voltammetric techniques

In **cyclic voltammetry** the scan is performed in both directions of the applied potential.

In this example, we first scan the potential to more positive values, resulting in the following oxidation reaction for the species R. When the potential reaches a predetermined switching potential, we reverse the direction of the scan toward more negative potentials. Because we generated the species O on the forward scan, during the reverse scan it reduces back to R.

As a result, the voltammogram has separate peaks for the oxidation reaction and for the reduction reaction, each characterized by a peak potential and a peak current. For a well-behaved system (reversible charge transfer), the anodic and the cathodic peak currents are equal $\left(i_{p,a} = i_{p,c}\right)$.

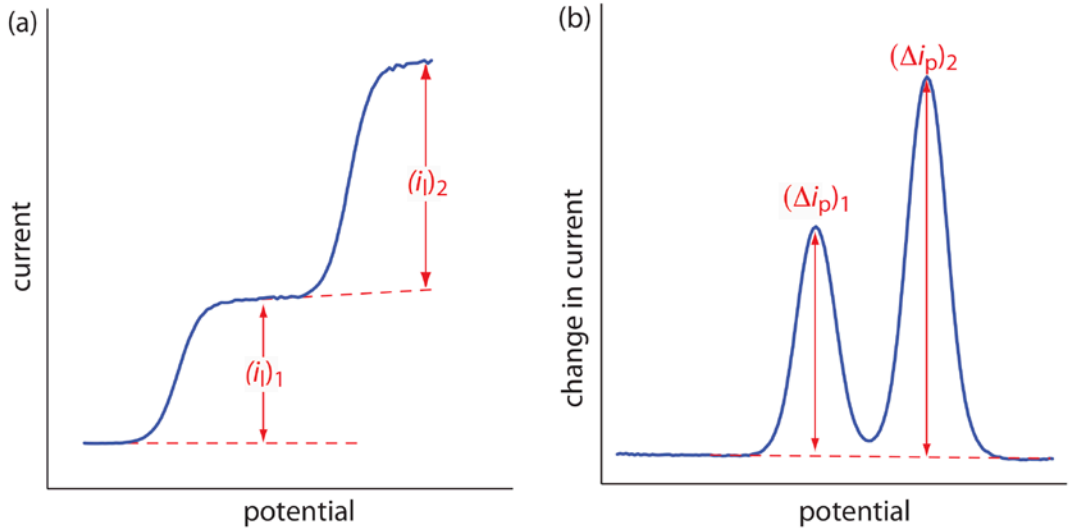


5.2 ELECTROCHEMICAL SENSORS

Voltammetric techniques

Voltammetry is an attractive technique for the analysis of samples that contain **two or more analytes**. Provided that the analytes behave independently, the **voltammogram of a multicomponent mixture is a summation of each analyte's individual voltammograms**.

If the separation between the half-wave potentials or between the peak potentials is sufficient, we can determine the presence of each analyte as if it is the only analyte in the sample. The minimum separation between the half-wave potentials or peak potentials for two analytes depends on several factors, including the type of electrode and the potential-excitation signal.



5.2 ELECTROCHEMICAL SENSORS

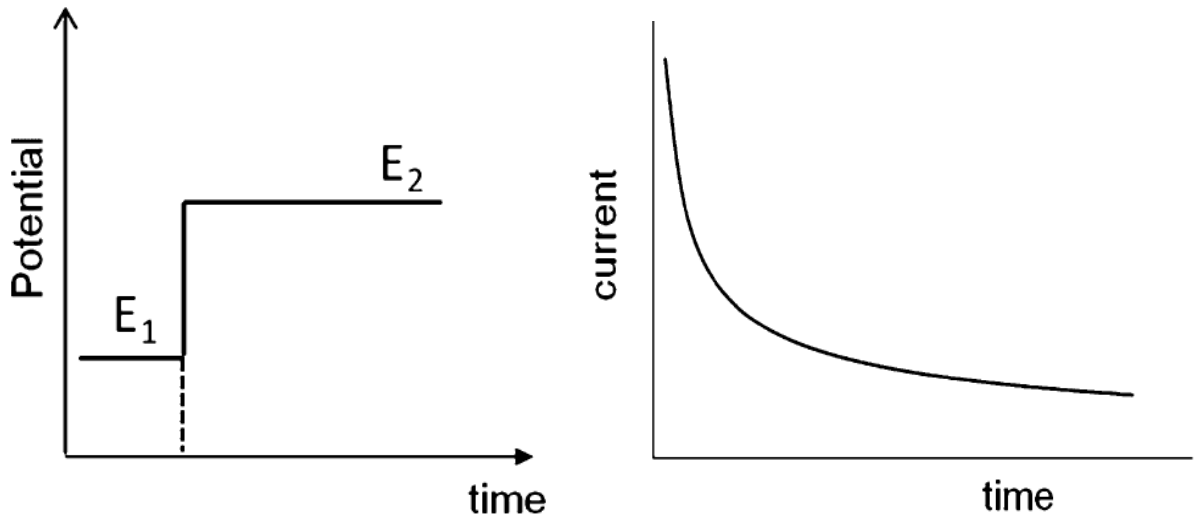
Amperometry

In amperometry, or chronoamperometry, a **constant potential is applied to the working electrode** and the **current is measured as a function of time**. Because we do not vary the potential, amperometry does not result in a voltammogram.

The WE potential is initially at a value at which no redox process takes place (E_1). Then, the potential is increased up to a at which the process occur (E_2). **In a chronoamperometric test the current is recorded as a function of the time spent since the application of E_2.**

For reversible charge transfer the current density can be calculated using the **Cottrell equation:**

$$i(t) = -\frac{nF\sqrt{D}}{\sqrt{\pi}}\frac{C_{bulk}}{\sqrt{t}} \qquad (5.30)$$



5.2 ELECTROCHEMICAL SENSORS

Example: Dissolved Oxygen

Quantification of **dissolved oxygen** is a common analysis in environmental monitoring of water samples. For this reason, a large number of electrochemical approaches have been developed to perform this task.

Among the different approaches, some of the most common are based on:

- **Membrane-covered electrodes**: Clark's electrode, Pt-LaF3-Sensing membrane, TiO_2 membrane coated sensor…
- **Modified electrodes**: Poly(Methylene Blue)-Modified Electrode, Metalloporphyrin-Modified Electrode, Nickel-Salen-Modified Electrode…
- **Miniaturized Dissolved Oxygen Sensors**: Solid-State Oxygen Sensor, Microelectrodes

5.2 ELECTROCHEMICAL SENSORS

Example: Dissolved Oxygen

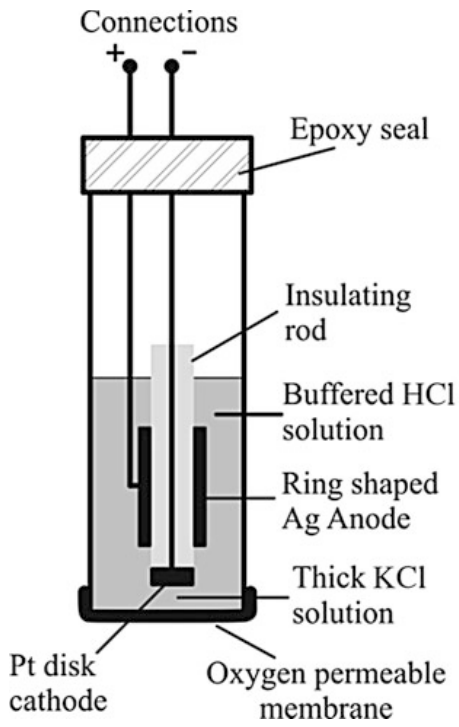
Clark's electrode is one of the most popular oxygen sensor. It is an **amperometric sensor** which consists of a working electrode, a reference electrode, and the electrolyte.

The working electrode (cathode) is made of noble metals such as platinum or gold, so the cathode material does not take part in the chemical reaction, whereas the anode is Ag in KCl.

A negative potential is applied to cathode relative to the anode (reference electrode) to **reduce the dissolved oxygen present in the solution** by the following reaction:

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

$$H_2O_2 + 2e^- \rightarrow 2OH^- \qquad (5.31)$$



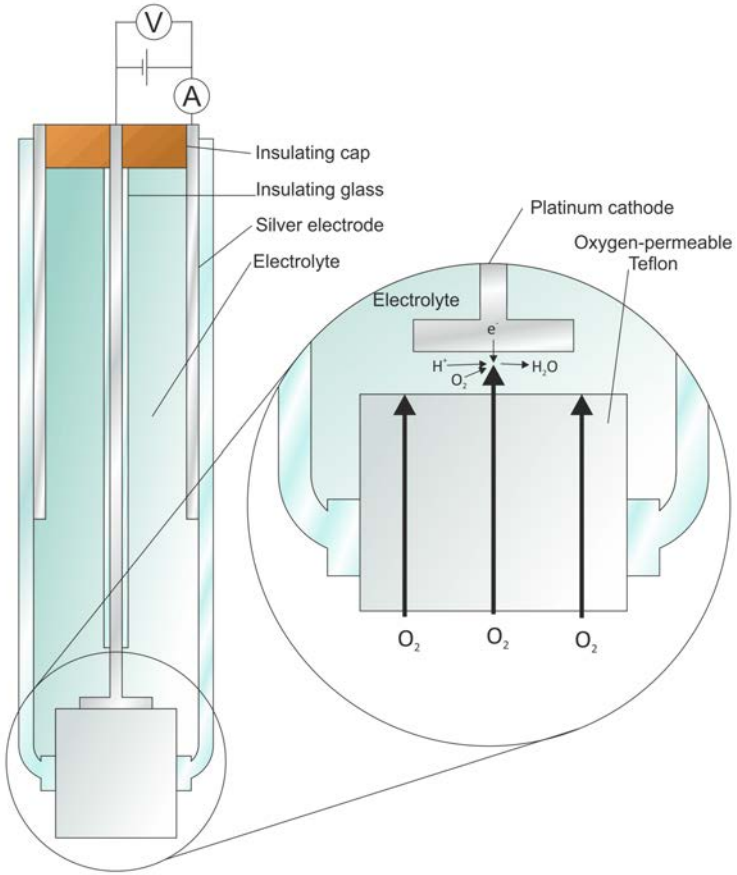
5.2 ELECTROCHEMICAL SENSORS

Example: Dissolved Oxygen

The electrode surface is isolated by the oxygen-permeable polymeric membrane in order to avoid the interference of any electroactive species present in the solution along with dissolved oxygen.

As a result, only dissolved oxygen present in the sample will **diffuse through the membrane and be reduced at the cathode surface** due to a negative external potential which will produce an electric current.

