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Title

A COMPREHENSIVE APPROACH TO NOXIOUS GASES DETECTION

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DOTTORATO DI RICERCA IN

INGEGNERIA DEI SISTEMI SENSORIALI E DI APPRENDIMENTO

XX CICLO

Titolo della tesi

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Foreword

This thesis provides the reader with a summary of the activities carried out within a three years cooperation between the Sensors and Microsystems Group of the Electronics Department at the University of Tor Vergata and “Centro Sviluppo Materiali SpA”.

The framework within which this study has been developed is the “*Innovative Materials and Technologies for Advanced Sectors*” Industrial Project, a peculiar framework that required a huge effort to be spent in keeping a result-oriented attitude during the entire PhD Course.

Thus, the reader should be aware that the discussion will often appear much less theoretical that in a standard PhD thesis, while it will be strongly focused on those practical aspects that could lead to an industrial implementation of the results that have been achieved.

The following list reports the main subjects covered during the three years period and that will be discussed in the following chapters:

- Development of a database on the state of the art of gas sensors;
- Development of a prototype of an innovative Carbon Monoxide sensor;
- Development of a prototype of an innovative DMMP sensor;
- Feasibility study about the potential application of QMB biosensors for CO and DMMP sensing.

It is worth pointing out that the each specific topic herein discussed requires the reader to keep an interdisciplinary approach, as all the results were obtained within a strong cooperation of several different experiences, such as:

- the industrial know-how at “Centro Sviluppo Materiali”;
- the strong experience in multisensors system design of the Electronics Department of Tor Vergata;
- the deep knowledge of sensitive layer synthesis at the Chemistry Department of Tor Vergata;
- the conditioning electronics know-how at the IMM Institute of CNR – Tor Vergata;
- the experience in Surface Acoustic Devices technologies at the IDAC Institute of CNR – Tor Vergata.
- the research activities at the Food Science Department of the University of Teramo.

I would like to acknowledge the people who supported the work and contributed in achieving the results.

Chapter 1

Database on the state of the art of gas sensors

1.1 Introduction

One of the main implications of an Industrial Project is the possibility of implementing the results achieved during the research phase and to develop a product which could be easily marketed.

Applying the above concepts to the matter of this work results in the extremely practical definition of the main goals that have been pursued:

- the realization of a prototype of a Carbon Monoxide sensor;
- the realization of a prototype of a DMMP sensor.

Obtaining the above goals required:

- a deep understanding of the working principles of the state-of-the-art already commercially available devices;
- the possibility of analyzing their performances and eventual limitations;
- the ability to focus the research activities on the innovative aspects which could lead to the development of a new sensor;
- know-how sharing among all the people involved in the realization of such products.

The latter immediately gained a relevant importance within the frame of this work, though being not extremely pertinent to a PhD Course in Electronics.

The reason can be easily explained in that a tool which enables the users to share theoretical and practical information concerning a production process provides the users themselves with numerous advantages.

Some of those advantages can be easily cited, as a system of that kind allows:

- easy understanding of the background the users are involved within, as far as the information model is complete;
- fast market analysis, as far as the characteristics of commercially available devices are detailed and described according to the information model;
- fast planning and identification of the feasible design strategies, in that the model description should avoid taking into account not feasible solutions.

Hence, part of the effort has been spent in developing a database of the working principles of the state of the art gas sensors.

The following paragraphs deal with the various phases that lead to the realization of the system:

- analysis of the scenario;
- information modelling: ENTITIES and ATTRIBUTES definition;
- architecture implementation;
- content development.

1.2 Scenario analysis

Databases design techniques often require a preliminary step that consists in determining the scenario within which the users will operate the system.

In the case here presented, the set of eventual profiles ranged from expert individuals to beginners, the latter requiring information to be provided with simple though complete descriptions.

Moreover, completeness of description was a milestone to be achieved, as the database was thought to cover the working principles of gas sensors and all their implications.

Content development should then be carried out taking into account an interdisciplinary approach, thus describing concepts developed within a wide range of fields, including:

- *chemistry*: chemical agents, sensing layers and standard analytical techniques;
- *electronics*: transduction elements and conditioning circuits ;
- *technology*: including the technological implication involved in the realization of each of the above elements;
- *marketing*: products and producers within the sensor field;
- *bibliography*: R&D institutes and literature.

Any of the above could be selected for accessing the database and should lead to retrieving equivalent data.

1.3 Information modelling [1-10]

Defining the correct model of information is the most important step in databases design, on which depends the usability of the system along with its usefulness in terms of clarity and completeness of description.

Achieving the above specifications when describing a huge interdisciplinary scientific field was really hard, requiring a lot of variables to be taken into account.

The model developed within this work will be discussed in the following.

The proposed description is based on the interpretation below:

Developing a gas sensor consists in designing a device which is able to detect concentration changes of a chemical (or biological) species, providing an easily measurable output signal, somehow proportional to the concentration change.

Such a device will be said to implement a transduction technique, whose character depends on the physical process which is involved in the interaction between the sensed species, defined as "analyte", and the sensor itself.

The above statement implies that the model of such a transduction technique should be composed by a number of building blocks, including:

- *Analyte*: chemical or biological;
- *Chemically Interactive Material (CIM)*: the sensitive layer where interaction between the sensor and the analyte takes place;
- *Transduction Element*: the element which detects the changes of a CIM's property as a consequence of the interaction with the sensed species;
- *Auxiliary Device*: the part of the sensor which keeps the optimal conditions for the system to operate.

A *Sensor* results from a peculiar arrangement of CIM, Transduction Element and Auxiliary Device.

The *Transduction Technique* results from the combination of a Sensor and *Transduction Electronics*, eventually coupled with an external Auxiliary Device (i.e.: an optical source), to detect concentration changes of a chemical analyte.

Fig. 1 reports a block scheme of the information model as implemented in the DB.

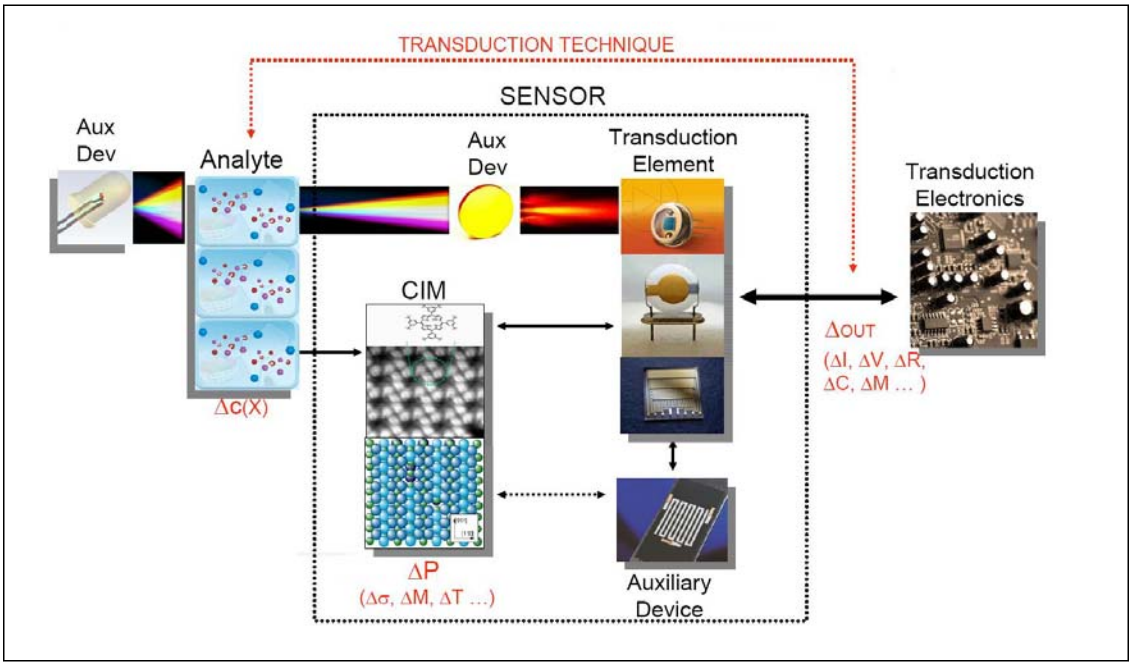


Fig. 1: schematic description of the model implemented in the database.

According to the most common database design procedure, each of the above blocks has been described by an ENTITY (a table) and a set of ATTRIBUTES.

The next sections report more detailed information concerning the entities related to the main blocks as well as the entities which complete the description:

- *Chemical Sensors Technologies;*
- *Standard Analytical Techniques;*
- *Products;*
- *R&D Institutes and Industries;*
- *Literature*

1.4 Model description

The model was validated using real examples as references.

Fig. 2 reports a block scheme of a metal oxide sensor, where the various modules could be identified:

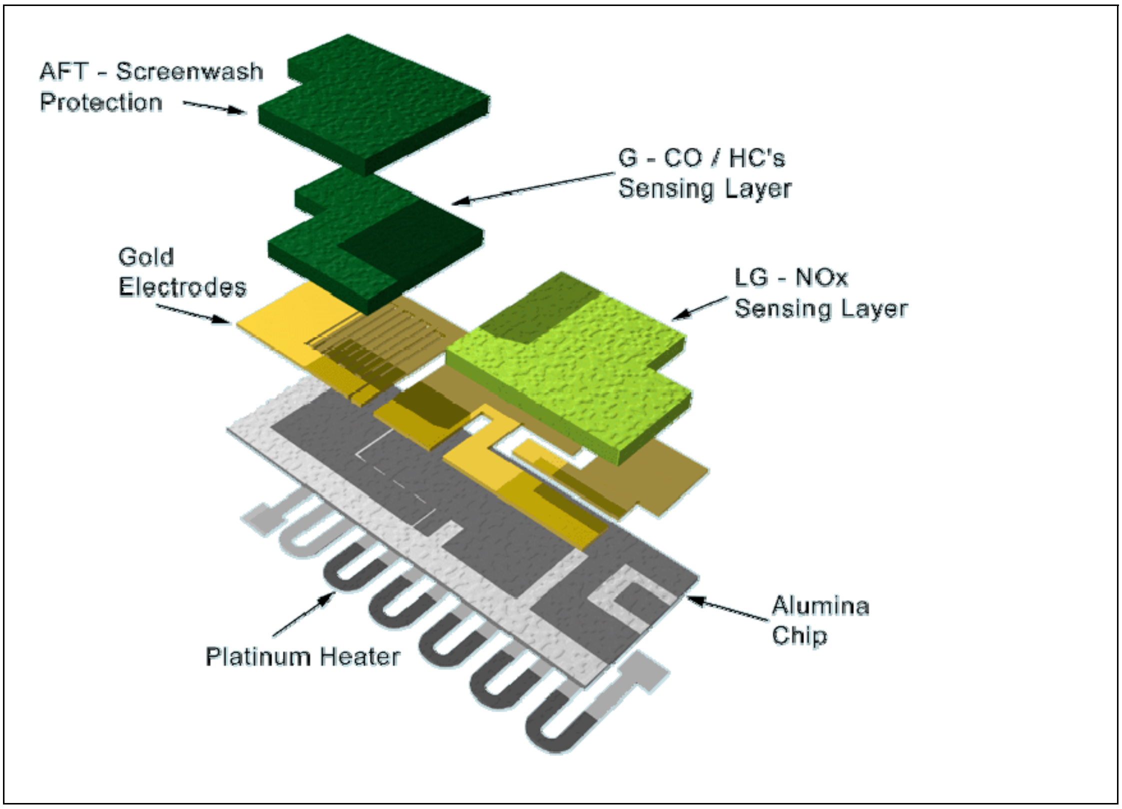


Fig. 2: block scheme of a MOX sensor.

- the CIM is a metal oxide layered on top of a pattern of interdigital electrodes;
- the electrodes represent the transduction element;
- the auxiliary device is a platinum heater;
- the interaction mechanism between the analyte and the sensing layer is a conductivity change: thus the transduction technique will be referred to as the *conductivity change*.

The model is then based on the transduction technique, which consists in implementing a procedure that allows detecting concentration changes of a target gas (analyte) by means of a sensor.

The criteria for identifying a transduction technique are based on the interaction mechanism between the analyte and the CIM, as reported in the following table:

ANALYTE-CIM Interaction	***TRANSDUCTION TECHNIQUES***	***CATEGORY***
Mass	Mass CHANGE	Acoustic/mechanical
Conductivity	Electrical conductivity CHANGE	Electrical
Temperature	Temperature CHANGE	Thermal
Refractive index	Refractive index CHANGE	Optical
Absorbance	Absorbance CHANGE	Optical
Work function	Work function CHANGE	Electrical
Electrochemical potential	Electrochemical potential CHANGE	Electrochemical
Ionic current	Ionic conductivity CHANGE	Electrochemical

Tab. 1: classification of the transduction techniques described in the DB.

1.4.1 Total Sensitivity of a Transduction Technique [11]

The main characteristic of a transduction technique is its TOTAL SENSITIVITY, defined as:

$$\mathbf{S_{TOT} = S_I * S_T * (S_A * S_F * S_{AD});}$$

where:

- S_{TOT} = total sensitivity;
- S_I = intrinsic sensitivity of the sensing layer (CIM);
- S_T = sensitivity of the transduction element;
- S_A * S_F * S_{AD}= sensitivity of the transduction electronics (amplification, filtering and A/D conversion).

The following table reports the intrinsic sensitivities of some of the CIM described in the database:

Interaction	$\mathbf{S_I}$	**CIM**
Mass	$\partial m/\partial c_{(X)}$	Organic layers
Conductivity	$\partial \sigma/\partial c_{(X)}$	Metal oxides
Temperature	$\partial T/\partial c_{(X)}$	Catalytic metals

Tab. 2: intrinsic sensitivities related to some transduction techniques.

A similar approach has been used for the transduction elements, as in Tab. 3:

Interaction	$\mathbf{S_T}$	**Transduction element**
Mass	$\partial f / \partial m$	TSMR
Conductivity	$\partial G / \partial \sigma$	Interdigital electrodes
Temperature	$\partial T / \partial c_{(X)}$	RTD

Tab. 3: sensitivities of the transduction elements.

Then the total sensitivities may be expressed as in the following table:

Interaction	$\mathbf{S_{TOT}}$	**Typical sensor**
Mass	$S_{TOT} = \frac{\partial m}{\partial c_{(X)}} * \frac{\partial f}{\partial m} = \frac{\partial f}{\partial c_{(X)}}$	QMB
Conductivity	$S_{TOT} = \frac{\partial \sigma}{\partial c_{(X)}} * \frac{\partial G}{\partial \sigma} = \frac{\partial G}{\partial c_{(X)}}$	MOX
Temperature	$S_{TOT} = \frac{\partial T}{\partial c_{(X)}} * \frac{\partial R}{\partial T} = \frac{\partial R}{\partial c_{(X)}}$	Pellistor

Tab. 4: total sensitivities of the main transduction techniques.

Tab. 4 also reports the most common sensors related to each transduction technique.

1.5 Architectural implementation

The model described in the previous sections has been implemented in collaboration with CSM personnel on a CSM's proprietary platform.

A detailed presentation of the development environment would be out of the scopes of this thesis, by the way the next pictures describe the user interface and the some available functionalities.

The main graphical user interface is the navigation page (Fig. 3), which allows the user to access information using any of the entities as starting point.