At a specific value of polarization potential which depends on the cathode material **the current is linearly proportional to the oxygen concentration.**

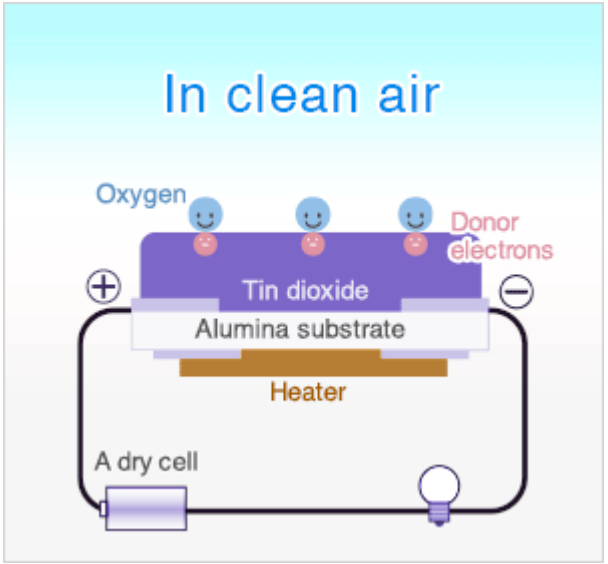


5.3 METAL-OXIDE SENSORS

Metal oxides sensors

Metal oxides (MOx) have been investigated for sensing applications, and more specifically for gas sensing applications, due to their affordability, significant **change in conductivity on exposure to the target molecule**, tunable properties by doping, and the ability to be easily interfaced with different transducing systems.

MOx sensors exhibit promise for detecting toxic pollutants (CO, H_2S, NO_x, SO_2, VOCs, etc.), explosive gases (H_2, CH_4, flammable organic vapors, etc.), and markers in exhaled breath.



5.3 METAL-OXIDE SENSORS

Metal oxides sensors: classification

Ceramic materials like metal-oxides have in general large bandgap energy resulting in an insulating behavior. For example, tin-oxide (SnO2), is characterized by a 3.6 eV bandgap, but **its resistivity is smaller compared to the one of common semiconductors**.

This phenomenon was associated for long time with the presence of donor levels near the conduction band (electrons conduction) due to the presence of oxygen vacancies in the material: in particular to the non-stoichiometry and oxygen-related intrinsic defects. In this case, the metal oxide is defined as **n-type** because of the conduction driven mainly from the electrons. Conversely, the **p-type** involves holes as the major charge carriers.

The MOxs employed for sensing applications include **transition MOx** (Fe_2O_3, WO_3, V_2O_5, CuO, etc.) and **non-transition MOx.** The non-transition MOx sensors include the **pretransition series** such as MgO and Al_2O_3 or **post-transition type** like In_2O_3 and **SnO_2**. The pretransition MOx possess high stability but poor electronic properties and hence have been generally less preferred for use as conductive gas sensors. The transition MOx sensors possess excellent conducting properties and variable chemical valency that enable **sensitive detection of even trace quantities of the analyte** but may sometimes have stability issues.

5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing mechanism

MOx have been mostly employed as **chemiresistors** where their **resistance is altered on exposure to the target molecule**. Chemiresistors exhibit both physisorption (van der Waal's) and chemisorption.

In this respect **oxygen plays a crucial role** not only because of its absence (vacancies) in the material structure but also because of his presence in ambient atmosphere **gives rise to change in sensor's conductivity**.

For temperatures between 150°C and 450°C, if the sensing material is in contact with an air mixture (and correspondingly with O_2 oxygen) a peculiar mechanism occurs generally defined as "ionosorption model". This step involves the **adsorption of oxygen molecules on the surface of the MOx**. Atmospheric oxygen adsorbs reversely on the metal-oxide open air surface as molecular (O_2^-), or atomic (O^{2-}, O^-) ions, which capture an electron from the conduction band (CB) of the semiconductor.

$$O_2(g) + e^- \rightarrow O_2(ads)$$
$$O_2(ads) + e^- \rightarrow O_2^-$$
$$O_2^- + e^- \rightarrow 2O^- \qquad (5.32)$$

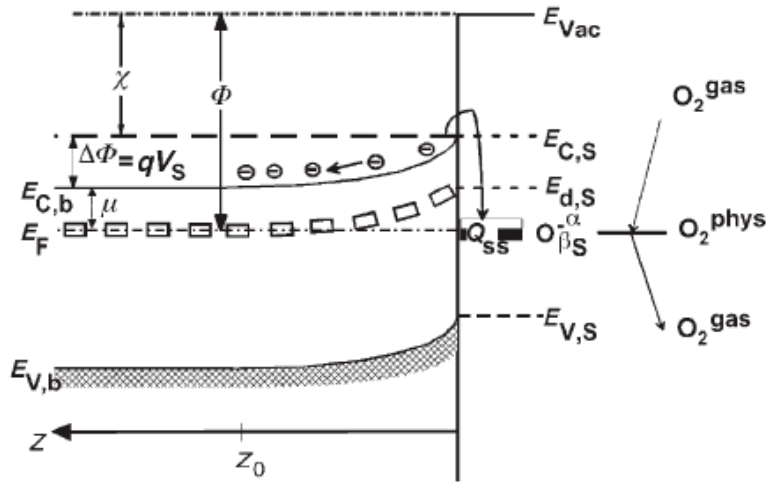
5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing mechanism

When the electrons move from the semiconductor to the surface leave behind the positive charges of the lattice, creating a so-called positive space charge region whose total charge is equal to the total charge of the electrons at the surface.

This **charge depletion induces an upward band bending at the surface** compared to the oxygen free case (Fermi level is still flat). Since in this area a lower number of electrons compared to the bulk is present, corresponding to a **more resistive region compared to the bulk material**, it is defined as **electron-depleted region** or layer. In equilibrium conditions, the magnitude of the barrier will be equal to qV_S with V_S which is a surface potential. The barrier determines the surface conductance equal to:

$$G = G_0 \exp\left(-\frac{q \cdot V_S}{kT}\right) \qquad (5.33)$$



5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing mechanism

The depth of the depleted surface region is defined as **Debye Length**:

$$\lambda_D = \sqrt{\frac{\epsilon\epsilon_0 kT}{q^2 n_b}} \tag{5.34}$$

where ϵ is the material dielectric coefficient, ϵ_0 is the vacuum permittivity, n_b is the bulk electrons concentration, q is the electron charge.

Once the surface of the MOx is oxygen rich, if the gas is introduced in the atmosphere it will interact with the adsorbed oxygen.

If the gas is a **reducing gas, it will reduce the oxygen** which will release the electron previously taken from the conduction band of the MOx and bonding to the electron of the reducing gas.

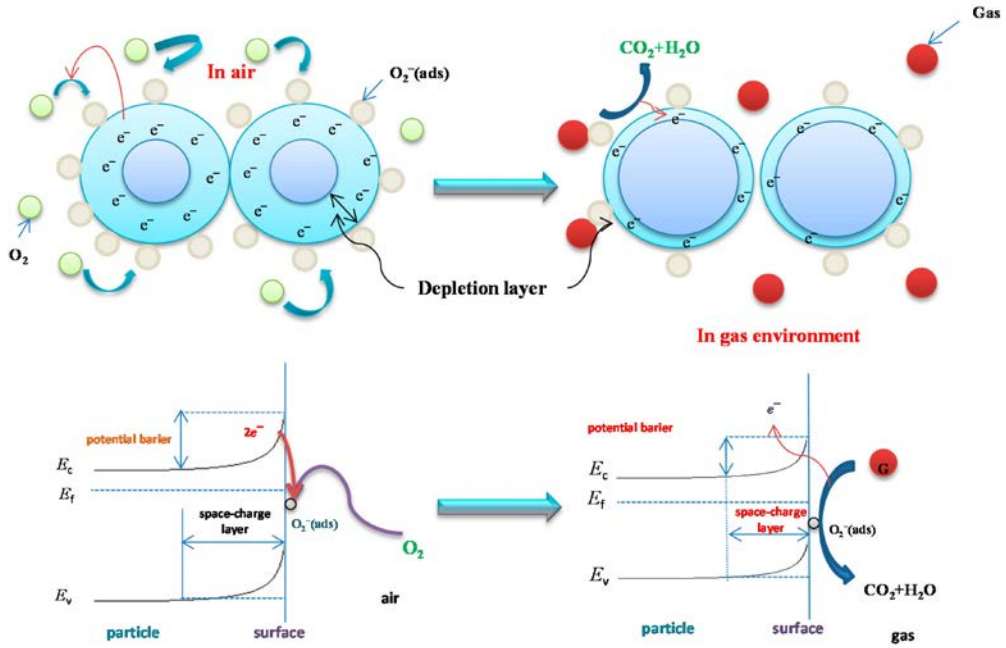
Conversely, if the **gas is an oxidizing gas** an analogous and competitive phenomenon to the oxygen adsorption will happen and the **oxidizing gas molecule/atom will take an electron** from the conduction band of the MOx .

5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing mechanism

- For **n-type Mox** sensor, the oxygen atoms extracted from the surface of reducing gases will behave as donors, whereas the oxygen atoms present in the surface of oxidizing gases act as acceptors. The involvement of the **reducing gases tends to increase conductance** while **oxidizing gases decrease conductance**.

- For **p-type MOx** sensor, the response in the presence of reducing and oxidizing gases **will be reversed** (increased conductance for oxidizing gases, decreased conductance for reducing gases).



5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing mechanism

Most MOx sensors are limited by a lack of specificity toward a target molecule. However, the specificity can be enhanced by altering the stoichiometry, porosity, and grain size of the MOx particles as well as introduction of appropriate dopants. The **performance of MOx-based chemical sensors is influenced by many factors** that can be broadly categorized as **chemical**, **structural**, and **environmental** parameters. The chemical composition and surface modifications of the MOx sensor are key factors that affect the sensing performance.

The **blending of more than one MOx** has been shown to have a positive impact on the sensing parameters for several analytes. For instance, when a blend of tin oxide and zinc oxide was employed for detection of butyraldehyde, it was found that while tin oxide dehydrogenated the analyte, zinc oxide catalyzed the decomposition of the analyte. Together the catalytic activities of the two MOx in the blend synergistically contributed to improved sensitivity toward the detection of butyraldehyde.

Alternatively, **the MOx layer can be doped** introducing small quantities of metal atoms. The metal centers act as **catalytic sites** that enhance the reactions at the MOx surface. In a typical example, palladium-doped SnO_2 sensors were employed for quantification of hydrogen gas where the palladium served as a catalyst that enhanced the sensor response.

5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing mechanism

The **morphology and dimensions of the MOx sensing element** play an important role in determining the **sensitivity**. Several nanostructures such as spheres, rods, flakes, flowers, and fibers have been explored for sensing and the results demonstrate that the **morphology of the structures** influence the sensing characteristics.

The microscopic local change in the number of carriers at the surface affects the total conductivity of the conductive material, which is fundamental for the functioning of the device. **The effects of local conductivity change on the MOx are enhanced in case of a high surface-to-volume ratio**, increasing the surface exposed to the atmosphere.

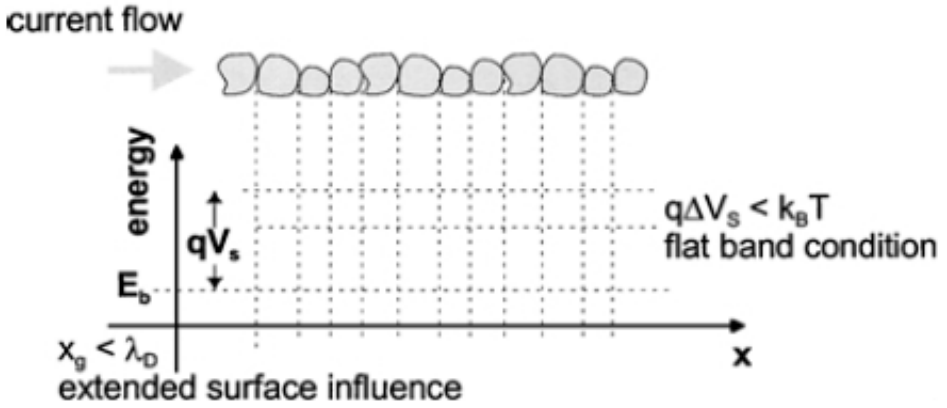
For this reason, this type of devices have generally a **porous morphology**, since is necessary for the gas interact with most part of the conducting volume, modulating positively or negatively the surface barrier created by the oxygen adsorption. Therefore, changing the ratio of the **Debye length and the grain size (*d*)** results in different behavior of the MOx sensor.

5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing mechanism

For porous layers the situation is complicated by the presence of **“necks” between grains**.

- If the **grain size is lesser than the thickness of the space charge layer ($d < \lambda_D$)**, the conductivity is dependent only on the surface reaction as there are no inner charge carriers. This is ideal for highly sensitive detection of an analyte as even lesser number of molecules interacting with the surface can produce a significant change in the conductivity of the MOx layer.

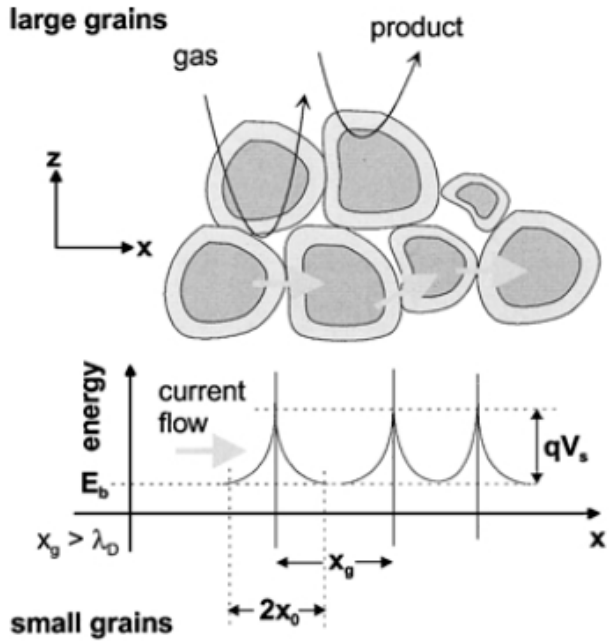


5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing mechanism

- If the **grain size is larger than the thickness of the space charge layer ($d > \lambda_D$)**, two cases can be distinguished: one with non-sintered grains and one with sintered grains.

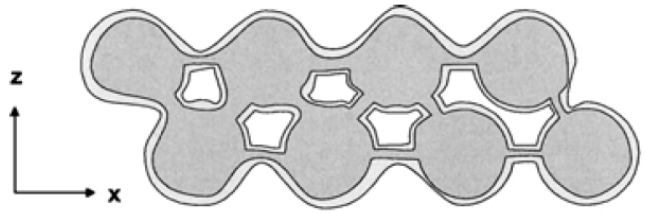
  I. In the first case, the **charges will see a single V_s barrier** when moving from grain to grain.



5.3 METAL-OXIDE SENSORS

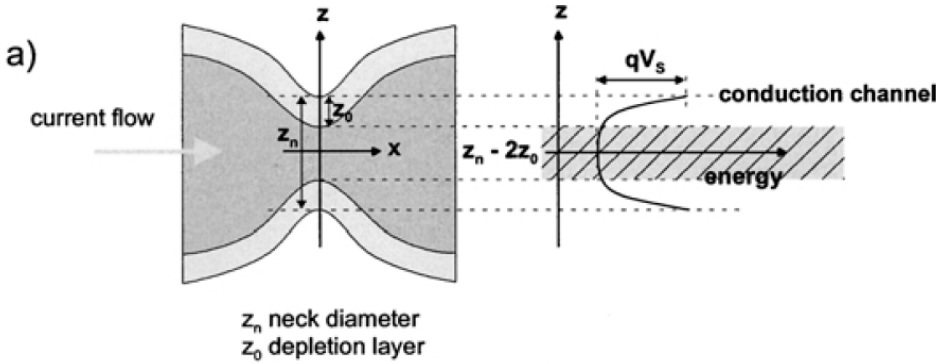
Metal oxides sensors: sensing mechanism

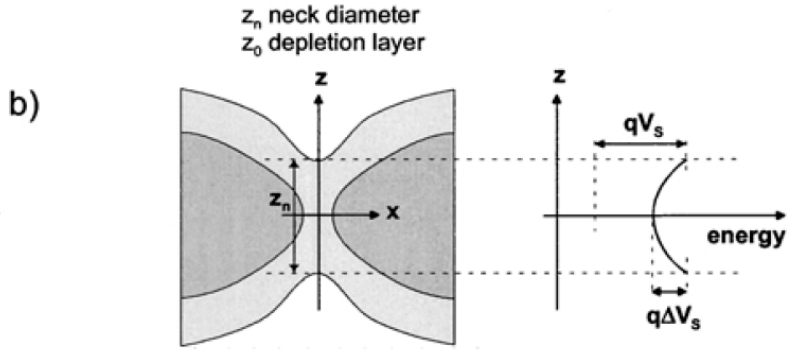
II. In the second case, the behavior depends on the **size of the contact area, z_n.**



a) If the **contact area is large** enough to not be influenced by the surface effects, a **conduction channel is created** (partly depleted necks).

b) If the **contact area is small**, the neck is completely depleted.





5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing performances

Humidity and moisture content in the environment have a negative impact on the sensing capabilities of a MOx sensor.

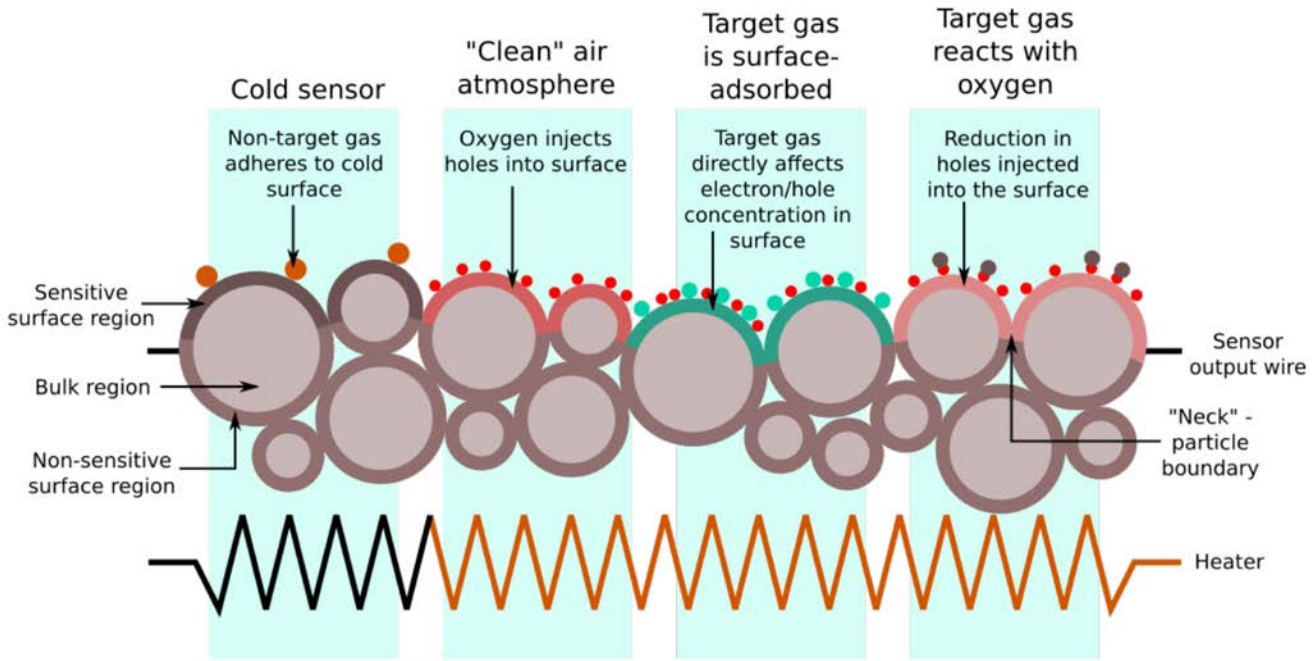
The **water molecules tend to chemisorb on the MOx surface** leading to formation of the hydronium and hydroxyl ions that are retained on the surface through electrostatic interactions with the metal cations. The hydronium ion transfers its proton to an O_2^- ion in the vicinity thereby forming OH^-. This process **not only depletes the surface oxygen but decreases the resistance of the MOx layer**.

The chemisorbed layer decreases the electron donation tendency, which in turn reduces the sensitivity of the MOx surface toward other gaseous analytes. **The chemisorbed layer promotes further physisorption of additional layers of water molecules** which are not very tightly associated with the surface. The strong electrostatic environment of the chemisorbed layer facilitates the dissociation of the physisorbed water molecules to form ions. The transfer of proton to O_2^- or H_2O depends on the surface coverage.

5.3 METAL-OXIDE SENSORS

Metal oxides sensors: sensing performances

The adsorbed water molecules further restrict the interaction of the analyte gases with the MOx surface. In order to reduce the number of physisorbed water molecules, most **MOx sensors are operated at elevated temperatures to remove the physisorbed water layer**. The chemisorbed hydroxyl ions are generally removed at temperatures exceeding 450°C, thereby further increasing the operating temperature of the sensor. This property has also been exploited for the development of MOx-based humidity sensors.

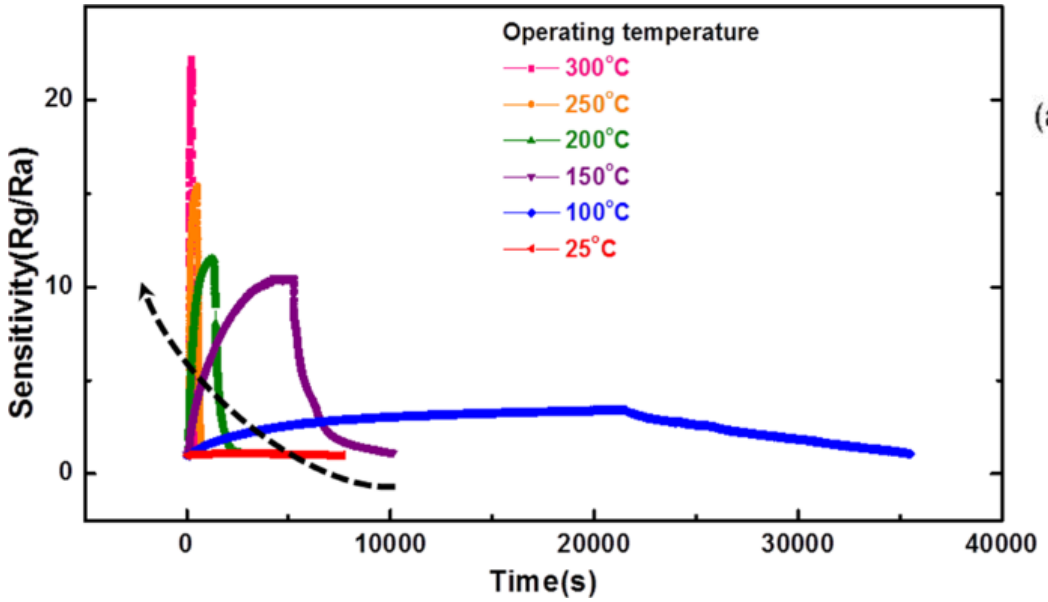


5.3 METAL-OXIDE SENSORS

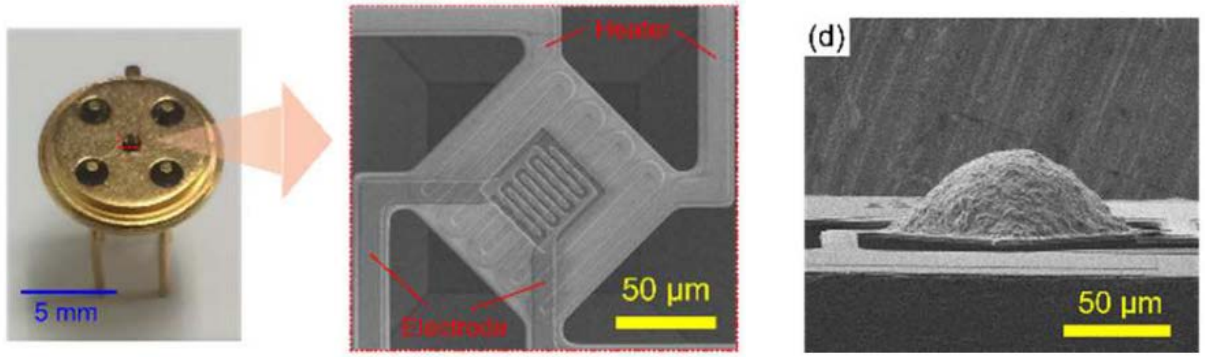
Metal oxides sensors: sensing performances

Temperature itself has an important role in determining the efficiency of detection.