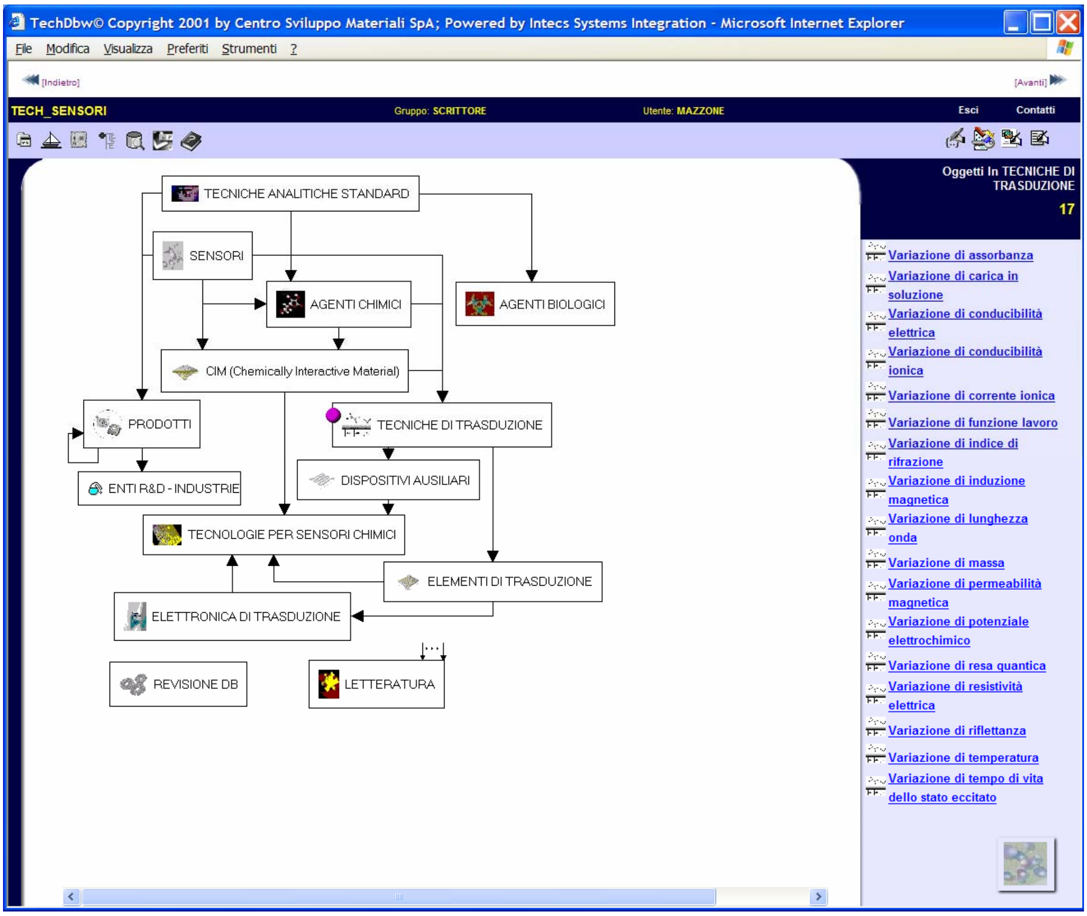


Fig. 3: database "navigation" page.

A search engine is also available (Fig. 4) allowing the user defining the search criteria.

Each object has a corresponding description page (Fig. 5), which lists all the objects attributes.

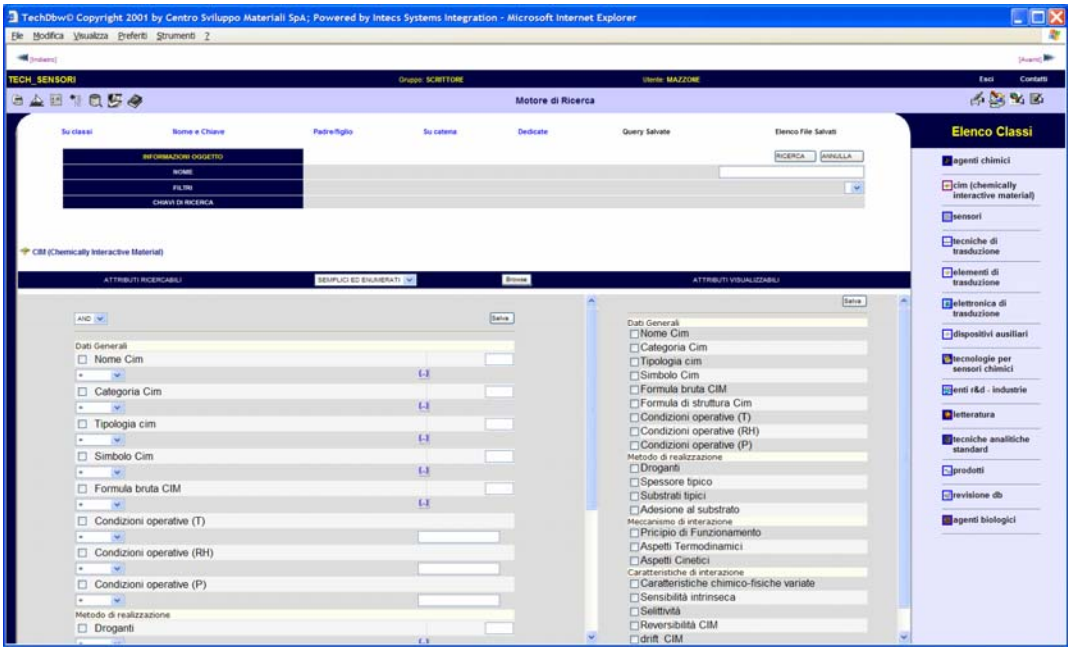
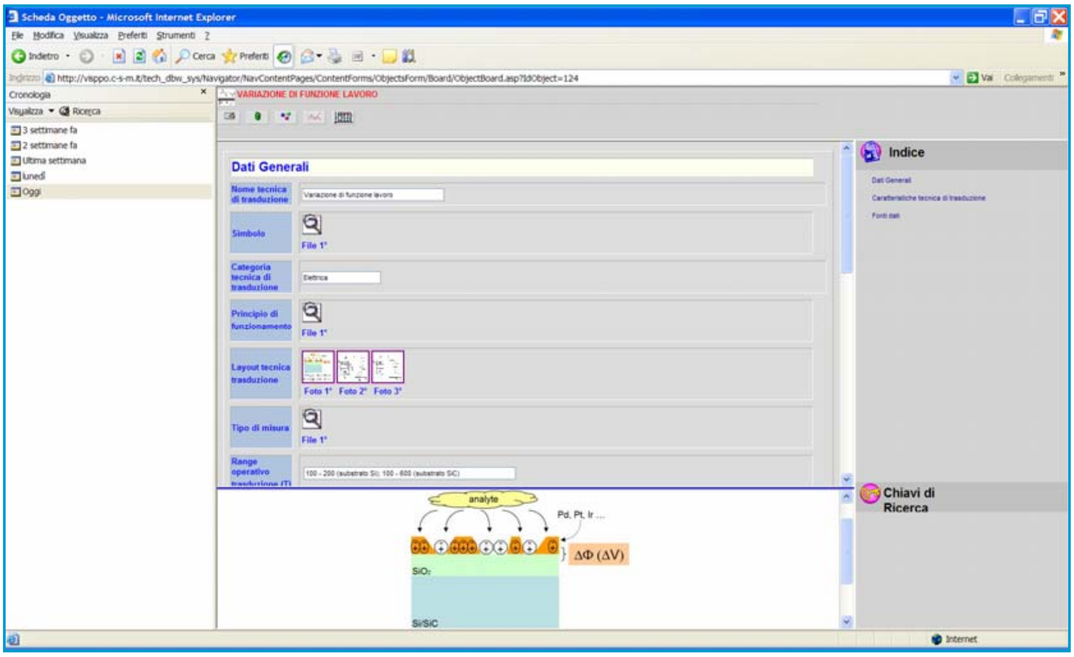


Fig. 4: DB search page.



http://visppo.c-s-m.it/tech_dbw_sys/Navigator/NavContentPages/ContentForms/ObjectsForm/Board/ObjectBoard.asp?IdObject=124

Nome tecnica di trasduzione: Variazione di funzione lavoro

Categoria tecnica di trasduzione: Elettrica

Range operativo trasduzione (T): 100 - 200 (substrato Si); 100 - 600 (substrato SiC)

Fig. 5: object description page.

1.5.1 Chemical Agents Entity [12-17]

The Chemical Analytes represent the species to be detected and their description has been obtained with the attributes reported in the following table.

Attributes categories	**Attributes**
General Data	Name IUPAC name CAS registry number RTECS registry number State @ 25 °C Symbol Chemical formula Chemical Structure Toxicity CWA category
Chemical-Physical properties	Atomic weight (u.m.a.) Molecular weight (u.m.a.) Odour Colour Vapour Phase density Liquid Phase density Solid Phase density Melting Point Boiling Point Flash Point Vapour Pressure a 25°C Volatility Solubility Heat of vaporization Decomposition Temperature Critical Temperature Stability (**c. s.**) L.E.L. U.E.L. Redox properties
Spectral data	IR spectrum Mass spectrum NMR spectrum VIS spectrum Spectral conditions
Physiological effects	Median Lethal Dosage Median Incapacitating Dosage Means of contact Eye toxicity Skin toxicity Respiratory Airways toxicity Physiological action Rate of action Detoxification Rate
Security information	Treatments Environmental Persistence Decontamination

1.5.2 Chemically Interactive Material (CIM) Entity [18-27]

The Chemically Interactive Material represents the interface between a sensor and an analyte, more specifically it represents the site of interaction between the target species and the sensor.

The description of the CIM has been obtained with the attributes reported in the following table.

Attributes categories	**Attributes**
General data	Name
	Category
	Typology
	Symbol
	Chemical formula
	Chemical structure
	Operating temperature
	Operating RH
	Operating pressure
Preparation method	Preparation technique
	Dopants
	Deposition technique
	Typical layer thickness
	Typical substrates
	Adhesion to substrate
Interaction mechanism	Working principle
	Thermal aspects
	Kinetic aspects
Interaction characteristics	Changing properties
	Intrinsic sensitivity (SI)
	Selectivity
	Reversibility
	Drift

1.5.3 Transduction Element Entity [28-37]

The Transduction Element represents the element which is able to detect a change of a determined property of the CIM when interaction with the sensed species occurs.

The transduction element has been described using the attributes reported in the following table.

Attributes categories	**Attributes**
General data	Name
	Description
	Layout
	Working principle
Characteristics	Sensitivity
	Noise
	Drift

1.5.4 Auxiliary Device Entity [38-43]

The Auxiliary Device entity includes the technological elements which may be used to keep the operating conditions required for implementing a transduction technique.

Some examples of auxiliary devices are listed below:

- Radiation sources;
- Optical filters and lenses;
- Choppers;
- Mirrors;
- Prisms;
- Heaters.

The auxiliary elements have been described using the attributes reported in the following table.

Attributes categories	**Attributes**
General data	Name Description
Typical layout	Layout
Typical composition	Composition

1.5.5 Sensor Entity [44-48]

The Sensor is a device basically composed by the CIM and the Transduction Element.

The sensor, coupled with proper Transduction Electronics and Auxiliary Devices, is able to detect a Chemical or Biological species, thus implementing a Transduction Technique.

The sensor has been described using the attributes reported in the following table.

Attributes categories	**Attributes**
General data	Name
	Category
	Structure
Reading technique	Technique layout
	I/O function
	Power supply
Characteristics	Sensitivity
	Selectivity
	Reversibility
	Resolution
	Noise
	Stability
	Drift
	Temperature dependence
	RH dependence
	Pressure dependence

1.5.6 Transduction Technique Entity [44-48]

The Transduction Technique represents the process which allows detecting a chemical or biological species by means of a sensor, whose output signal is proportional to the concentration change of the analyte.

The transduction technique has been described using the attributes reported in the following table.

Attributes categories	Attributes
General data	Name
	Symbol
	Category
	Working principle
	Block scheme
	Measurement
	Operating temperature range
	Operating RH range
	Operating pressure range
	Operating magnetic field range
Characteristics	Sensitivity (ST)
	Selectivity
	Resolution
	Drift
	Typical applications
	State-of-the-art
	Technological limitations
	Means of improvement

1.5.7 Transduction Electronics Entity [49-53]

The Transduction Electronics entity includes the descriptions of the most common circuital solutions adopted for conditioning a sensor's output signal.

The following table reports the set of attributes used for describing the elements of this entity.

Attributes categories	**Attributes**
General data	Circuit name
	Description
	Circuit typology
	I/O function
Typical layout	Circuit layout

1.5.8 Chemical Sensor Technologies Entity [54-56]

This entity includes the descriptions of the most common technologies that may be used within the field of sensors development and applications, including:

- synthesis and deposition of sensitive layers;
- realization of transduction elements;
- realization of auxiliary devices.

The following table reports the set of attributes used for describing the elements of this entity.

Attributes categories	**Attributes**
General data	Name
	Use
	Tools
	Typical substrates
Process description	Process phases
Typical layout	Process layout

1.5.9 Products Entity [57-69]

The PRODUCTS entity reports the information about the products for a selected application.

A product can be described by the following set of attributes.

Attributes categories	**Attributes**
General data	Model
Performances	Range Sensibility Selectivity Calibration curve Power consumption (qualitative) Response time Stability Temperature dependence RH dependence Pressure dependence Lifetime
Mechanical data	Dimensions Packaging Weight
Operating conditions	Device temperature Environmental temperature RH Flow Pressure
Electrical characteristics	Operating voltage Operating current Heater operating voltage Heater operating current Typical frequency Power consumption Output Warm-up Time
Commercial Data	Availability Price Data-sheet

1.5.10 R&D Institutes and Industries Entity [57-69]

This entity reports the list and description of the institutes which are involved in sensors production and applications.

The description is obtained using the following set of attributes.

Attributes categories	**Attributes**
General data	Name
	Type
Administration	Address
	Town
	Postal Code
	Nation
Factory	Address
	Town
	Postal Code
	Nation
Contacts	Website
	Contacts

1.5.11 Literature Entity

This entity reports the information about the available literature products for a selected argument.

All entities link to literature and description of all of them is obtained through the following set of attributes.

Attributes categories	**Attributes**
General data	Resource type
	Subject
	Title
	Authors
	Date of publication
	Website

1.5.12 Standard Analytical Techniques Entity [70]

This entity describes the most common analytical procedures used for detecting a selected analyte.

The description is obtained through the following set of attributes.

Attributes categories	Attributes
General data	Name
	Acronym
	Description

1.5.13 Biological Analytes Entity [16]

This entity describes the biological agents that may be detected using a selected transduction technique.

A biological analyte can be described by the following set of attributes.

Attributes categories	**Attributes**
General data	Name
	Related disease
	Type of agent
	BWA category
	Biochemical structure
	Molecular weight (u.m.a.)
	Agent origin
	Agent description
Epidemiological data	Transmissible person to person
	Infectivity rate
	Mortality rate
	Stability
	Natural hosts
	Means of delivery
	Means of contact
Pathological data	Incubation period
	Duration of illness
	Rate of action
	Toxicity
	Symptoms
Countermeasures	Vaccination
	Treatments

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Chapter 2

Development of QMB sensors based on Fe-porphyrins for Carbon Monoxide detection

2.1 Introduction [1-2]

Carbon monoxide is a colourless, odourless gas which is formed when carbon containing substances are burned with an insufficient air supply.

The combustion of fuels, such as petrol, gas, coal and woods generate CO emissions, while the main source of carbon monoxide pollution in urban areas are motor vehicles.

The importance of measuring CO depends mainly on its high toxicity and the following list reports some of the application areas where carbon monoxide sensors are used:

- Domestic safety;
- Industrial safety;
- Medicine;
- Automotive;
- Emissions (OAQ);

Carbon Monoxide is a colourless, odourless gas which has no taste and is also non-irritating, it is flammable and mixtures of carbon monoxide and air in the flammable range will ignite if a flame or a spark is present.

The importance of measuring CO is based on its high toxicity even at lower concentration levels.

This is why it was chosen as a target analyte for the studies carried out during the course.

2.2 Health effects of carbon monoxide [2]

When carbon monoxide is inhaled it passes through the upper respiratory system down into the lungs.

Almost all the carbon monoxide entering the body leaves the lungs and passes directly into the bloodstream through the alveoli (air sacs).

Carbon monoxide is not changed chemically while in the body and interferes with the ability of the blood to transport oxygen.

Haemoglobin, a protein present in the red blood cells, normally binds oxygen (to form *oxyhaemoglobin*) and transports it to all parts of the body.

Carbon monoxide competes with oxygen and binds to haemoglobin (to form *carboxyhaemoglobin* or COHb) much more easily.

Carbon monoxide is therefore a chemical asphyxiant, meanings that it prevents sufficient oxygen from reaching the tissues, the most sensitive being the nervous system and the heart.

The effects of carbon monoxide in the body are determined by the amount inhaled.