At **low temperatures**, the detection **efficiency of MOx sensors is poor owing** to slow kinetics of interaction. The **efficiency progressively increases with increase in operating temperatures** and peaks at a specific value that is unique for the type of gaseous analyte and MOx being employed. **Further increase in temperature decreases the sensor efficiency** due to desorption of the gaseous analyte from the MOx surface. Thus, it is essential to ensure that the operating temperature of every MOx sensor does not exceed the working range.



(a)



5.3 METAL-OXIDE SENSORS

Metal oxides sensors for environmental monitoring

Several MOx have been explored for the detection of various pollutant gases.

- SnO_2 sensor is among the most extensively investigated for a wide range of gaseous analytes like **NO**, **NO_2**, and **NH_3**.
- Fe-doped WO_3 mesoporous hollow nanospheres displayed a sensing range of 10–1000 ppb toward **NO_2** at 100–140 °C emphasizing the catalytic role of the dopant.
- ZnO nanoparticles is another extensively investigated MOx that has been used in several configurations like platelets, rings, combs, rods, etc., for the detection of **flammable gases**.
- Functionalized ZnO nanorods along with AlGaN/GaN heterostructures have been investigated for monitoring of **NH_3 in air**.

Real time and remote monitoring of gaseous pollutants are also under active development with attempts to enable optimum sensor performance at ambient conditions.

5.3 METAL-OXIDE SENSORS

Metal oxides sensors for environmental monitoring

Modifier	LOD	Linear range	Response time (sec)	Gas
CuO nanowires (FET)	5 ppm	50–800 ppm	<10	CO
Al-doped ZnO	<750 ppb	5–50 ppm	6–8	CO
ZnO nanowires/Au nanoparticles	—	5–100 ppm	40	CO
SnO_2/RGO composite	2 ppm		4–12	NO_2
ZnO nanorods	10 ppm	10–140 ppm	4	H_2S
ZnO thin film	—	5–100 ppm	20	NH_3
CZO nanoflowers	10 ppm	10–100 ppm	32.3	NH_3
V_2O_5/PVAC composites	100 ppb	0.8–8.5 ppm	50	NH_3
RGO/CO_3O_4 composite	—	5–100 ppm	4	NH_3
ZnO nanopencils	5 nM	15 nM–0.5 mM	<10	NH_3
SnO_2/Ppy	—	10–100 ppm	3–4	NH_3
CuO decorated Gr hybrid nanocomposite	—	0.25–100 ppm	70–76	CO
$LaFeO_3$ nanocrystalline powder	—	500–2000 ppm	4 min	CO_2
ZnO/MWCNT	40 ppm	40–200 ppm	8–23	CO

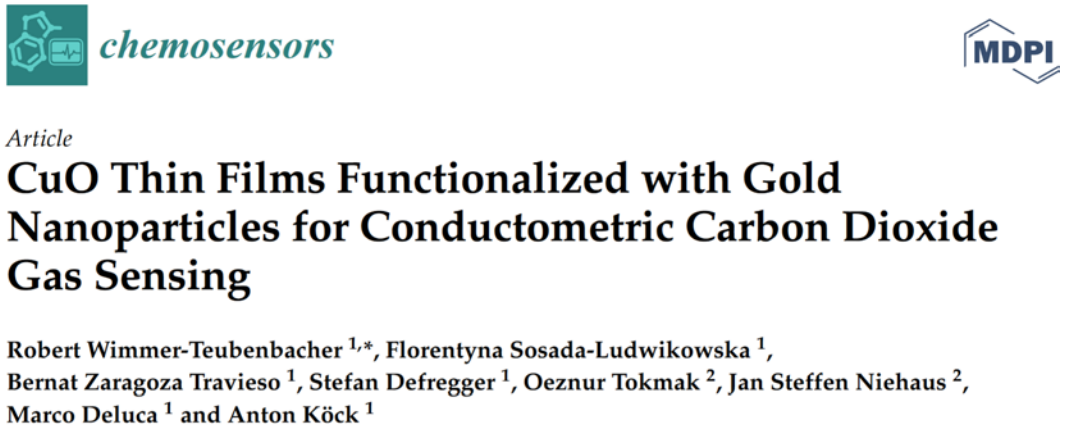
Modifier	LOD	Linear range	Response time (sec)	Gas
Reduced GrO-WO_3 nanocomposite	0.5 ppm	5–20 ppm	9 min	NO_2
Fe_2O_3 thin film	—	10–200 ppm	12	NO_2
Ppy-WO_3 hybrid nanocomposite	5 ppm	5–100 ppm	—	NO_2
ZnO hierarchial nanostructures	1 ppm	1–100 ppm	50	NO_2
Nano-$BiFeO_3$	5 ppm	—	20	SO_2
(i) RGO/SnO_2	10 ppm	10–500 ppm	2.4 min	SO_2
(ii) MWCNT/SnO_2			5.3 min	
Nano crystalline $BaSnO_3$	10 ppm	10–40 ppm	—	SO_2
LaCaFeO	3 ppm	1–10 ppm	86 s	SO_2
WO_3 nanoplates	5 ppm	1–100 ppm	3 min	NO_2
Ag/mesoporous WO_3	100 ppb	0.1–1 ppm	5.05 min	NO_2
Poly crystalline CuO	sub ppm	0.5–10 ppm	—	H_2S

5.3 METAL-OXIDE SENSORS

Metal oxides sensors for environmental monitoring

https://doi.org/10.3390/chemosensors6040056

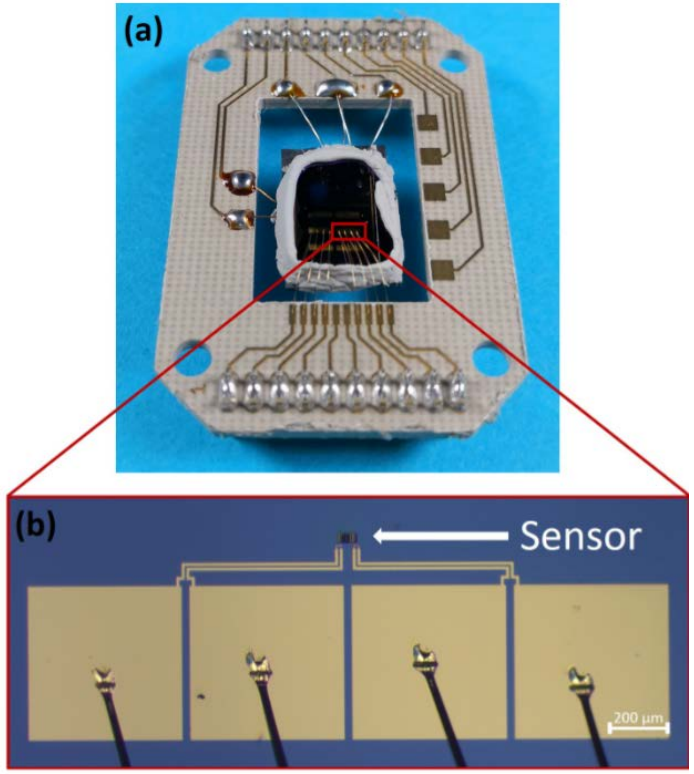
- **CuO thin film sensors** fabricated by thermal oxidation of patterned copper layers.
- Comparison among sensitivities of **pristine CuO sensors** and sensors functionalized with **gold (Au) nanoparticles.**
- Sensitivity evaluated towards CO_2 at **different humidity levels.**



- **Sensitivity** calculated as $\boldsymbol{S = \frac{R_{gas} - R_{air}}{R_{air}} \cdot 100}$, thus evaluating the sensor resistance in presence of target gas respect to the value measured in synthetic air (N_2~80%, O_2~20%)

5.3 METAL-OXIDE SENSORS

Metal oxides sensors for environmental monitoring



Functionalized material

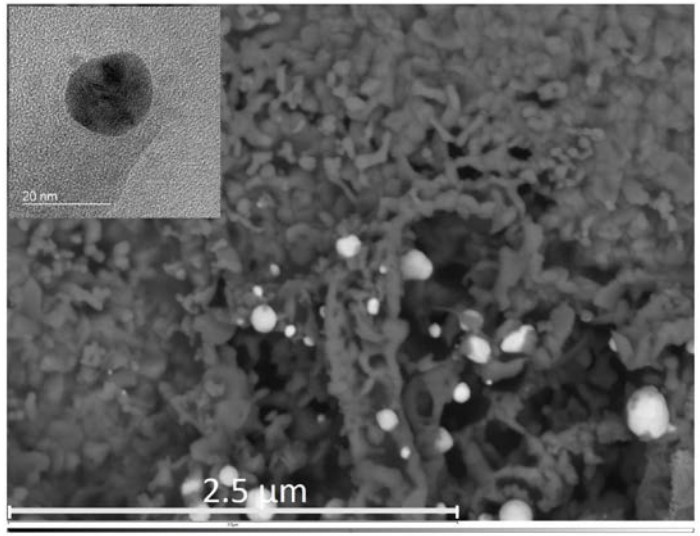


Figure 3. SEM image of the investigated sensor surface area containing Au nanoparticles. The insert shows a TEM image of a single nanoparticle.