Factors which affect the dose include:

- concentration of carbon monoxide in air;
- length of exposure;
- rate of work (how much air we inhale).

Three other factors that determine the effect carbon monoxide has on the body are:

- age;
- individual susceptibility;

- smoker versus non-smoker (smokers have higher levels of carbon monoxide in their blood and may experience harmful effects at lower concentrations).

Prolonged or repeated exposures to low levels of CO are typical at workplaces and sources include cigarette smoking and motor vehicles.

At airborne concentrations of about 50 ppm, specific effects may not be immediately noticeable, but exposure may reduce:

- alertness;
- perception;
- performance of fine motor tasks.

These subtle effects may not be recognized by the person affected and they usually occur at or above standards established for workplace exposure.

Similar effects are produced by other causes which may be confused with those produced by carbon monoxide, including:

- common drugs;
- beverages;
- food;
- fatigue.

Effects produced by exposure to carbon monoxide are generally reversible, that is: the effects disappear following removal from exposure.

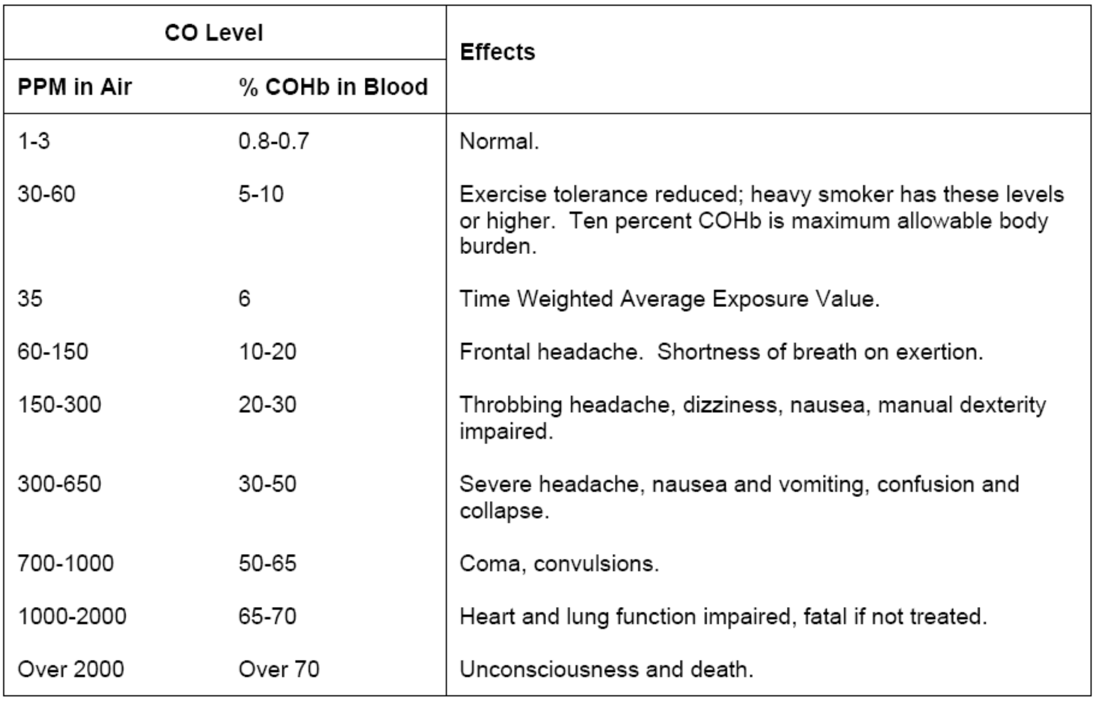
In addition, effects produced during one exposure are usually independent of those produced during any other.

Massive overexposure can cause permanent damage most likely in the nervous system.

These effects can include:

- loss of memory;
- increased irritability;
- impulsiveness;
- mood changes;
- violent behaviour;
- verbal aggression;
- personality changes;
- learning disabilities;
- mental deterioration;
- instability when walking.

The following table reports the physiological effects of varying levels of carbon monoxide.



CO Level		Effects
PPM in Air	**% COHb in Blood**	
1-3	0.8-0.7	Normal.
30-60	5-10	Exercise tolerance reduced; heavy smoker has these levels or higher. Ten percent COHb is maximum allowable body burden.
35	6	Time Weighted Average Exposure Value.
60-150	10-20	Frontal headache. Shortness of breath on exertion.
150-300	20-30	Throbbing headache, dizziness, nausea, manual dexterity impaired.
300-650	30-50	Severe headache, nausea and vomiting, confusion and collapse.
700-1000	50-65	Coma, convulsions.
1000-2000	65-70	Heart and lung function impaired, fatal if not treated.
Over 2000	Over 70	Unconsciousness and death.

2.2.1 Exposure limits to carbon monoxide [3]

Current safety standards vary from agency to agency, but the most conservative agency is the American Conference of Governmental and Industrial Hygienists [www.ACGIH.org].

The ACGIH 2004 guidelines list the TLV/TWA for CO at 25 ppm, i.e., 25 ppm for 8 hours, and do not offer the usual ceiling value of 400 ppm [used by OSHA].

Instead of a ceiling value, ACGIH guidelines give a maximum exposure of 3 to 5 times the TLV, explained as: the maximum exposure for 30 minutes should not exceed 3 times the TLV, and one should never be exposed to more than 5 times the TLV.

Putting this into practice for Carbon Monoxide, would limit exposures to a maximum of 75 ppm for 30 minutes and set a never to exceed ceiling value of 125 ppm CO.

One more indicator is the BEI, or Biological Exposure Indices.

The CO that is inhaled is bound to the haemoglobin in the red blood cells making them incapable of carrying oxygen.

Therefore, CO exposure causes a type of anaemia and symptoms are like asphyxiation, with dizziness, drowsiness, nausea to the degree of the insult suffered. The CO poison is in equilibrium in the lungs, and a person with 3.5% COHb (3.5% poisoning of the haemoglobin) will emit about 20 ppm CO in the exhaled lung alveolar air.

It takes about 8 hours breathing CO free, clean air to clear one half of the CO poisoning from a person, i.e. go from 3.5% to 1.75% COHb.

2.3 Carbon monoxide detectors [4-10]

Devices for sensing carbon monoxide and triggering an alarm in the presence of excess concentrations are widely available.

These devices are based mainly on four transduction techniques:

- *conductivity changes*: MOX sensors;
- *absorbance changes*: IR sensors;
- *ionic current changes*: electrochemical sensors;
- *temperature changes*: pellistor sensors.

The next sections report some details about the working principles of market available carbon monoxide sensors.

2.3.1 MOX sensors

The discovery in 1953 that adsorption of a gas onto the surface of a metal oxide semiconductor produced a large change in its electrical conductivity signalled the advent of mixed metal oxide semiconductor sensor (MOX) technology.

The effect is commercially exploited for only a few oxides due to the requirement for a unique combination of resistivity, magnitude of resistance change in gas (sensitivity) and humidity effects.

Amongst the oxides which are used as MMOS sensors are Cr2TiO3, WO3 and SnO2.

The conductivity change is caused by a loss or a gain of surface electrons as a result of adsorbed oxygen reacting with the target gas, as shown in Fig. 6.

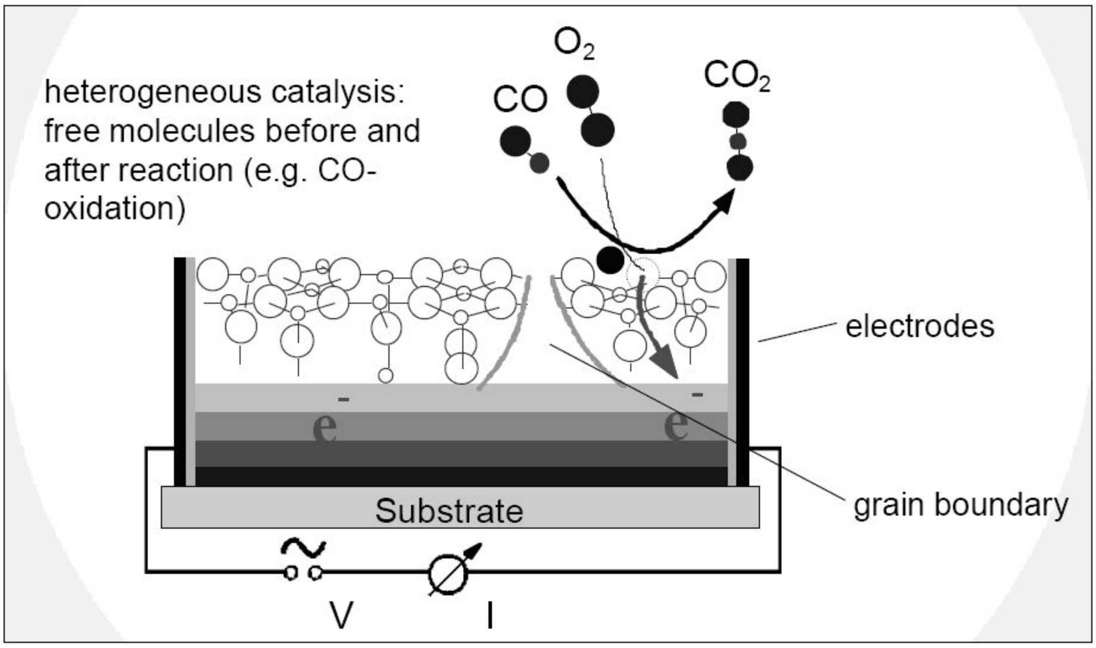


Fig. 6: schematic diagram of a MOX sensor.

If the oxide is an n-type, there is either a donation (reducing gas) or subtraction (oxidising gas) of electrons from the conduction band.

The result is that n-type oxides increase their resistance when oxidising gases such as NO2, O3 are present while reducing gases such as CO, CH4, EtOH lead to a reduction in resistance.

The converse is true for p-type oxides, such as Cr2TiO3, where electron exchange due to gas interaction leads either to a rise (oxidising gas) or a reduction (reducing gas) in electron holes in the valence band.

This then translates into corresponding changes in electrical resistance.

Unlike some other gas sensing technologies, MOX sensors can be made quantitative, as the magnitude of change in electrical resistance is a direct measure of the concentration of the target gas present.

Since the change in electrical resistance in the sensing oxide is caused by a surface reaction, it is advantageous to maximise the surface area to intensify the response to gas.

Accordingly, commercial gas sensors take the form of highly porous oxide layers, which are either printed down or deposited onto alumina chips.

The electrodes are usually co-planar and located at the oxide/chip interface.

A heater track is also present usually on the backside of the chip to ensure the sensors run “hot”.

This is a necessary requirement as both the interference from humidity is minimised and the speed of response is increased.

MOX sensors do not normally discriminate between different target gases.

As such, considerable care is taken to ensure the microstructure of the oxide, its thickness and its running temperature are optimised to improve selectivity.

In addition, selectivity is further enhanced through the use of catalytic additives to the oxide, protective coatings and activated-carbon filters.

2.3.2 INFRA-RED sensors

It has long been known that:

- a wide range of materials absorb infrared radiation (due to intramolecular vibrations);
- for any material, the strength of absorption (absorbance) varies with wavelength (its absorption spectrum);
- different materials have different absorption spectra.

The basic principles of operation of infrared gas sensors rely on the exploitation of these facts.

Typical infra-red spectra for carbon monoxide, propane, n-hexane and carbon dioxide are shown in Fig. 7.

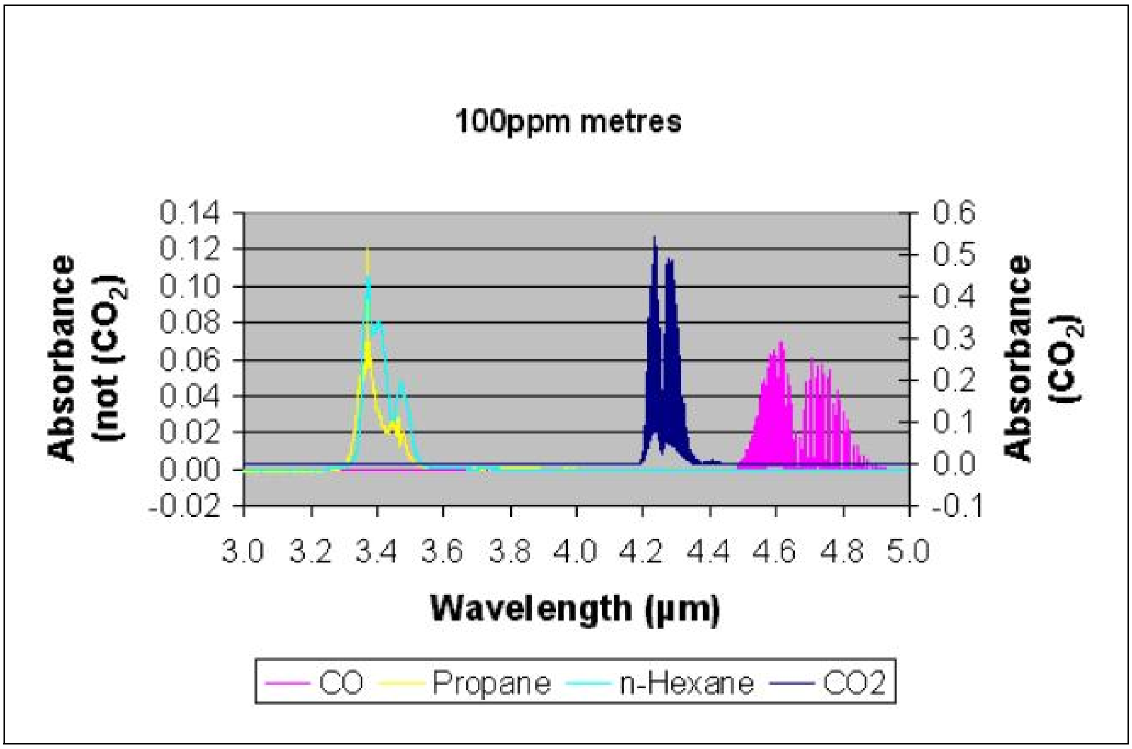


Fig. 7: absorption spectra of CO, CO2, n-Hexane, Propane.

There are certain basic components common to all infrared gas sensors:

- an infrared source (e.g. incandescent lamp);
- a detector (e.g. thermopiles, pyroelectric detectors);
- a means to select appropriate wavelengths (e.g. band pass interference filter);
- a sample cell.

Radiation from the source passes through the sample cell and wavelength selector. The choice of wavelength has a large bearing on the relative selectivity of the sensor. The radiation NOT absorbed by the sample is then detected and the ratio of this to the incident provides a measure of the concentration of target gas in the sample.

A second detector (or channel) tuned to a different wavelength that is not attenuated by any species likely to be present in the sample is normally used to provide this reference measurement.

A further component that enhances the performance of IR gas sensors is a temperature sensor.

All these components have temperature dependencies which must be compensated to provide an accurate measure of gas concentration.

This temperature sensor (typically a thermistor) should be sited within, or in very close proximity to, the detector(s).

Infrared sensors effectively give a measure of the number of target gas molecules in the light path between source and detector.

Consequently, the output signal not only varies with concentration but also barometric pressure i.e. they are partial pressure devices.

For very high measurement accuracy, compensation for barometric pressure is, therefore, required.

This dependency also infers that sensors with longer optical path lengths (i.e. distance travelled by radiation between source and detector(s)) will have increased sensitivity and tend to have a lower dynamic range but increased resolution.

In a single target gas, fixed optical light path device under constant barometric pressure, the signal output (and signal/noise ratio) approximately exponentially decays with increasing concentration i.e. infrared gas sensors are inherently non-linear.

The measurement accuracy decreases with increasing concentration.

The components described above form a typical infrared gas sensor.

However, some supporting electronics is required in any practical system.

The more common detector technologies provide very small analogue signal outputs that require amplification.

Basic analogue filtering of the amplified output signal can then enhance measurement accuracy.

The source also requires a driver circuit.

It is usual practice to modulate the source output by pulsing (although some older design used fixed illumination and mechanical choppers).

This creates periodic variations in the emitted intensity and so allows the use of synchronous detection techniques.