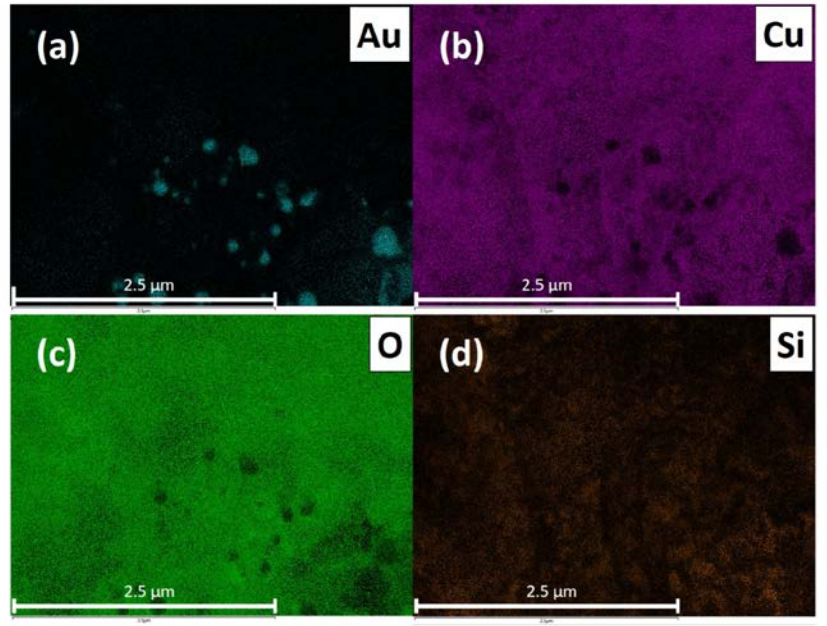


Figure 4. Elemental mapping of a 4 µm × 4 µm section on the copper oxide surface with 5 keV (primary beam energy). **(a)** Au elemental map, **(b)** Cu elemental map, **(c)** O elemental map and **(d)** Si elemental map.

5.3 METAL-OXIDE SENSORS

Metal oxides sensors for environmental monitoring

Evaluation of the gas sensors' performance towards CO_2:

- gas sensor was operated at three different temperatures (300 ◦C, 350 ◦C, 400 ◦C)
- for each operating temperature three RH levels (25%, 50%, 75%) considered.

Sensor tested at different CO_2 concentrations: 250 ppm, 500 ppm, 1000 ppm, 1500 ppm and 2000 ppm. **Target gas was flushed for 5 minutes.**

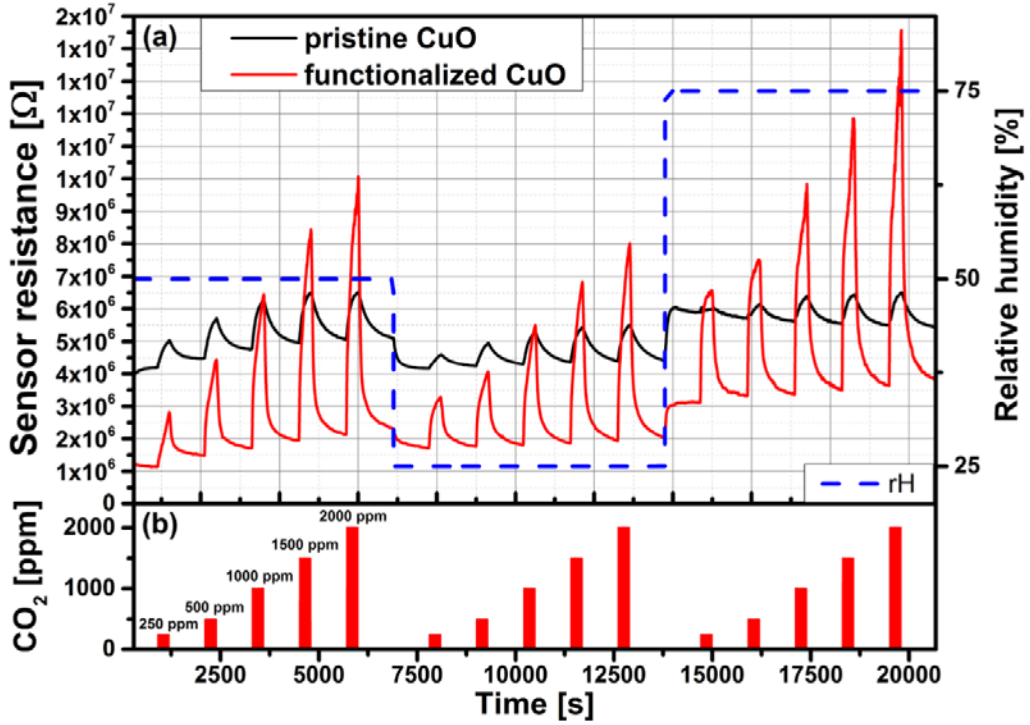
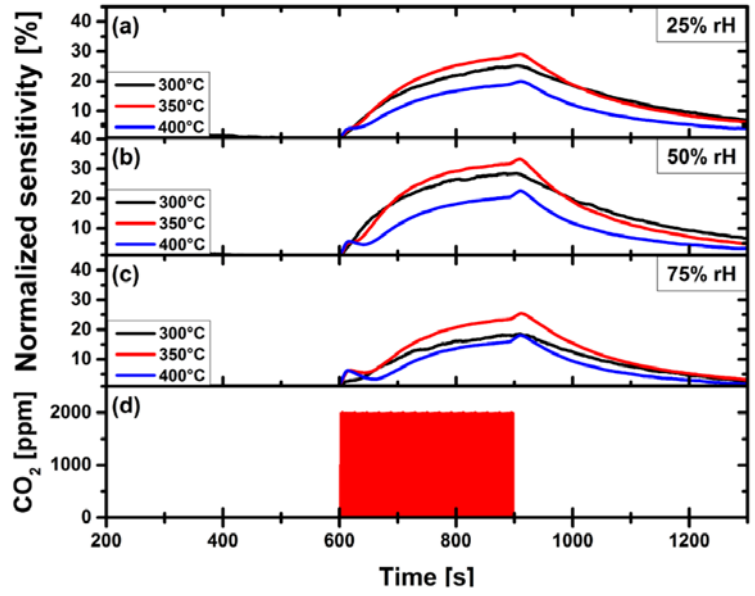


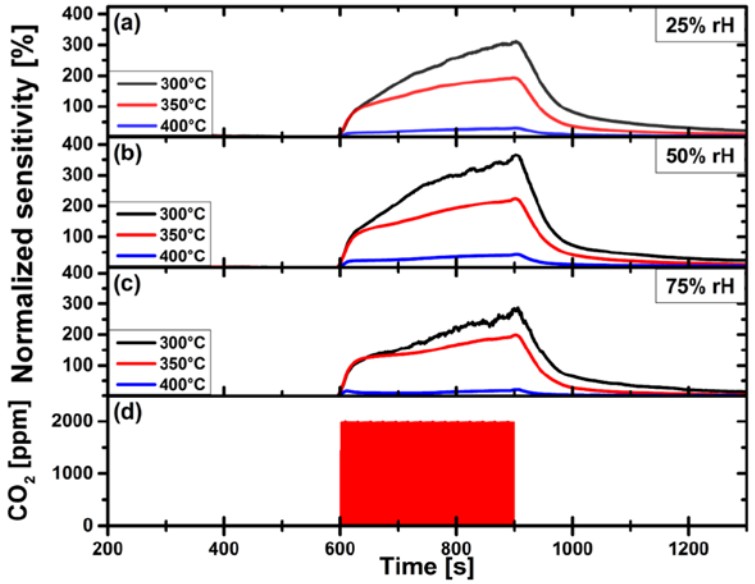
Figure 6. (**a**) Carbon dioxide measurement of the pristine and functionalized CuO gas sensors at an operation temperature of 300 °C and rH levels of 25%, 50% and 75%. (**b**) CO_2 gas pulses: 250 ppm, 500 ppm, 100 ppm, 1500 ppm and 2000 ppm.