An overall block schematic of a typical 2 channel IR gas sensor with separate supporting electronics is shown in Fig. 8.

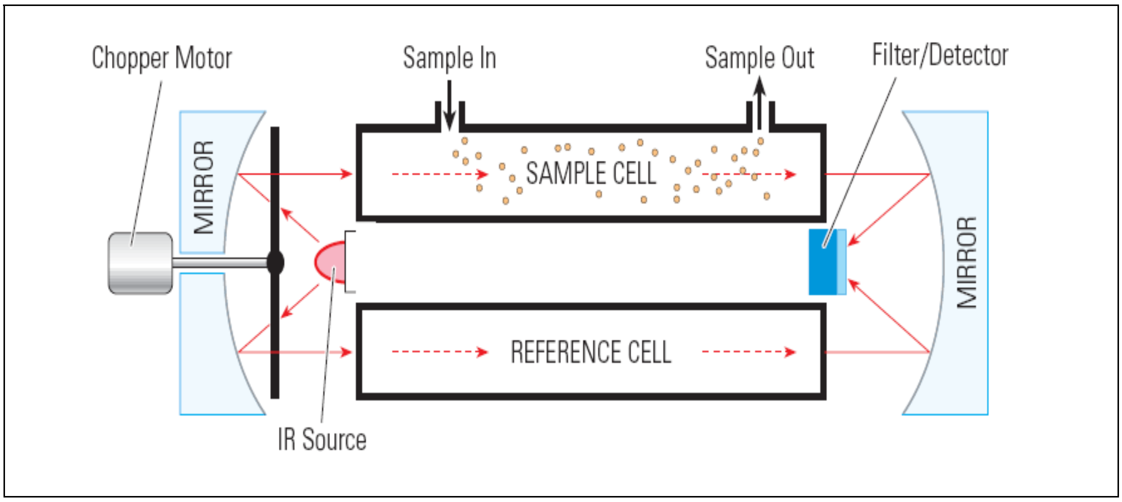


Fig. 8: block scheme of an infrared sensor.

2.3.3 Electrochemical sensors

They have a direct response to volume concentration of gas rather than partial pressure.

The simplest form of electro-chemical sensor comprises two electrodes: sensing and counter, separated by a thin layer of electrolyte.

This is enclosed in a plastic housing that has a small capillary to allow gas entry to the sensing electrode and includes pins which are electrically attached to both electrodes and allow easy external interface.

These pins may be connected to a simple resistor circuit that allows the voltage drop resulting from any current flow to be measured.

Gas diffusing into the sensor is either oxidised or reduced at the sensing electrode and, coupled with a corresponding (but converse) counter reaction at the other electrode, a current is generated through the external circuit.

Since the rate of gas entry into the sensor is controlled by the capillary diffusion barrier, the current generated is proportional to the concentration of gas present outside the sensor and gives a direct measure of the toxic gas present.

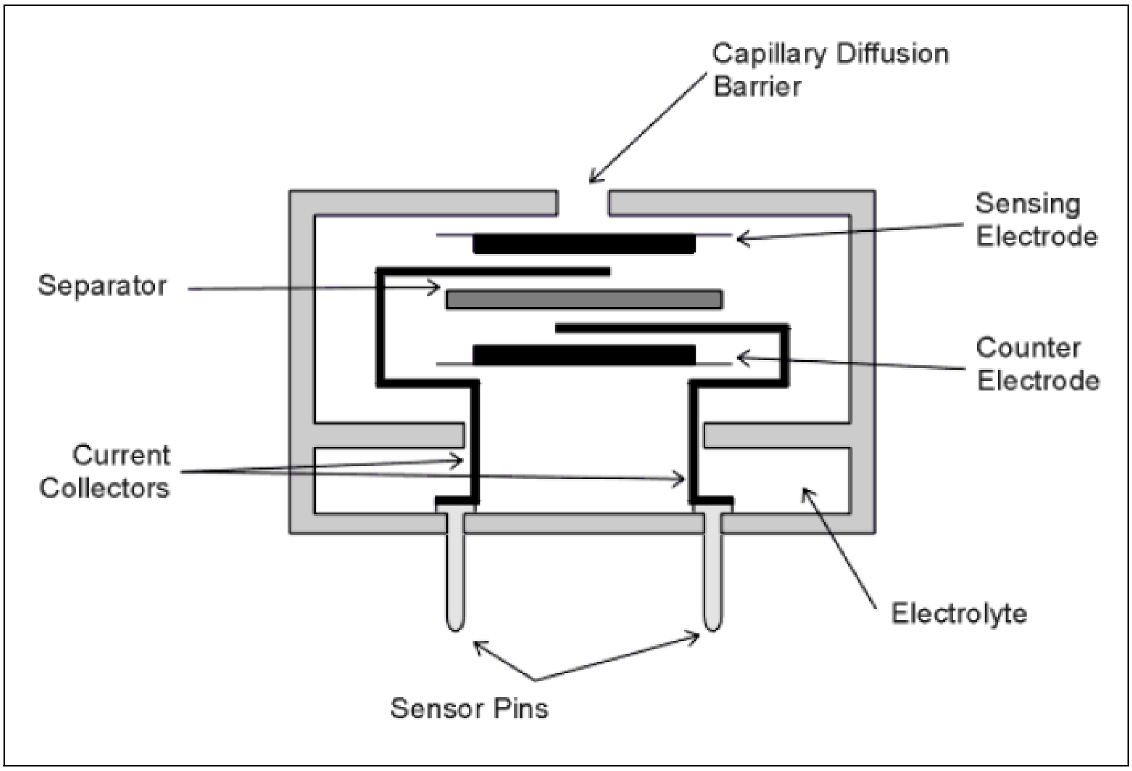


Fig. 9: schematic diagram of an electrochemical gas sensor.

The electrode is therefore able to react all target gas as it reaches its surface, and still has electrochemical activity in reserve.

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

- *Sensing*: CO + H2O CO2 + 2H+ + 2e–
- *Counter*: ½O2 + 2H+ + 2e- H2O
- *And the overall reaction is*: CO + ½O2 CO2

Similar reactions take place for all other toxic gases that are capable of being electrochemically oxidised or reduced.

From the reaction at the counter electrode, it is evident that oxygen is required for the current generation process to take place.

This is usually provided in the sample stream by air diffusing to the front of the sensor, or by diffusion through the sides of the sensor (a few thousand ppm is enough).

2.3.4 Pellistor sensors

Combustible gas mixtures will not burn until they reach an ignition temperature. However, in the presence of certain chemical media, the gas will start to burn or ignite at lower temperatures.

This phenomenon is known as a catalytic combustion.

Most metal oxides and their compounds have these catalytic properties.

Platinum, palladium, and thoria compounds are also excellent catalysts for combustion.

This explains why the automobile exhaust system is treated with platinum compounds and is called a catalytic converter.

This kind of gas sensor is made on the basis of the catalytic principle, and therefore is also called the *catalytic gas sensor*.

A gas molecule oxidizes on the catalyzed surface of the sensor at a much lower temperature than its normal ignition temperature.

All electrically conductive materials change their conductivity as temperature changes.

This is called the *coefficient of temperature resistance* (Ct).

It is expressed as the percentage of change per degree change in temperature.

Platinum has a large Ct in comparison to other metals.

In addition, its Ct is linear between 500°C to 1000°C, which is the temperature range at which the sensor needs to operate.

Because the signal from the sensor is linear, this means that the gas concentration is directly proportional to the electrical signal.

This improves the accuracy and simplifies the electronic circuitry.

Also, platinum possesses excellent mechanical properties, it is physically strong and can be transformed into a fine wire which can be processed into small sensor beads.

Furthermore, platinum has excellent chemical properties:

- it is corrosion resistant and can be operated at elevated temperatures for a long period of time without changing its physical properties;
- it is capable of producing a constant reliable signal over an extended period of time.

The standard sensor consists of a matched pair of elements, typically referred to as a detector and compensator (reference element), see Fig. 10.

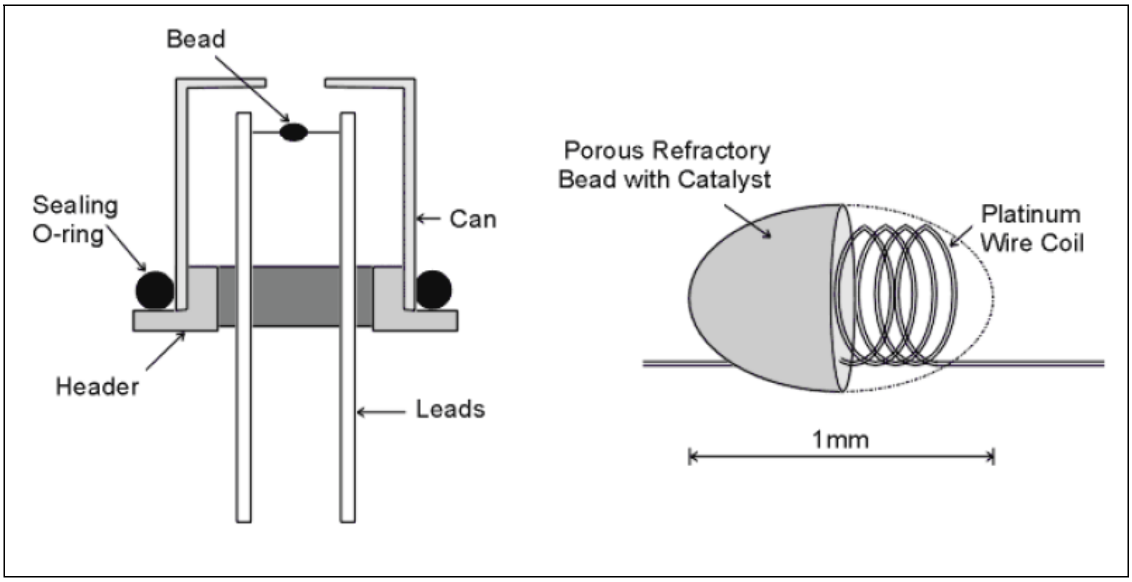


Fig. 10: schematic diagram of a pellistor sensor.

The detector comprises a platinum wire coil embedded within a bead of catalytic material.

The compensator is similar except that the bead does not contain catalytic material and as a consequence is inert.

Both elements are normally operated in a Wheatstone bridge that will produce an output if the resistance of the detector differs from that of the compensator (Fig. 11).

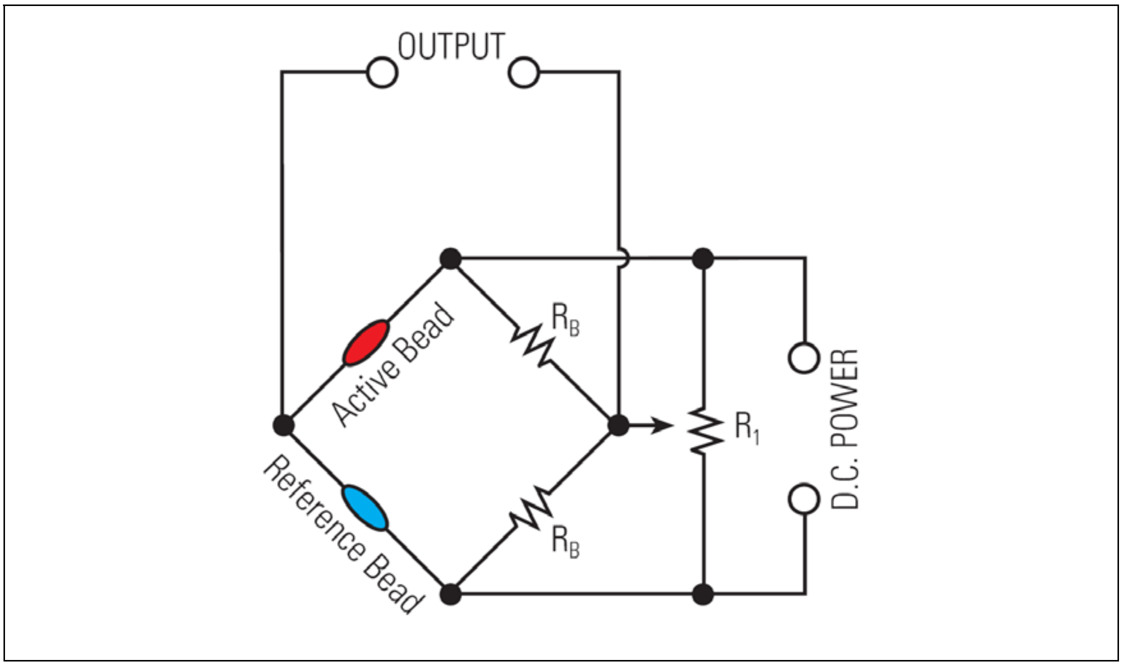


Fig. 11: typical layout for a pellistor sensor.

The bridge is supplied with a constant DC voltage that heats the elements to 500-550°C.

Target gases are oxidised only on the detector element, where the heat generated increases its resistance, producing a signal proportional to the concentration of combustible gas.

The compensator helps to compensate for changes in ambient temperature, pressure and humidity, which affects both elements equally.

2.4 An innovative approach to CO detection [5]

Since the activities reported in this thesis have been carried within the frame of an innovation project, the development strategy of a new carbon monoxide sensor required studying the feasibility of using a transduction technique alternative to those already implemented in commercial devices.

The selected technology is based on a biomimetic approach, trying to exploit the biological phenomena which lead to CO poisoning for developing a highly sensitive, selective sensor.

The biomimetic approach requires discussing some basic principles of the oxygen transportation within blood.

In normal conditions haemoglobin (Hb), which is the oxygen-carrying pigment and predominant protein in the red blood cells (in mammals the protein makes up about 97% of the red cell’s dry content, and around 35% of the total content, including water), forms an unstable, reversible bond with oxygen.

In its oxygenated state it is called oxyhaemoglobin and is bright red, while in the reduced state it is called deoxyhaemoglobin and is purple-blue.

Oxyhaemoglobin is formed during respiration when oxygen binds to the heme component of haemoglobin.

This process occurs in the pulmonary capillaries adjacent to the alveoli of the lungs.

The oxygen then travels through the blood stream to be dropped off at cells where it is utilized in aerobic glycolysis and in the production of ATP by the process of oxidative phosphorylation.

Deoxyhaemoglobin is the form of haemoglobin without the bound oxygen.

The name haemoglobin is the concatenation of heme and globin, reflecting that each subunit of haemoglobin is a globular protein with an embedded heme group.

Each heme group contains an iron atom and this is responsible for the binding of oxygen.

The most common type of haemoglobin in mammals contains four such subunits, each with one heme group, as reported in Fig. 12.

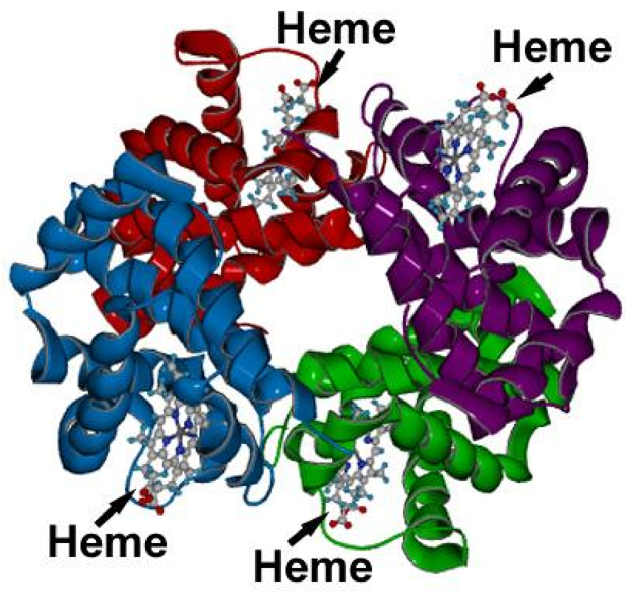


Fig. 12: haemoglobin structure and heme groups.

In humans, each heme group consists of an iron ion held in a heterocyclic ring, known as porphyrin, as shown in Fig. 13.