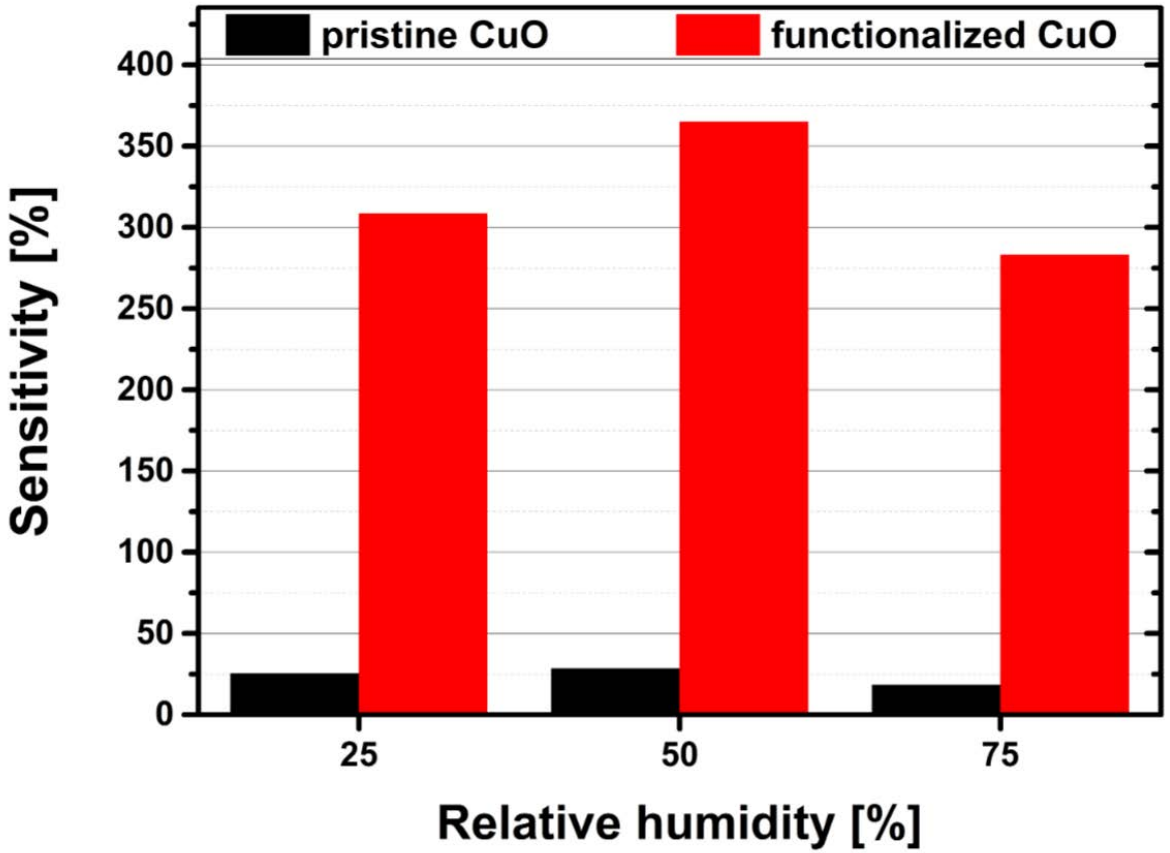
5.3 METAL-OXIDE SENSORS

Pristine CuO sensor



Functionalized CuO sensor



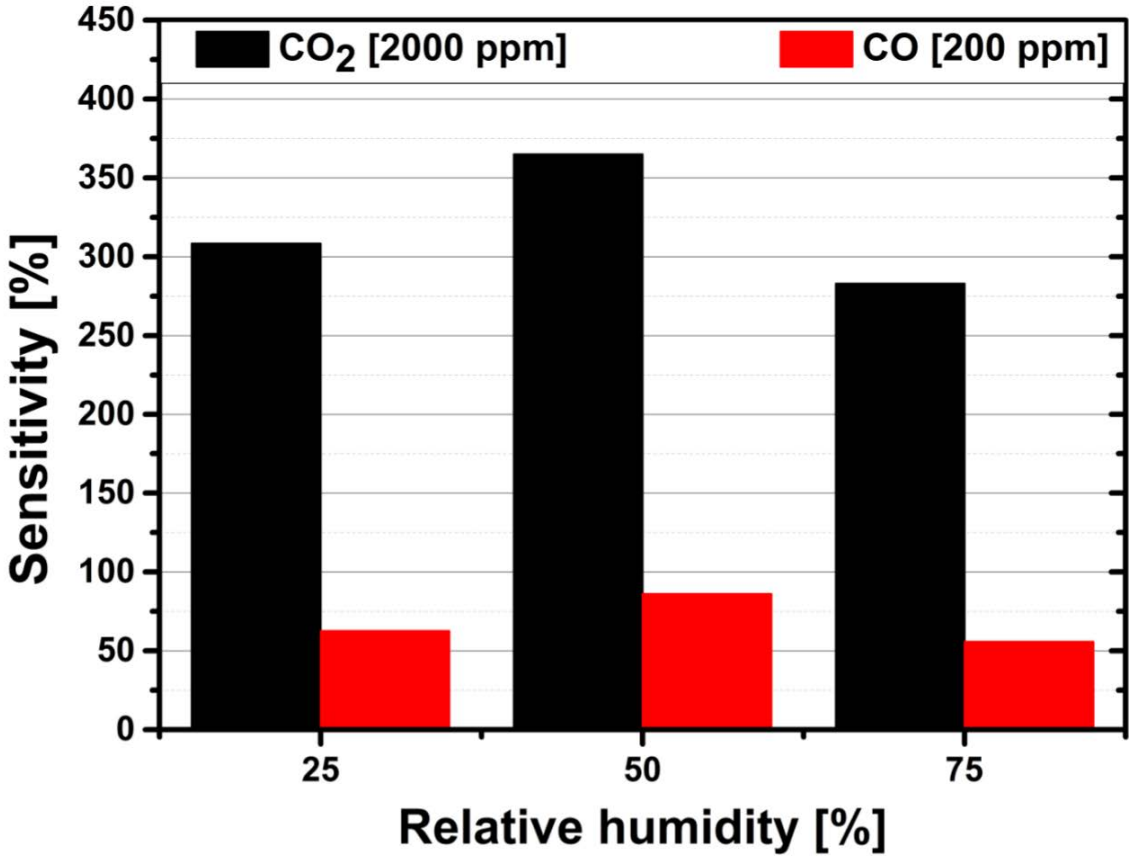


Strong performances increase for functionalized sensors with respect to the pristine sensor.

5.3 METAL-OXIDE SENSORS

Metal oxides sensors for environmental monitoring

- **Cross selectivity versus carbon monoxide (CO) was tested.**
- The CuO-based sensors show a response of less than 5% at CO concentrations around 20 ppm.
- To achieve a relevant response (>50%), the concentration of CO was increased up to 200 ppm and compared with the response to a CO_2 concentration of 2000 ppm.
- The cross selectivity was tested under different RH conditions, at 300°C.



5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Smart sensors

The current paradigm in environmental monitoring is to employ **a panel of sensors to detect different gases in a mixture rather than individual gases.**

The term **smart or intelligent sensor** refers to an instrument in digital technology **combining data acquisition and their internal processing and incorporates new features**. In general, these sensors integrate an embedded microcontroller to perform internal processing and calculations and have a bidirectional communication capability that means receiving external commands and sending measurements and status information. They are **equipped with one or more sensor matrices** for measuring the **target and influence quantities** and other integrated algorithms for the analysis of these measurements and therefore provide decision support.

The sensors to be employed can be based on electrical, optical, piezoelectric, mechanical, electrochemical, gas chromatography, mass spectrometry, or a combination of these. These sensors are trained through data and learning.

5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Smart sensors

One such a device or a system is the **electronic-nose (e-nose)** which is known to be an intelligent system which senses the presence of analytes around it. It then makes a decision and identifies a specific vapor among other analytes. Such a system comprises sensors array, necessary circuitry, and signal processing.

This kind of system works electronically and mimics the human nose. The concept of e-nose was first introduced by Persaud and Dodd and Ikegami and Kaneyasu in 1982 which consisted of **nonspecific sensors arranged in the form of array and a patterns recognition technique**.

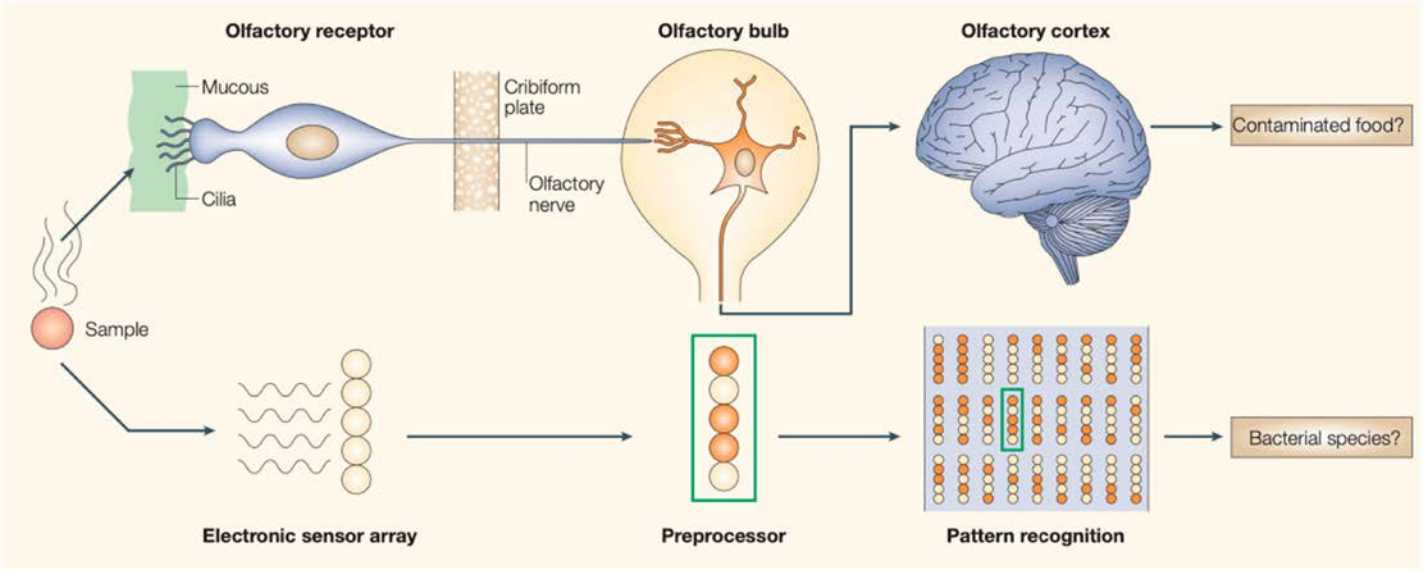
In 1988, the term “e-nose” was defined by Gardner and Bartlett as “an instrument which comprises of an array of electronic chemical sensors with **partial specificity and appropriate pattern recognition system**, capable of recognizing simple or complex odors”

5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose

An electronic nose exploits mechanical and electronic components to **emulate the human olfactory system**. Compared to the human olfactory system, an e-nose uses a **gas sensor array** to convert the gas molecular signals into electric signals.

Although **no highly specific receptors** are used in an e-nose, **unique patterns can be generated** for various odors as their fingerprints for future predictions through proper machine learning techniques.



5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose

The optimizations adopted in e-nose systems can be classified in three main categories:

- **sensitive material selection and sensor array optimization**
- **feature extraction and selection method**
- **pattern recognition method**

The general machine learning framework of the E-Nose for specific applications involves feature extraction, modeling, and drift compensation.

An e-nose produces high-dimensional time-series raw signals in responding to target gases, which contain noises and redundant information. Feature extraction preserves only the information uniquely characterizing the pattern of an odor signal. **The extracted features can be used for qualitative and quantitative analysis assisted by proper modeling techniques.**

5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose – sensor array optimization

The sensors used in the array are nonspecific and give response to vapors differently. The properties of these sensors respond to the change in the ambient. **The properties could be any of the physical property of the material**. With the advent in the nanotechnology, the sensing response of the materials has touched heights.

The most common type of sensors used in an array are MOx based.

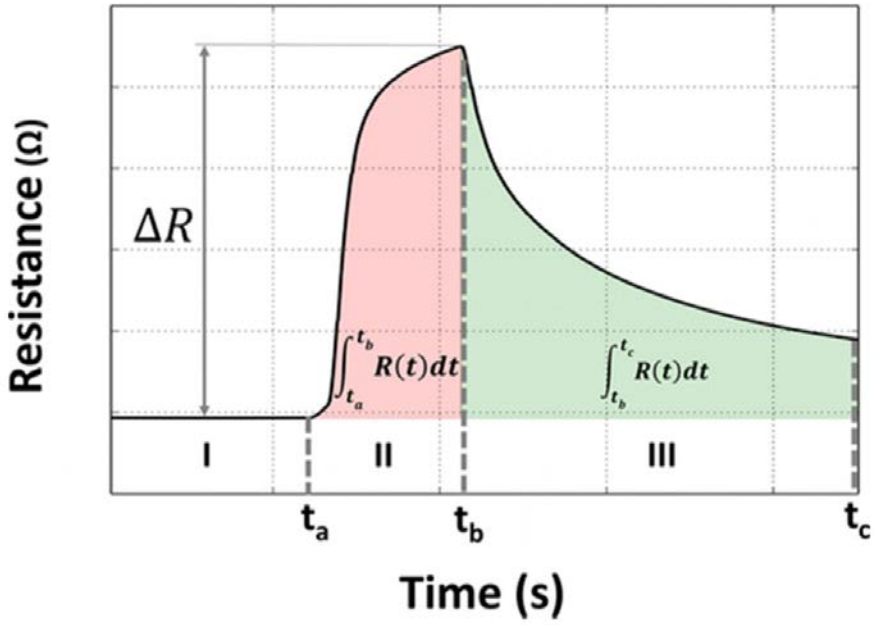
These sensors are very sensitive but operate at high temperatures, which makes their power consumption very high and increases the fabrication complexity. This problem even piles up when sensors are used in an array. Thus, **sensors with high sensitivity and room temperature operation are likely to have best suitability in an array**. Such room temperature operation can be achieved by playing with physics of materials and tuning their band gaps. This can be made possible by using heterostructures with near band gaps and literature has evidenced that this dissimilarity has been taken as an advantage in sensing applications.

5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose – feature selection

E-Nose data are collected as a **time-series array of high dimensionality that reflects the concentration of target gas**. The signal strength increases during the response phase and decreases during the sensor recovery phase in each measurement.

The analytes are **distinguished and identified based on their distinct features** at both phases in their responses. The features can either be manually extracted or learned from a neural network.



5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose – feature selection

Manually extracted features are selected based on the prior knowledge of data processing and e-nose data. Features extracted from raw signals can be either from the **time domain** or **frequency domain.**

Time-domain features can be extracted from the original response curve. Those features characterize the local pattern and can be calculated based on a small section of complete signals. Among the other, time-domain features includes: maximum response; responses at specific time; area; integral; derivative; difference; higher order derivative.

In addition to the low-level features abstracting local characteristics of e-nose signals, there are also high-level feature extraction practices such as parametric fitting with predefined functions.