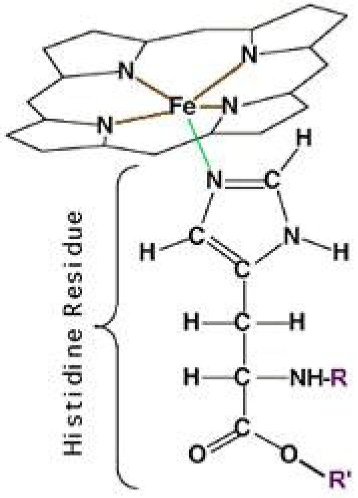


Fig. 13: heme structure and iron porphyrin.

The iron ion, which is the site of oxygen binding, bonds with the four nitrogens in the centre of the ring, which all lie in one plane.

The iron ion may either be in the Fe(II) or Fe(III) state, but ferrihaemoglobin (Fe(III)) cannot bind oxygen.

In binding, oxygen temporarily oxidizes Fe to Fe(III), so iron must exist in the Fe(II) oxidation state in order to bind oxygen.

The enzyme methaemoglobin reductase reactivates haemoglobin found in the inactive (Fe(III)) state by reducing the iron centre.

Each heme group is able to bind one oxygen molecule and thus one haemoglobin molecule can bind four oxygen molecules.

Haemoglobin's oxygen-binding capacity is decreased in the presence of carbon monoxide, because both gases compete for the same binding sites on haemoglobin, carbon monoxide binding preferentially in place of oxygen.

While carbon dioxide occupies a different binding site on the haemoglobin and is more readily dissolved in deoxygenated blood, facilitating its removal from the body after the oxygen has been released to tissues undergoing metabolism, CO competes with oxygen at the same binding site, displacing it, and is carried through the blood stream.

Haemoglobin binding affinity for CO is 200 times greater than its affinity for oxygen, meaning that small amounts of CO dramatically reduce haemoglobin's ability to transport oxygen.

This phenomenon has been the guideline for developing a carbon monoxide sensor using iron porphyrins as sensing layer (CIM).

The following paragraph will deal with the sensor design and development.

2.5 Prototype design and development

As already introduced, the feasibility study of an innovative carbon monoxide sensor has been inspired by the biological mechanism of the interaction between CO and haemoglobin.

In normal conditions, haemoglobin bind oxygen molecules reversibly, but the affinity towards carbon monoxide is much greater, as evidenced in the phenomenon of CO poisoning.

The new approach, which is presented in the next sections, was then aimed at synthesizing iron porphyrins to use as sensitive layers in quartz microbalance (QMB) sensors.

2.5.1 CIM: iron porphyrins [6-11]

The synthesis strategy brought to developing 3 different iron compounds, basically two Fe(III) porphyrins and one of Fe(II):

- Fe(III)[T(3,5(OH)2P)P](Cl)
- Fe(III)[T(2,5(OH)2P)P](Cl)
- Fe(II)[T(2,5(OPiv)2P)P](NMeIm)

This choice can be explained by the following reasons:

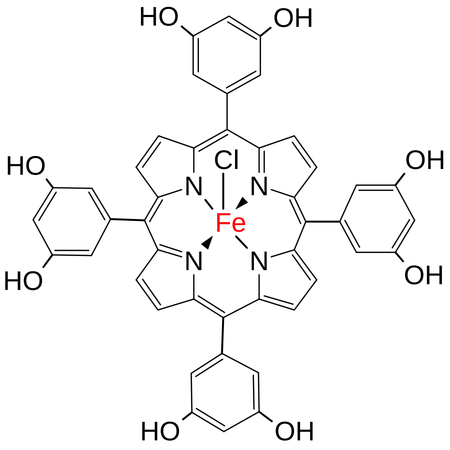
1. Though the best iron oxidation state for interacting with CO is Fe(II), porphyrins of Fe(II) are not stable in air, as Fe(II) rapidly oxidises to Fe(III) thus loosing any capability of binding carbon monoxide. To limit this process, the Fe(II) porphyrin contains an N-Metil-Imidazole ligand, which has the property of stabilizing the Fe(II) state.

2. The molecule structure of Fe(III) porphyrins is such that carbon monoxide can be trapped inside the porphyrin structure.

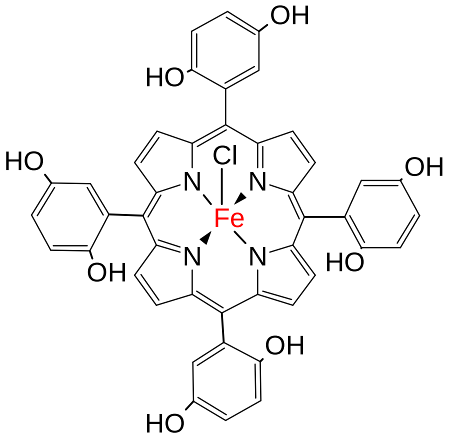
Both Fe(II) and Fe(III) layers have been deposited on the transduction element in the form of highly porous layers, to let CO diffusing through the layer itself.

The following pictures report the chemical structure of the 3 compounds.

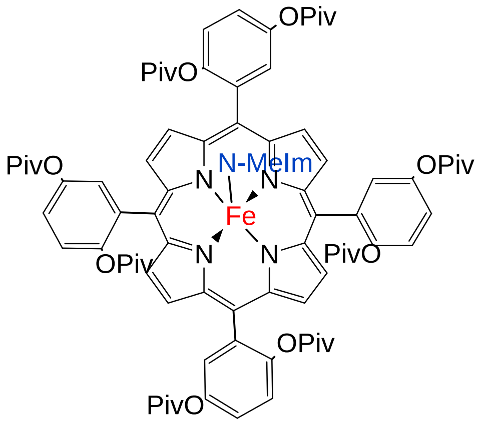
Fe(III)[T(3,5(OH)$_2$P)P](Cl)



Fe(III)[T(2,5(OH)$_2$P)P](Cl)



Fe(II)[T(2,5(OPiv)$_2$P)P](NMeIm)



2.5.2 Transduction element: TSMR resonator [12]

A TSMR resonator is composed by a piece of piezoelectric crystal (typically a circular slab of SiO2) with a couple of thin film metal contacts.

Such a device is shown in Fig. 14.

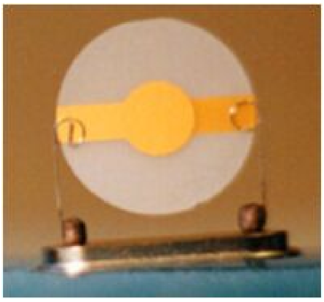


Fig. 14: the TSMR resonator.

The TSMR resonator allows exploiting the reverse piezoelectric effect to obtain acoustic bulk vibrations as a consequence of alternating voltages excitations.

Thus, any mass change of the oscillating device results in a variation of the oscillating frequency.

In more detail, the relationship between frequency shift and mass change can be expressed by the Sauerbrey equation:

$$\Delta f = -\frac{2 f_0^2}{A\sqrt{\mu_q \rho_q}} \cdot \Delta m$$

.

A TSMR device can be used to develop a Quartz Microbalance sensor (QMB), a sensor which implements the mass change transduction technique.

2.5.3 Device assembly: QMB sensor [6]

In this case, such a sensor was obtained by covering the TSMR with layers of the iron porphyrins described in the previous section.

Deposition was made using the spray casting technique.

Fig. 15 Reports the working principle of a QMB chemical sensor.

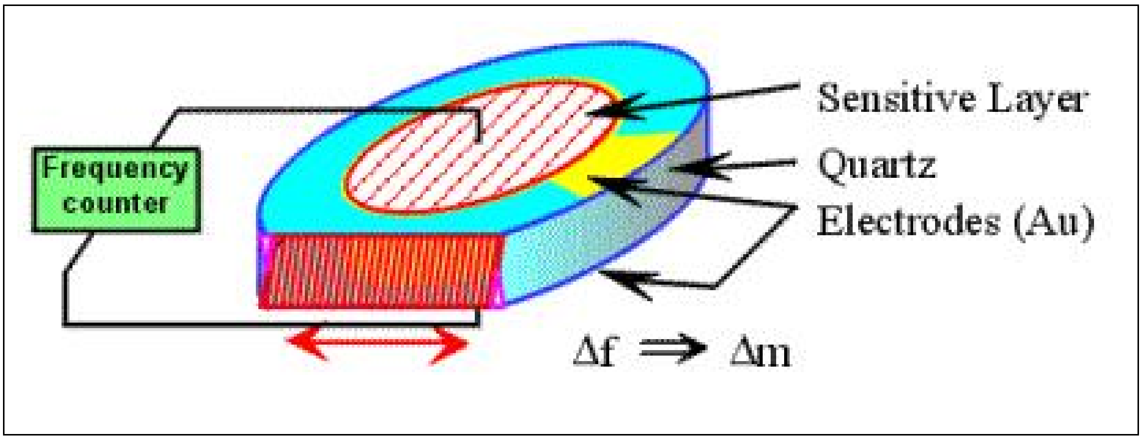


Fig. 15: block scheme of a chemical sensor based on a TSMR resonator.

2.6 Prototype set-up

Tests have been performed on a set of 6 different sensors and 2 empty resonators as references, for compensating the environmental parameters such as temperature, relative humidity and flow rate.

Prototype devices have been mounted in an Electronic Nose measurement chamber, as reported in Fig. 16:

Fig. 16: prototypes inside the measurement chamber.

The following list reports the composition of the membranes according to their position in the chamber:

QMB1: reference

QMB2: Fe(III)[T(2,5(OH)2P)P](Cl)

QMB3: Fe(III)[T(2,5(OH)2P)P](Cl)

QMB4: Fe(III)[T(3,5(OH)2P)P](Cl)

QMB5: reference

QMB6: Fe(III)[T(3,5(OH)2P)P](Cl)

QMB7: Fe(II)[T(2,5(OPiv)2P)P](NMeIm)

QMB8: Fe(II)[T(2,5(OPiv)2P)P](NMeIm)

2.6.1 Measurement set-up

The measurement set-up used for testing the prototypes' performances is reported in Fig. 17, and was composed by the following main blocks:

CO-500ppm cylinder;

N2-100% cylinder (carrier gas);

N2-100% cylinder (cleaning gas);

Bubbler;

Nafion filter (PERMAPURE);

Mass Flow Controller set (MKS200);

Electronic Nose.

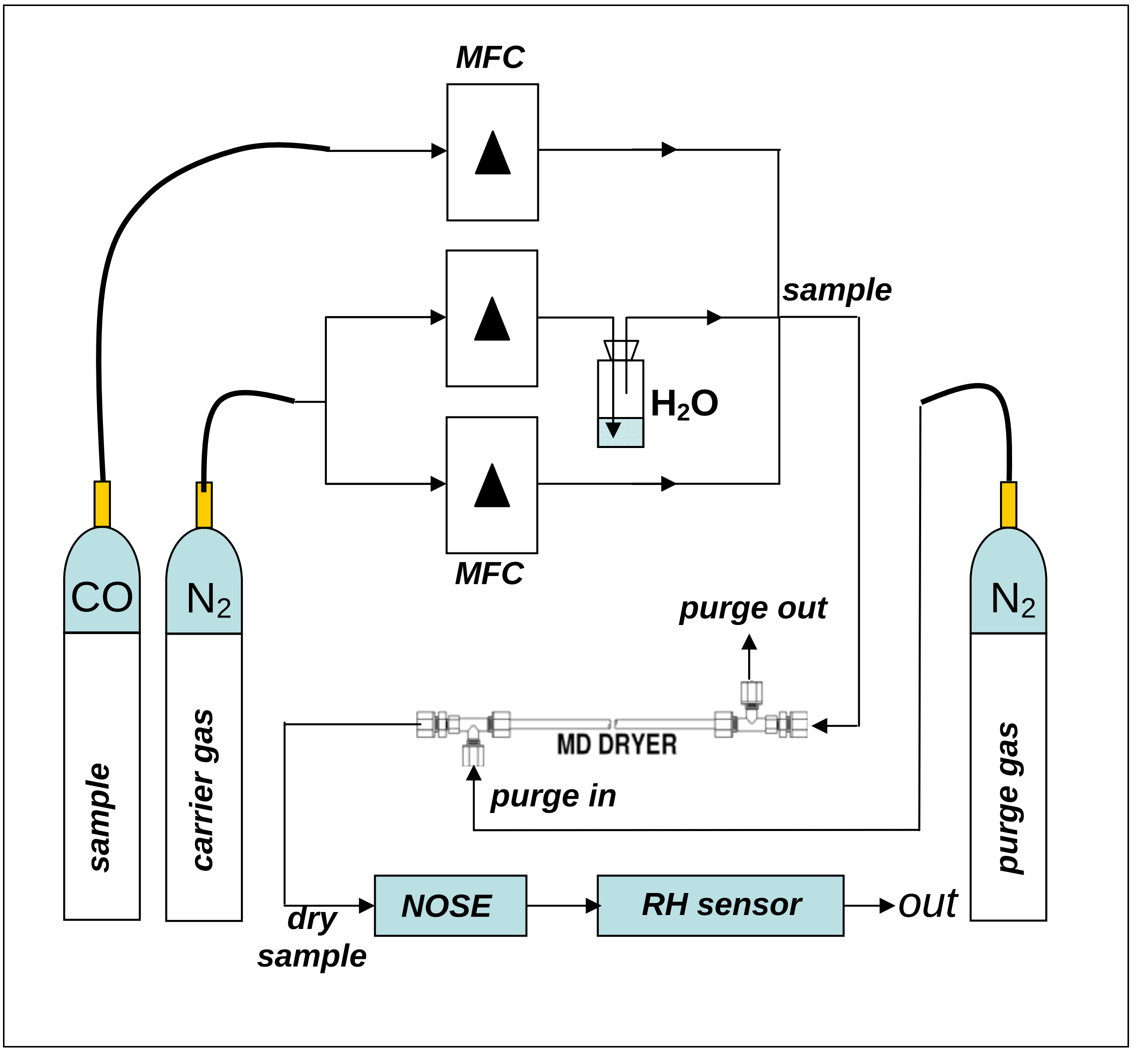


Fig. 17: measurement set-up schematic.

2.6.2 Calibration of the NAFION filter

This session was aimed at defining the performances of the NAFION filter when used as humidity trap.

A humidity trap is necessary when using porphyrin based QMB sensors, as the porphyrins themselves are highly sensitive to water vapour and then the results would be influenced by the sample's humidity content.

The measurement set-up used for calibrating the NAFION filter is reported below:

N2-100% carrier gas cylinder;

N2-100/ cleaning gas cylinder;

MFC for controlling the CG flow;

MFC for controlling the RH level;

PERMAPURE MD-070-12;

RH/T sensor;

Fig. 18 reports a scheme of the measurement set-up.

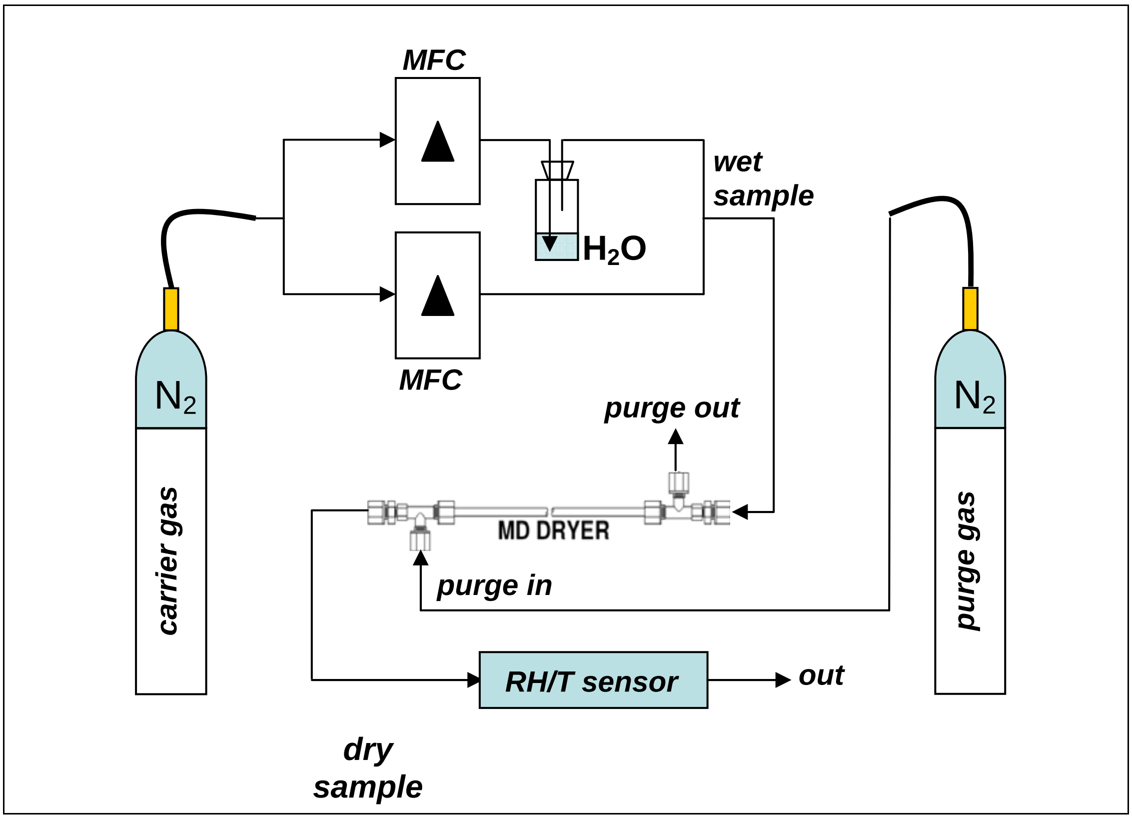


Fig. 18: measurement set-up for NAFION calibration.

The following table reports the measurement protocol.

Input RH level	Output RH level	Measure duration (min)
10%	11,29%	30
20%	16,38%	30
30%	19,21%	30
40%	21,43%	30
50%	22,40%	30
60%	23,49%	30

These measurements allowed defining a calibration function (see Fig. 19) to make an estimation of the sample’s residual humidity level after transition through the filter:

$$RH_{out} \cong 6.869\log(RH_{in}) - 4.316$$

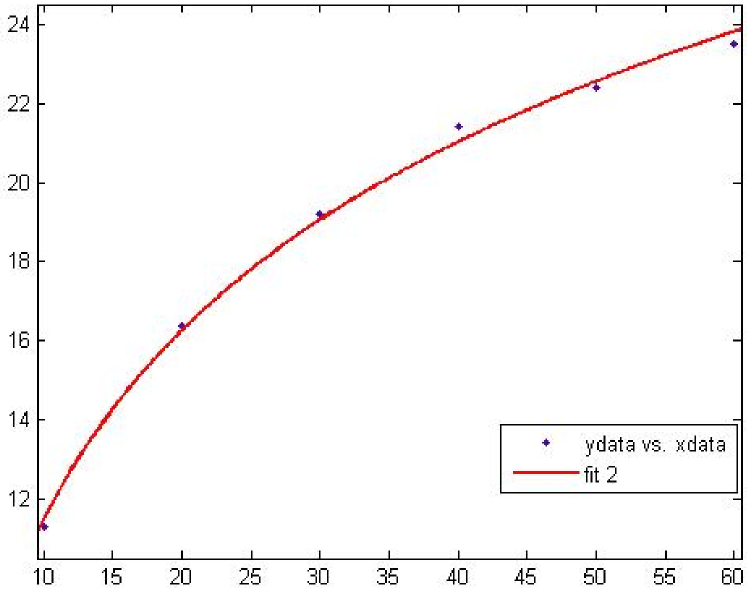


Fig. 19: calibration curve of the NAFION filter.

2.7 Measurements sessions

Prototype sensors have been tested according to a multiple session protocol, according to the following list:

- CO measurements without NAFION filter;
- CO measurements with NAFION filter;
- CO, CO-H2O mixture and H2O measures with NAFION filter;
- CO, CO-H2O mixtures and H2O measures without NAFION filter.

The results are reported in the following sections.

2.7.1 CO measurements without NAFION filter

This session has been carried out according to the following protocol:

Experiment phase	CO concentration (ppm)	Duration (min)
cleaning	0	60
measure	50	15
cleaning	0	45
measure	50	15
cleaning	0	45
measure	50	15
cleaning	0	45
measure	10	15
cleaning	0	45
measure	10	15
cleaning	0	45
measure	20	15
cleaning	0	45
measure	40	15
cleaning	0	45
measure	20	15

Tab. 5: protocol for session 1.

The results showed that the 3 porphyrins exhibit different sensitivity to carbon monoxide, the following list reports the sensitive materials ordered by their sensitivity level, Porf1 being the most sensitive:

- Porf1: Fe(III)[T(3,5(OH)2P)P](Cl) [sensors 4 and 6]
- Porf2: Fe(III)[T(2,5(OH)2P)P](Cl) [sensors 2 and 3]
- Porf3: Fe(II)[T(2,5(OPiv)2P)P](NMeIm) [sensors 7 and 8]

The sensors' responses to CO are reported in pictures from Fig. 20 to Fig. 22.

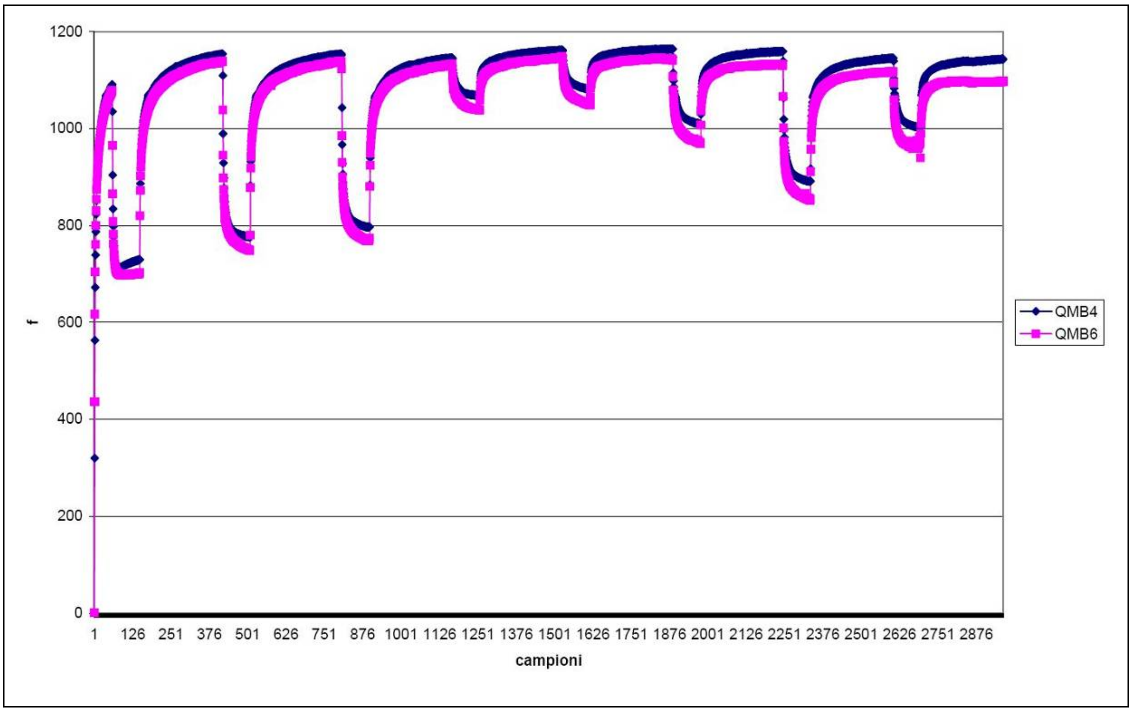


Fig. 20: response curves of sensors 4 and 6 to the protocol reported in Tab. 5.

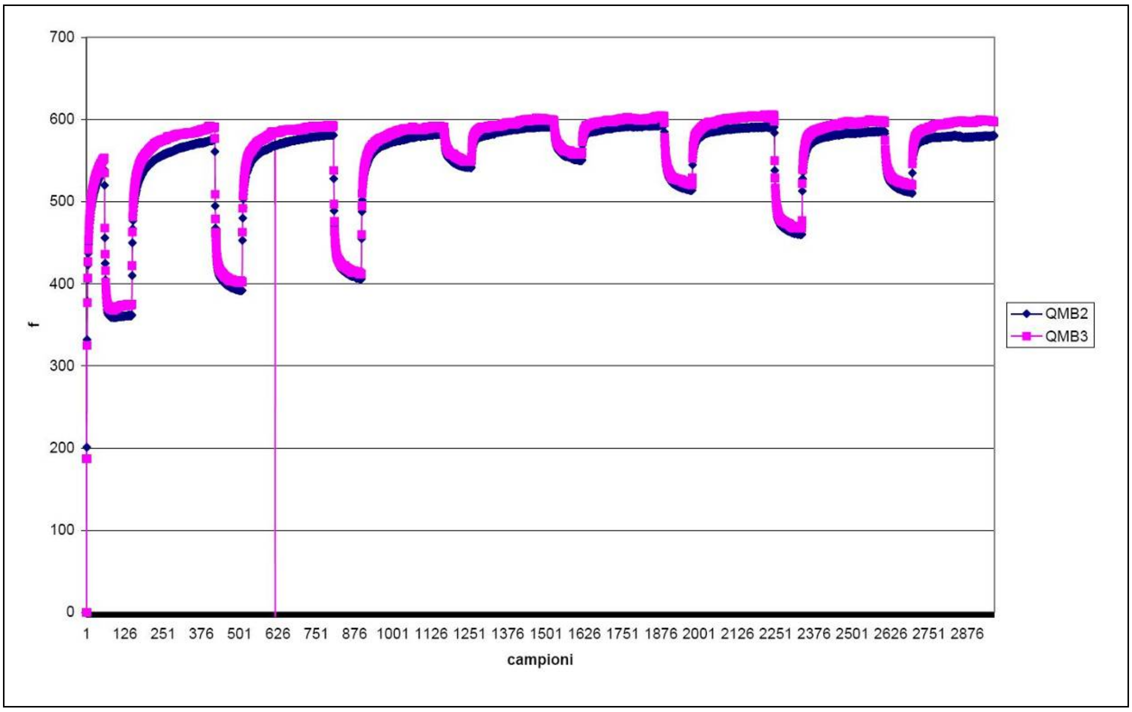


Fig. 21: response curves of sensors 2 and 3 to the protocol reported in Tab. 5.

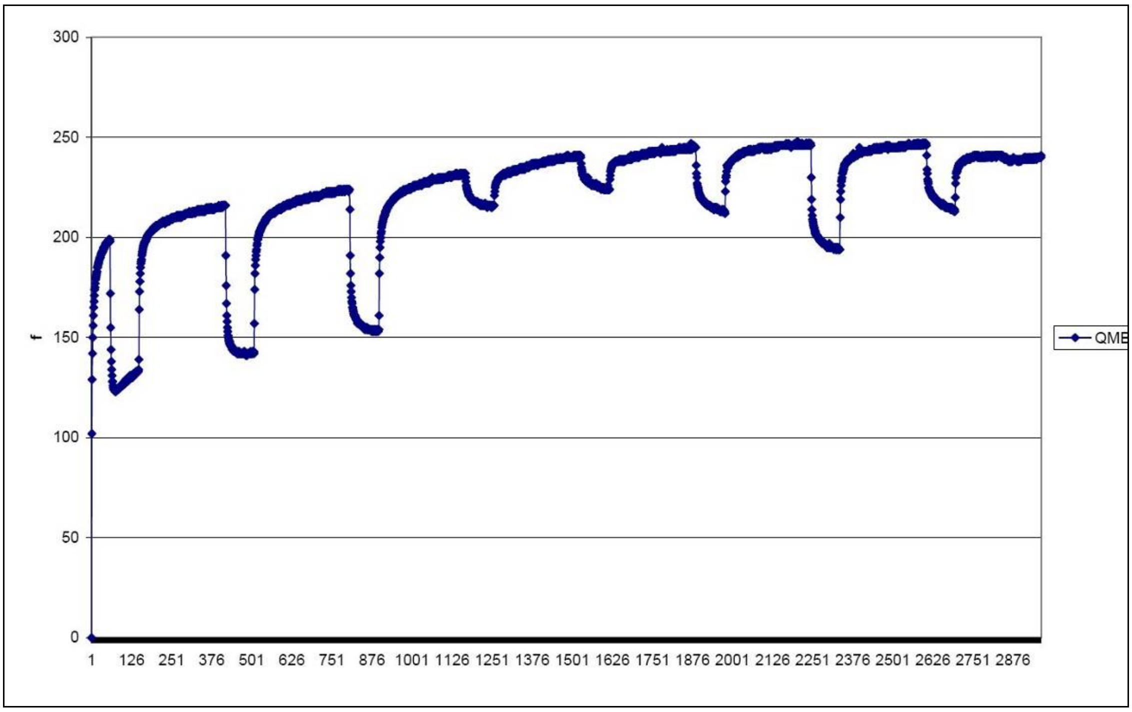


Fig. 22: response curves of sensor 7 to the protocol reported in Tab. 5.

This session included a second measurement cycle, in order to verify to what extent the results could be repeatable.

The protocol is reported in Tab. 6.

Experiment phase	CO concentration (ppm)	Duration (min)
cleaning	0	90
measure	5	15
cleaning	0	45
measure	5	15
cleaning	0	45
measure	5	15
cleaning	0	45
measure	10	15
cleaning	0	45
measure	5	15
cleaning	0	45
measure	50	15
cleaning	0	45
measure	20	15
cleaning	0	45
measure	30	15
cleaning	0	45
measure	30	15
cleaning	0	45
measure	30	15
cleaning	0	45
measure	100	15
cleaning	0	45
measure	150	15
cleaning	0	45

Tab. 6: protocol for the repetition of session 2.

The results obtained during the repetition of session 1 are reported in the pictures from Fig. 23 to Fig. 25.

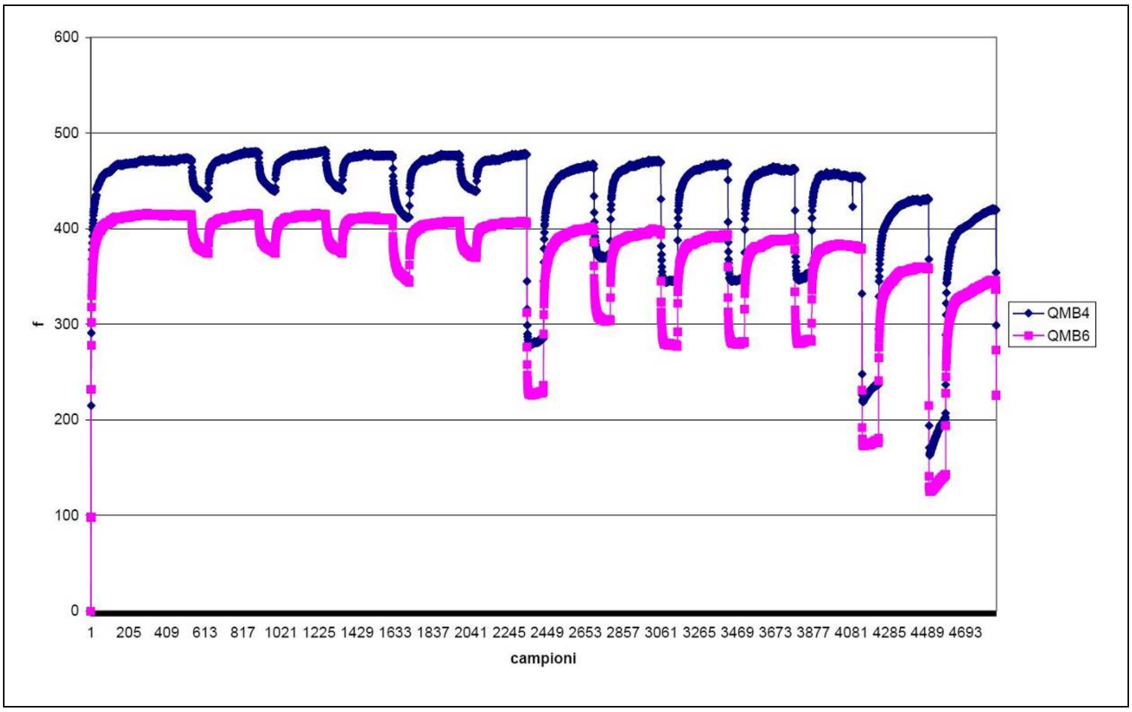


Fig. 23: response curves of sensors 4 and 6 to the protocol reported in Tab. 6.