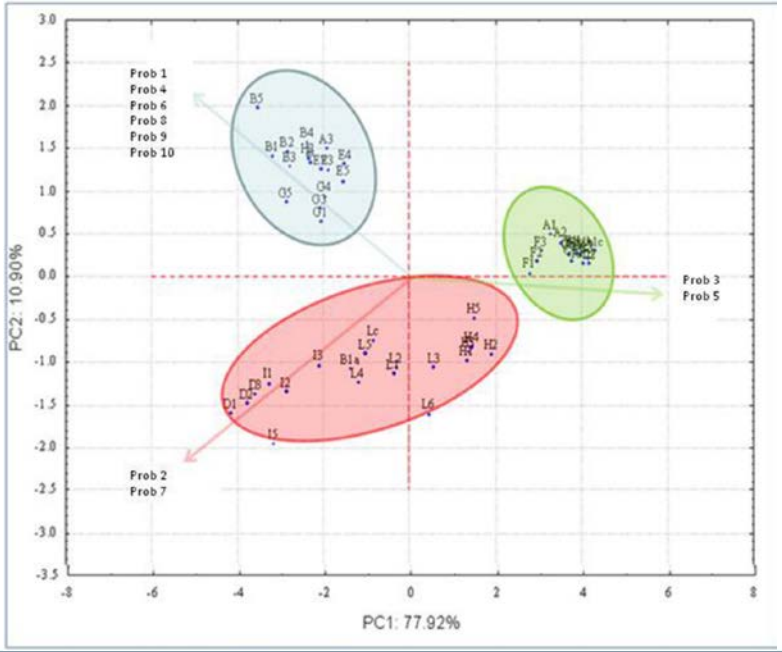
Frequency-domain features can be extracted after transforming the original time-domain signal to a frequency domain through **Fourier transform** or wavelet transform.

5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose – data analysis

In addition to manual feature extraction that requires domain knowledge about the E-Nose and gas sensors, features can also be extracted through dedicated data analysis techniques.

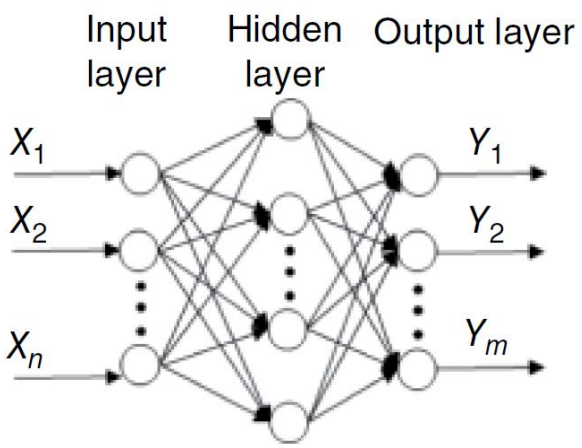
- **Multivariate analysis**, a set of techniques which operate reducing the dimensions in a multivariate problem so that the existing correlation among variables can be identified and filtered for an efficient classification or regression. One of the most common techniques in multivariate analysis is Principal Component Analysis (PCA) which is a mathematical process that transforms a number of correlated variables into number of uncorrelated variables called principal components.

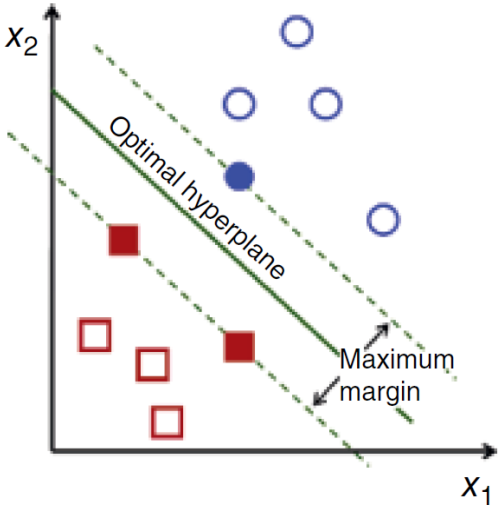


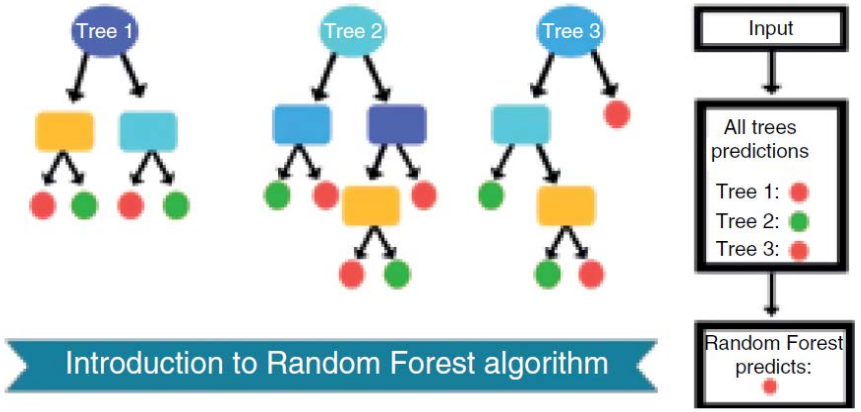
5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose – data analysis

- **Pattern recognition methods**, which include artificial neural networks, support vector machines, and machine learning algorithms (random forest). For classification purposes, these are usually based on unsupervised learning methodology. There is an input layer and a completion layer. The first layer has the input data and then through order weighing the output numerical value is given at the output layer.







5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose for environmental monitoring

Ultra-Low-Power Smart Electronic Nose System Based on Three-Dimensional Tin Oxide Nanotube Arrays

Cite this: *ACS Nano* 2018, 12, 6, 6079−6088
Publication Date: May 24, 2018

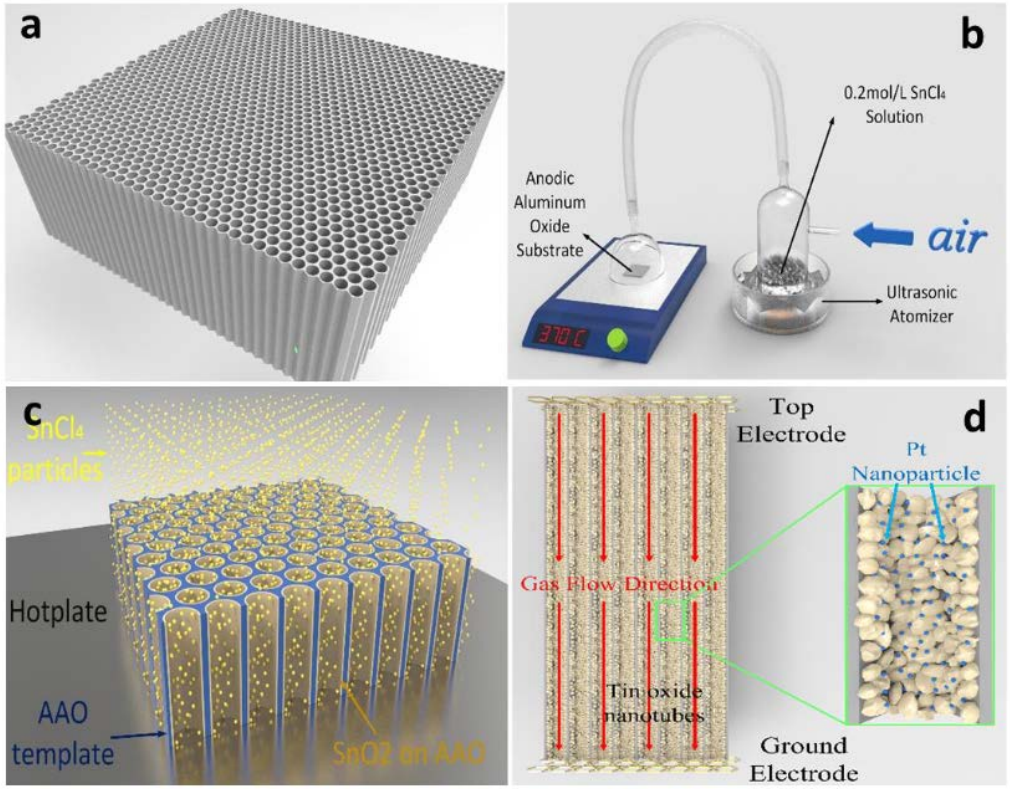
Jiaqi Chen, Zhuo Chen, Farid Boussaid, Daquan Zhang, Xiaofang Pan, Huijuan Zhao, Amine Bermak, Chi-Ying Tsui, Xinran Wang, and Zhiyong Fan*

- High-performance smart electronic nose (E-nose) system consisting of a multiplexed **tin oxide (SnO_2) nanotube sensor array**, read-out circuit, wireless data transmission unit, mobile phone receiver, and **data processing application**.
- Fabricated E-nose sensor achieved state-of-the-art sensitivity for hydrogen (H_2) and benzene detection at **room temperature**.
- **Reduced power consumptions** compared to conventional thin film SnO_2 sensor: average power consumption of ~12.5µW, representing 1‰ of required power of the state-of-art commercial SnO_2 sensors.

5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose for environmental monitoring

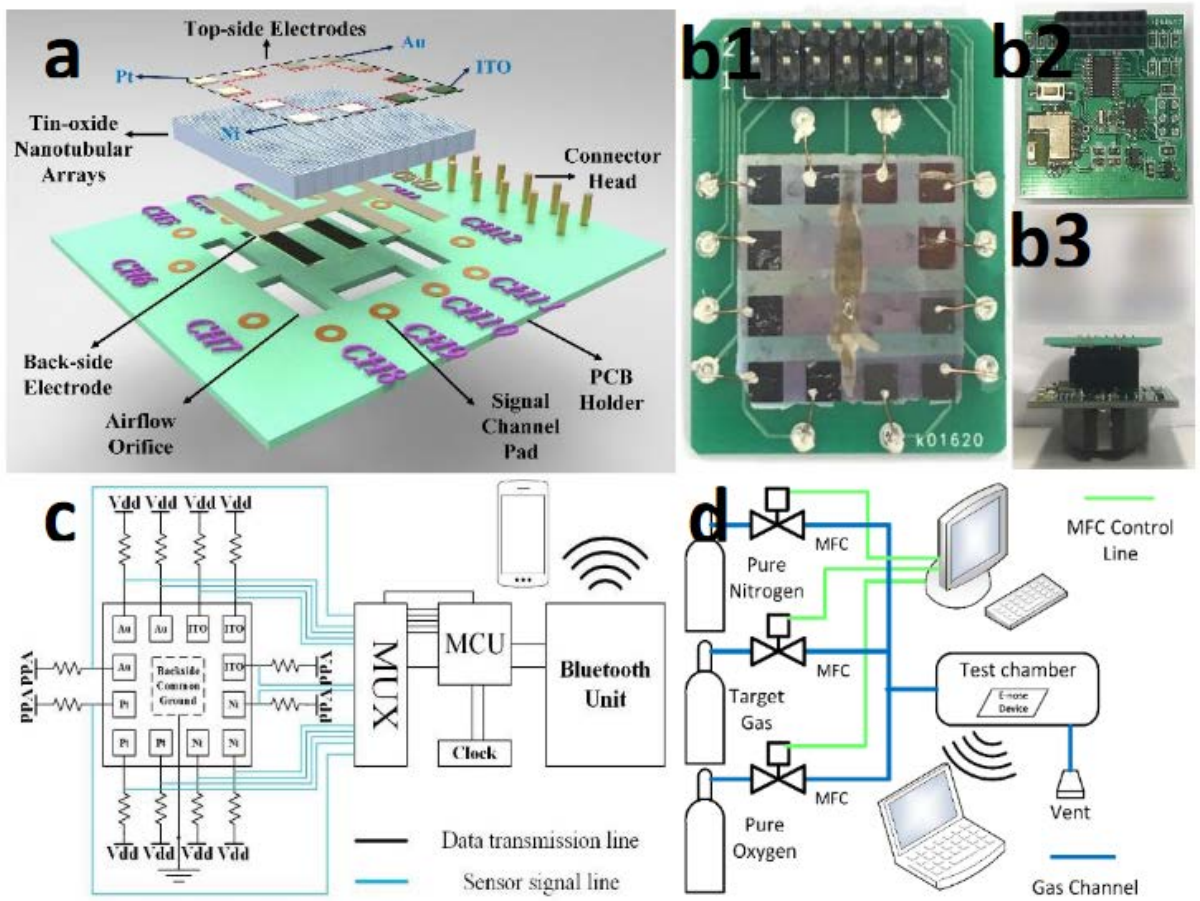
- **Nanotube array** used to enhance surface-to-volume ratio of sensing material (porous alumina membrane, PAM)
- PAM used to host sensing material: **polycrystalline SnO_2 film** with ~70nm grain size deposited into the PAM using ultrasonic spray pyrolysis (USP) to form a SnO_2 nanotube array.
- 5 nm diameter **Pt nanoparticles** decorated on the entire surface of the SnO_2 nanotubes (catalyst for H_2).
- Four different materials deposited on the top side of SnO_2 nanotubes at different locations to form the **top electrode** array: **gold** (Au), **platinum** (Pt), **nickel** (Ni) and **indium tin oxide** (ITO).