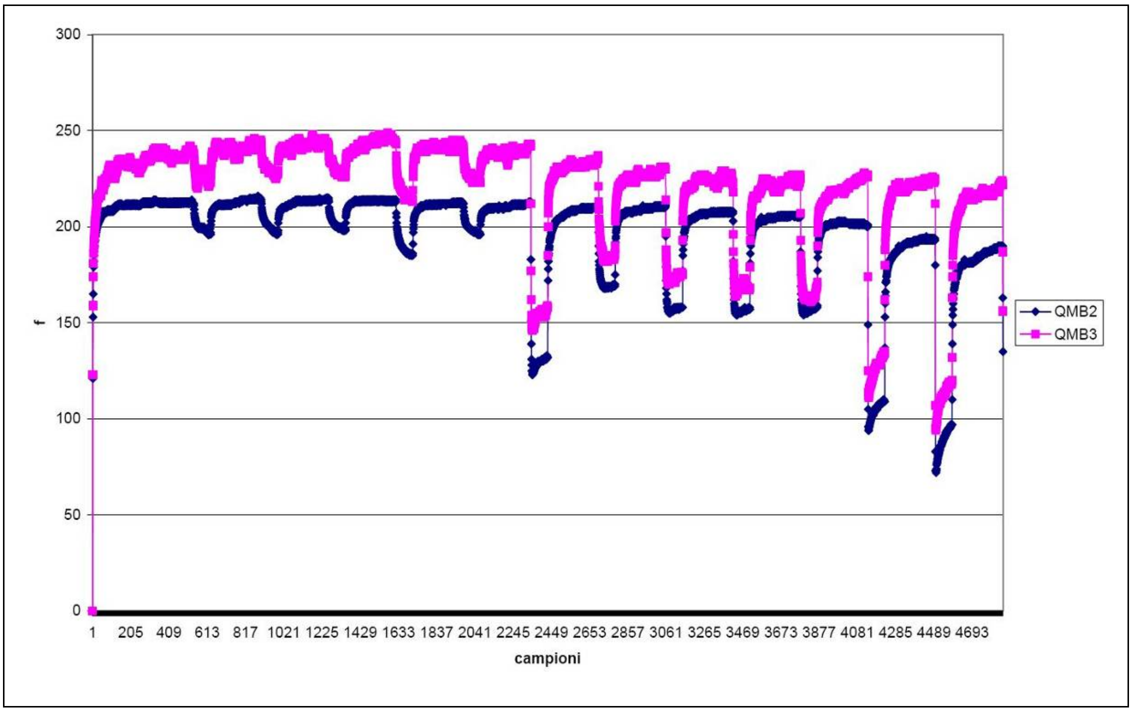


Fig. 24: response curves of sensors 4 and 6 to the protocol reported in Tab. 6.

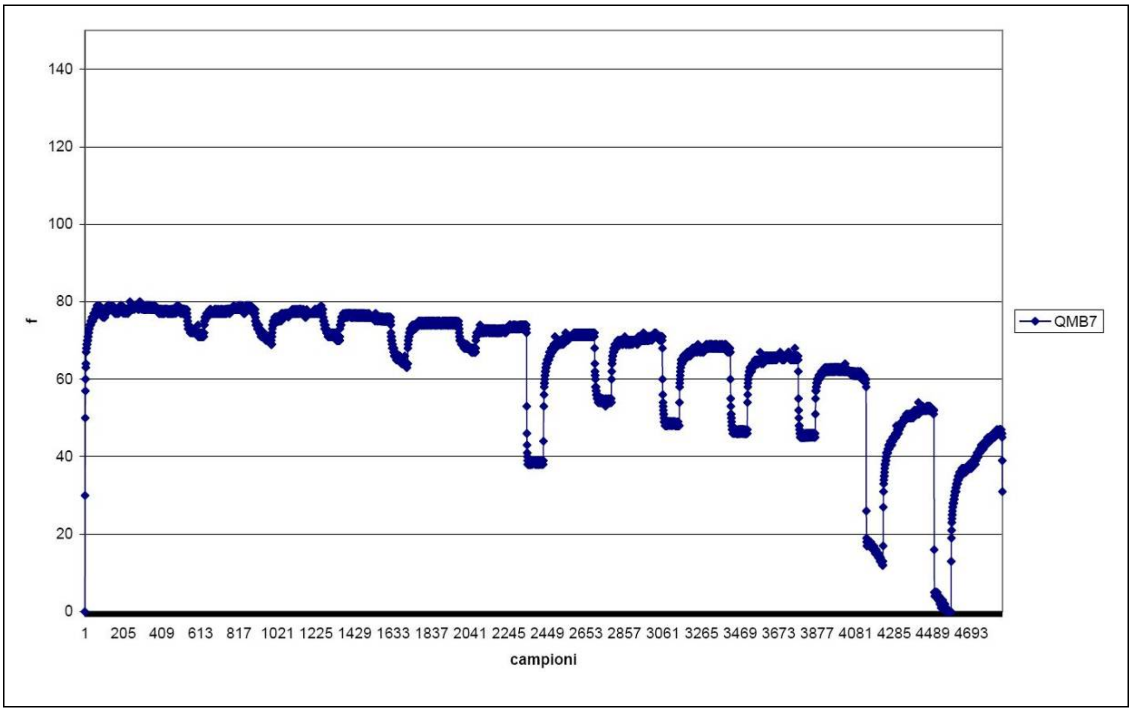


Fig. 25: response curves of sensors 4 and 6 to the protocol reported in Tab. 6.

The results obtained during the repetition evidenced that the sensitivity level was slightly reduced, thus leading to the conclusion that this kind of sensors suffer from a certain degree of slow reversibility.

These results can be easily explained due to the high affinity between Fe ions and carbon monoxide molecules.

This phenomenon required some counteractions to be taken in order to increase the reversibility.

2.7.2 CO measurements with NAFION filter

This session has been carried out according to the following protocol:

Experiment phase	CO concentration (ppm)	Duration (min)
cleaning	0	90
measure	50	15
cleaning	0	45
measure	50	15
cleaning	0	45
measure	50	15
cleaning	0	45
measure	10	15
cleaning	0	45
measure	10	15
cleaning	0	45
measure	20	15
cleaning	0	45
measure	20	15
cleaning	0	45

Tab. 7: protocol for the repetition of session 3.

The main goal was determining if the NAFION filter could influence the results by reducing the carbon monoxide content of the sample.

The results confirm that the filter does not remove CO from the sample, thus it can be efficiently used as humidity trap in applications of iron-porphyrins based QMB sensors for carbon monoxide detection.

The filter induces, as expect, a modification of the response shape.

Fig. 26 reports the response curves of sensors 4 and 6 to carbon monoxide when the filter is not used.

Fig. 27 reports the response curves of the same sensors I presence of the humidity trap.

The frequency change is not altered.

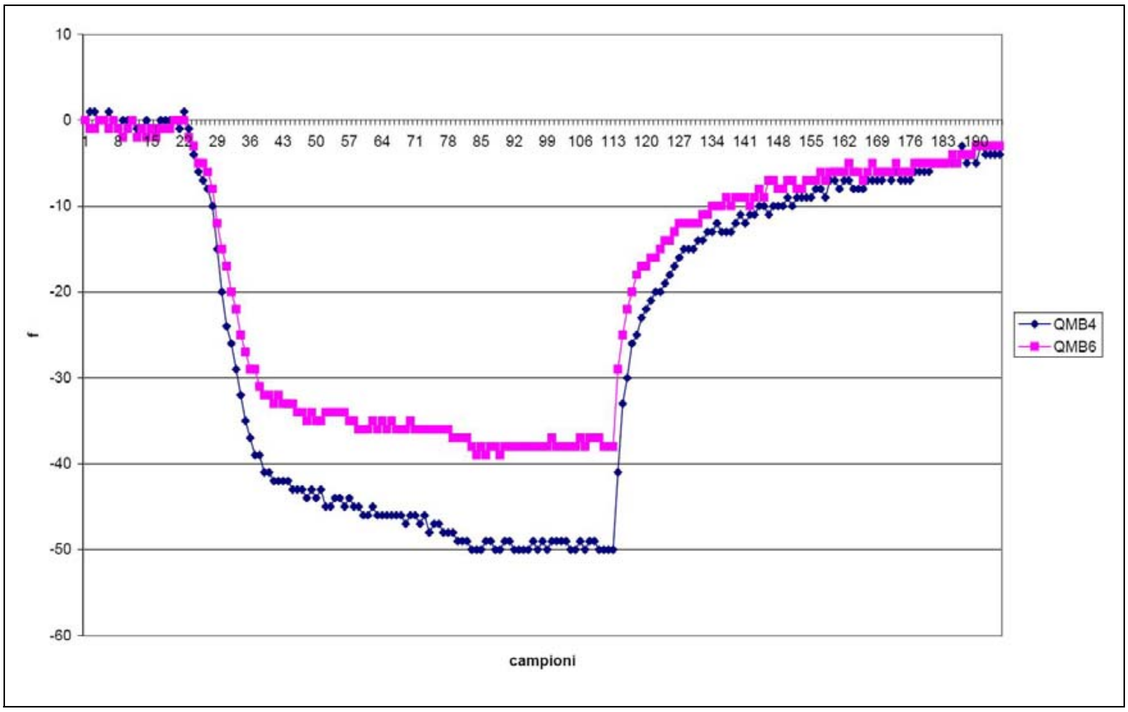


Fig. 26: response curves of sensors 4 and 6 to the protocol reported in Tab. 7.

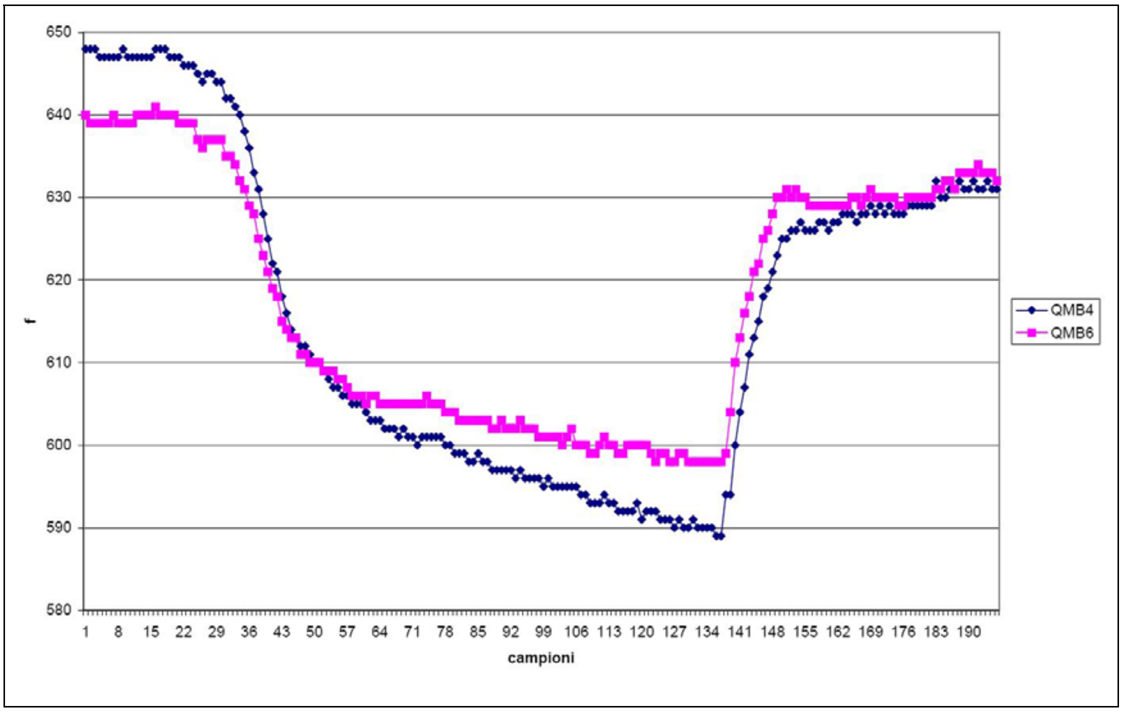


Fig. 27: response curves of sensors 4 and 6 to the protocol reported in Tab. 7.

2.7.3 CO measurements with NAFION filter with humidity level

This session was aimed at testing the carbon monoxide sensors in working conditions similar to the real case, i.e.: with a RH level different from zero, according to the following strategy:

- a 30% RH input level was obtained using a bubbler filled with water;
- the NAFION filter was used to reduce the RH level to a value of about 20%;
- CO concentration = 20ppm.

The results, reported in Fig. 28 to Fig. 30, show that the sensors' responses to the CO-H2O mixtures is the sum of the single responses to CO and water vapour.

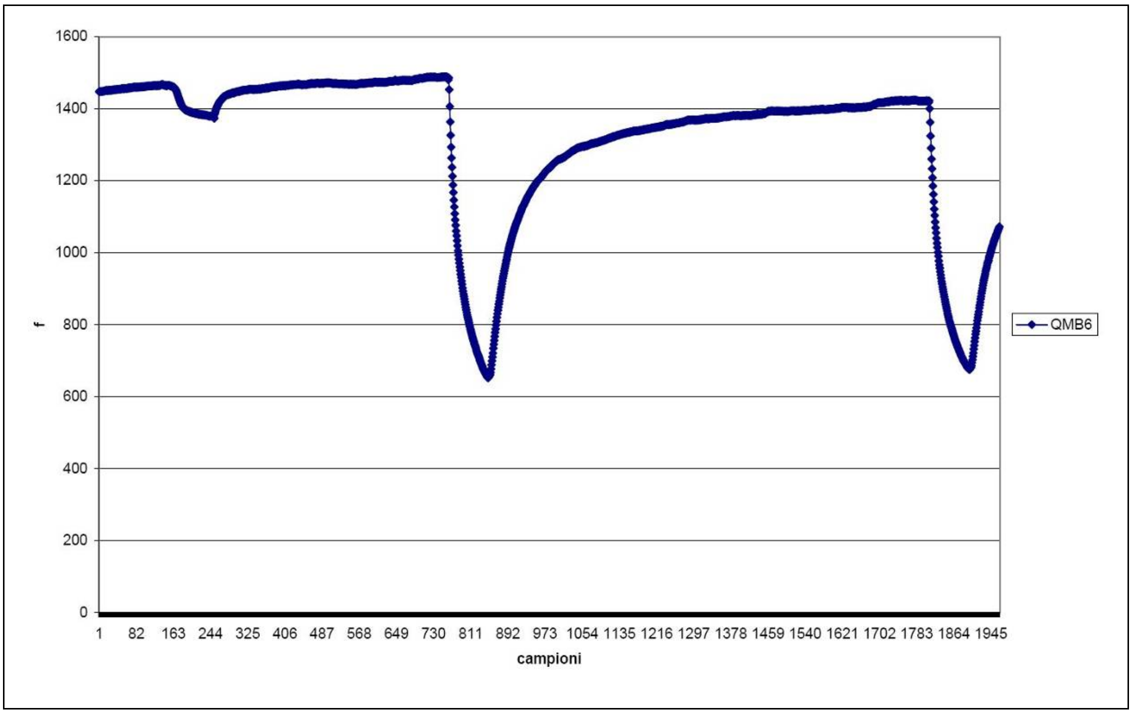


Fig. 28: response curve of sensors 6 to CO, CO-H2O and H2O.

Tab. 8 reports the frequency shifts for sensor 6 related to each measured sample, showing that the summing error is about 1%.

	CO20ppm	**CO20ppm** **H2O 20%**	**H2O 20%**
Frequency shift (Hz)	83	835	744

Tab. 8: frequency shifts for sensor 6 during the session.