5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose for environmental monitoring

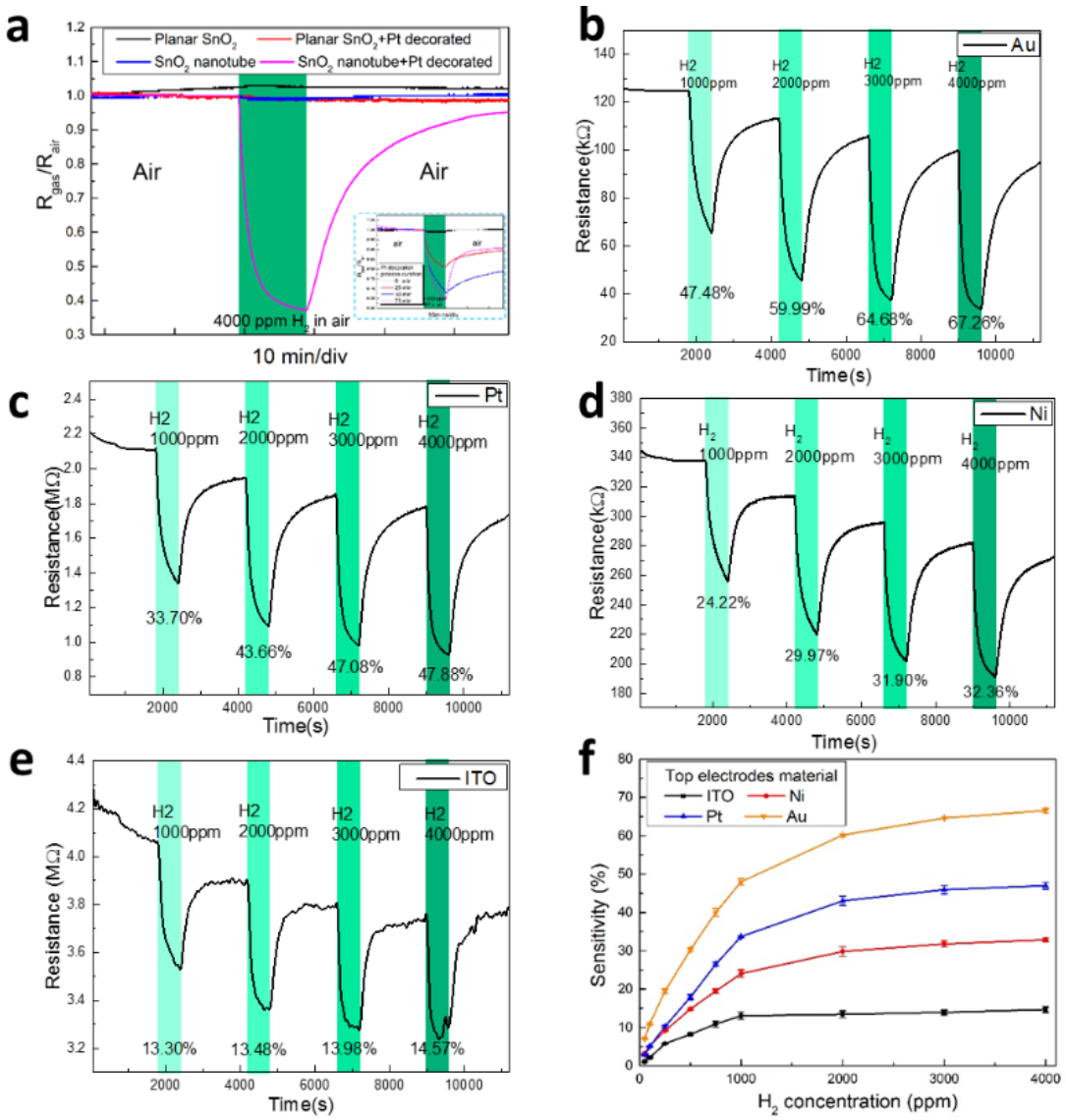
- **Monolithically integrated sensor array** packaged on a printed circuit board (PCB), with the top electrode of each sensor connected to a signal channel pad.
- Additional **data acquisition PCB**, including multiplexer and microcontroller unit (MCU) with an embedded analogue-to-digital converter.
- Target gas and balance gas injected into the test chamber using computer-programmed **mass flow controllers** (MFC) with a **proper mixture ratio**.



5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose for environmental monitoring

- **H_2 detection performances preliminary compared to different SnO2 sensors at room temperature** (planar, planar with Pt particles, nanotubes only)
- Sensor response is evaluated acquiring the conductance measurements performed by the 4 **top electrodes**: Au, Pt, Ni, and ITO.
- Electrodes' sensitivities are evaluated at different H_2 concentrations and compared. **Nonlinear (saturated) response for concentration higher than 1000 ppm**.
- **Minimum detection limit**: 10 ppm



5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

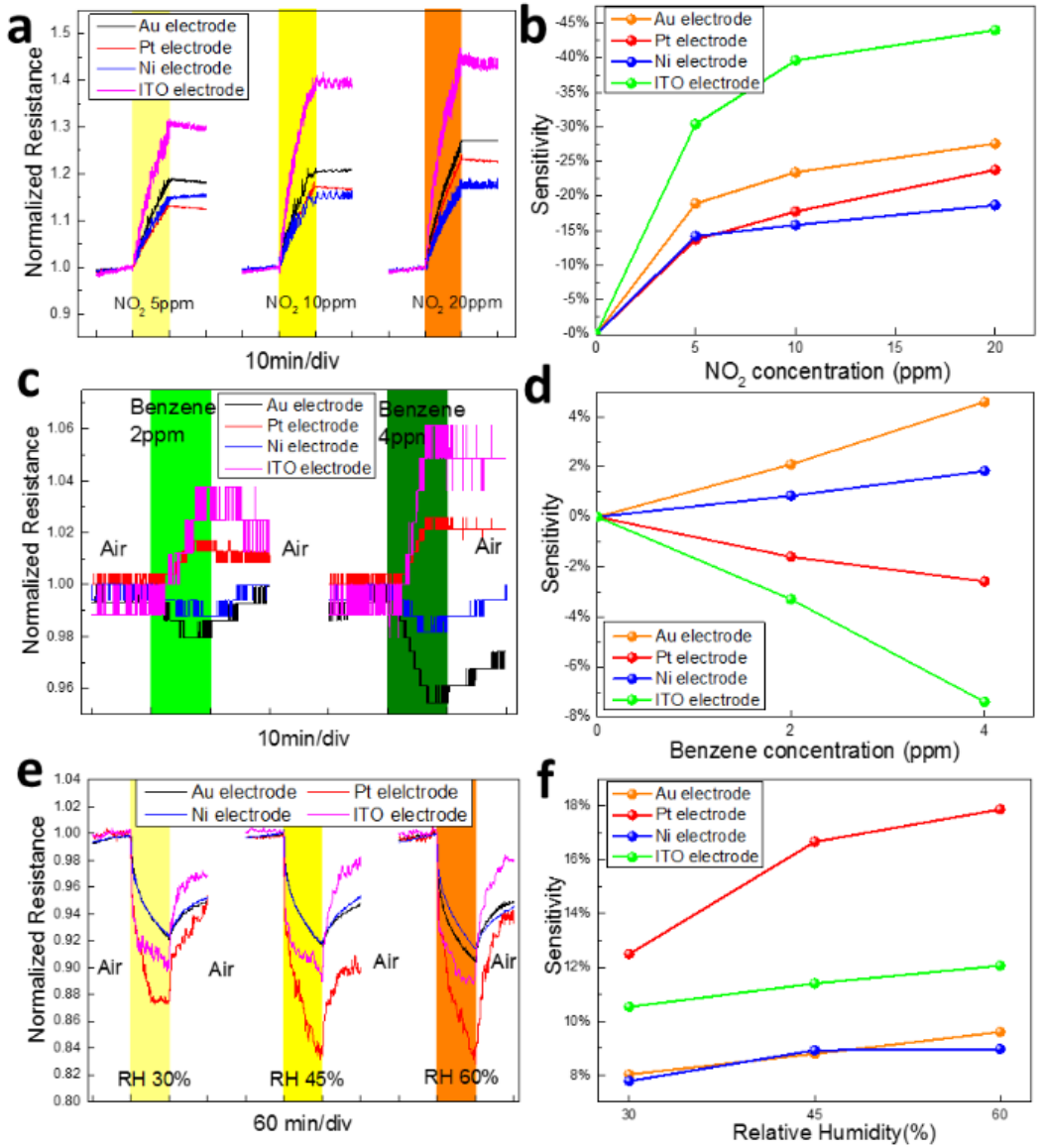
Electronic nose for environmental monitoring

Detection of nitrogen dioxide and benzene with nanotube sensors was evaluated.

- Nonlinear **exponential dependence of sensitivity** versus **NO_2** concentration. **Long sensor recovery** time due to oxidizing properties of NO_2 (~hours at room temperature)

- **Linear dependence** of sensitivity for benzene in the investigated range (**2-4 ppm**). Benzene acting as oxidizing gas for ITO and Pt electrodes and as reducing gas for Au and Ni electrode sensors.

Evaluation of the impact of humidity on sensors considering 30%, 45% and 60% relative humidity levels.



5.4 SMART SENSORS FOR ENVIRONMENTAL MONITORING

Electronic nose for environmental monitoring

Learning vector quantization (LVQ) used as identification tool.

- Training data used to define training vectors. Testing data defines testing vector to be discriminated by comparison with training data.
- **Vector orientation representing the signature** of a given gas type.
- When an unknown gas is sensed by the E-nose, the **orientation and length of the acquired vector** associated to its **sensitivity pattern** can be obtained and **matched with the vectors pre-stored in the identification library.**