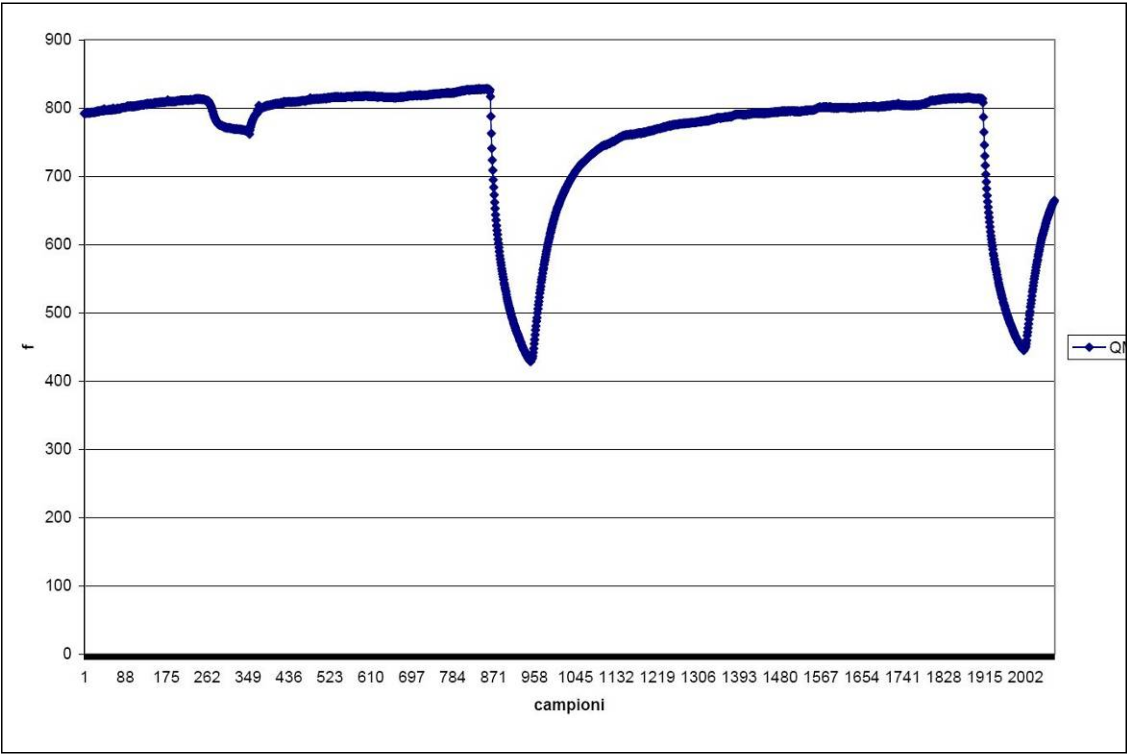


Fig. 29: response curve of sensor 2 to CO, CO-H2O and H2O.

Tab. 9 reports the frequency shifts for sensor 2 related to each measured sample, showing that the summing error is about 3,5%.

	CO20ppm	**CO20ppm** **H2O 20%**	**H2O 20%**
Frequency shift (Hz)	45	398	367

Tab. 9: frequency shifts for sensor 2 during the session.

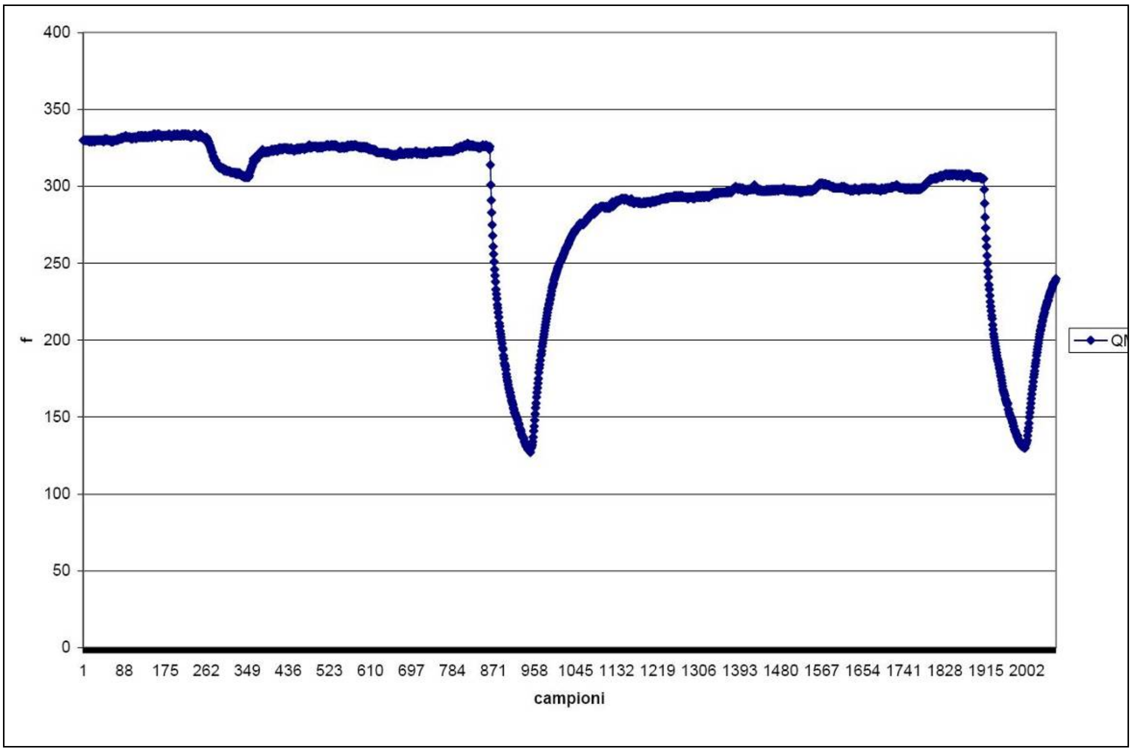


Fig. 30: response curve of sensor 7 to CO, CO-H2O and H2O.

Tab. 10 reports the frequency shifts for sensor 7 related to each measured sample, showing that the summing error is about 1%.

	CO20ppm	**CO20ppm** **H2O 20%**	**H2O 20%**
Frequency shift (Hz)	25	198	175

Tab. 10: frequency shifts for sensor 7 during the session.

The results obtained during this session lead to the following conclusions:

- the NAFION filter can be efficiently used to reduce the water vapour content of the sampled gas, without influencing the carbon monoxide concentration;
- the response to carbon monoxide can be extrapolated from the output signal if the calibration curve of the NAFION filter was determined and an RH sensor is present in the measurement chamber.

2.7.4 CO measurements without NAFION filter with humidity level

Also this session was aimed at testing the carbon monoxide sensors in working conditions similar to the real case, i.e.: with a RH level equal to 20% without the NAFION filter.

The sensors showed that the responses to CO at a certain humidity level are the sum of the single responses to carbon monoxide and 20% water vapour.

Of course the observed frequency shifts where similar to those described in the previous section.

What is worth to be pointed out here is that half of the sensors were treated thermally (8 hours at 120°C) before the session, while half of the sensors were cleaned in a constant N2 stream for the same time.

The results obtained during this session confirm that the thermal treatment is more efficient for enhancing the sensors’ recovery after exposure to CO (and water vapour) than the simple cleaning in nitrogen.

Moreover, the sensors’ performances can be recovered almost at the original level.

2.8 Demo system assembly

The results obtained during the measurement sessions showed that this technology is very promising for developing low cost, selective CO sensors.

Though reversibility is a critical problem, it can be improved by implementing simple counteractions such as:

- optimization of the measurement protocol with an effective trade off between the durations of the measurement and cleaning phases;
- development of integrated heaters to enhance reversibility and speed up the recovery time.

For the above reason the feasibility study has been considered successful and a demo system has been set-up to establish a starting point for further industrial developments.

The demo system is composed by the following modules:

- a single sensor, transparent, measuring chamber;
- a single sensor transduction electronics (single supply oscillator circuit);
- a portable frequency counter (AGILENT) for signal acquisition;
- USB-GPIB board for connecting the counter to a notebook;
- an ad-hoc developed acquisition software and user interface (AGILENT VEE).

The QMB sensor is a 20MHz TSMR resonator with a sensitive layer realized by spray casting deposition of the membranes reported in section 5.

Fig. 31 Reports a schematic of the demo system.

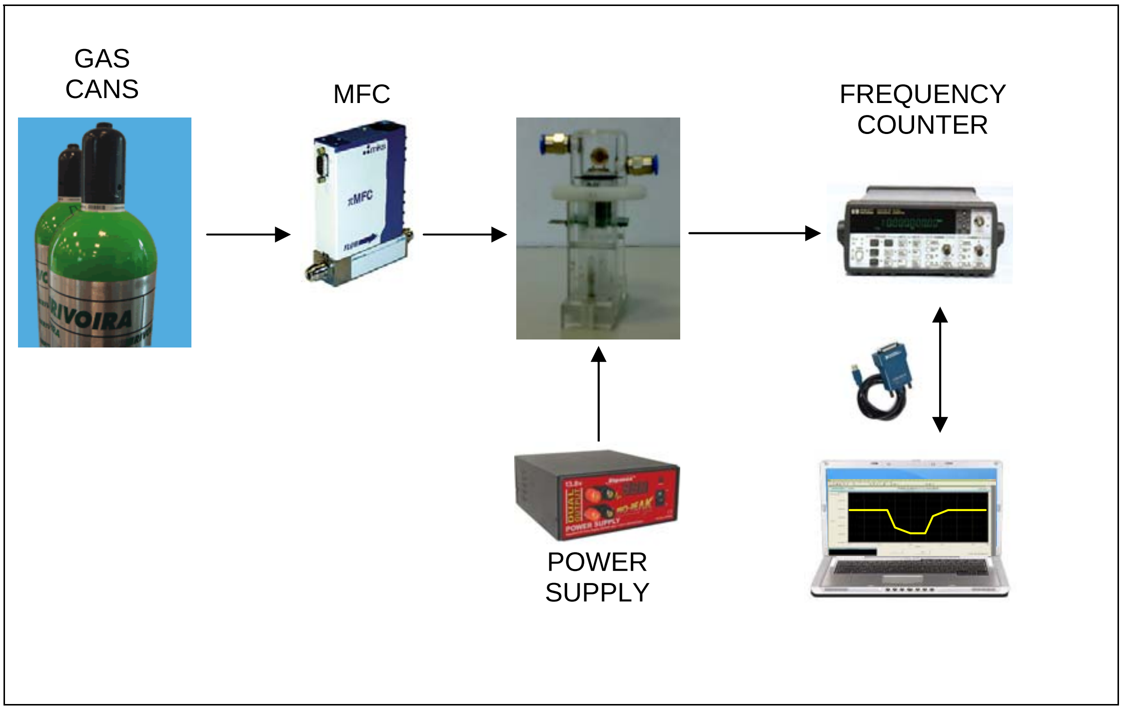


Fig. 31: block scheme of the demo system.

The following picture reports the measurement chamber and the oscillator circuit.

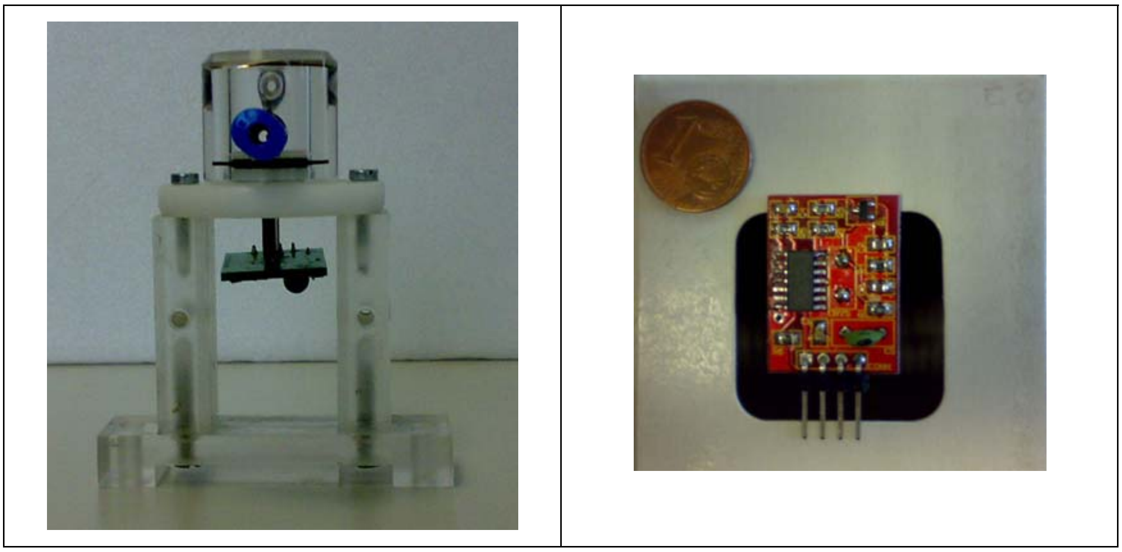


Fig. 32: measurement chamber and oscillator circuit PCB.

2.9 Comparison with the state of the art [3, 13-18]

The results obtained during this feasibility study show that the QMB sensors technology can be exploited for developing highly sensitive carbon monoxide sensors with high resolution levels.

Data concerning QMB6 (CIM = *Fe(III)[T(3,5(OH)2P)P](Cl))* are listed below:

- Response level @ 10ppm CO = 95,5 Hz (CO in N2);
- Sensitivity @ 10ppm CO = 6.45 Hz/ppm (CO in N2);
- Resolution @ 10ppm CO = 800 ppb (CO in N2).

The resolution level has been estimated considering a noise level of about 5Hz and then multiplying that level by 3, thus providing a high overestimation.

The following table compares the performances of the carbon monoxide sensor developed within the PhD course with some results published during the same period.

Sensor type	**Performances**	**Reference**
QMB	Sensitivity = 1,6Hz/ppm LOD= 0,91ppm	[13]
MOX	LOD = 0,8ppm	[14]
MOX	Range = 100-4000ppm	[15]
CNT	Range = 10-200ppm LOD = 0,01ppm	[16]
MOX	LOD = 10ppm	[17]
MOX	Range = 25-1000ppm	[18]

Though the literature data are not expressed according to a standard, it is worth pointing out that the feasibility study reported within this thesis lead to developing a prototype of an innovative carbon monoxide sensor whose performances, though at a demo level, are already comparable with the state of the art reported in literature.

2.10 Discussion

This chapter reported the results of the feasibility study about the possibility to develop a carbon monoxide sensor based on Quartz Microbalance devices.

The target gas was chosen because its toxicity level and wide field of applications require highly sensitive and selective sensors possibly thought to be low cost.

Since the framework the PhD course was developed within was an industrial innovation project, the choice for the transduction technique was aimed at finding an alternative technique with respect to optical, thermal, conductometric or electrochemical devices.

TSMR resonators were selected as transduction elements, while the Chemical Interactive Materials have been deployed according to a biomimetic approach: Fe-porphyrins exploiting the iron ions affinity towards CO, as it happens with the haemoglobin molecule in blood.

The biological phenomenon that unfortunately may lead to CO poisoning, becomes here the basic assumption for developing innovative carbon monoxide sensors.

Prototypes have been tested at various concentration levels and a solution for reducing the humidity influence has been obtained through the use of a NAFION filter.

Though still a prototype, the QMB sensors demonstrated promising features, in terms of sensitivity and resolutions, even if compared with the state of the art reported in literature.

The successful results obtained during the testing phase, lead to the decision of designing and developing a demo system to be used as a starting point for a future industrialization of the sensor.

A low cost, small size dosimeter can be envisaged as one of the practical implementation of the technology developed during this study.

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Chapter 3

Development of SAW sensors based on lanthanide complexes for DMMP detection

3.1 Introduction [1]

The list of most toxic chemical compounds includes about 70 substances, whose properties can be used to kill, injure or incapacitate a person.

According to the UN *Chemical Weapons Convention* of 1993, lethal toxic chemicals have been classified in 3 main groups:

- *Schedule 1*: have legitimate use only for research (medical, pharmaceutical) or for protective purposes (testing of sensors or protective clothing). Examples: Nerve Agents, Lewisite, Mustard gas.
- *Schedule 2*: have legitimate small-scale industrial use. Examples: DMMP (Sarin precursor) used as flame retardant, Thiodiglycol (Mustard precursor) used as solvent in inks.
- *Schedule 3*: have legitimate large-scale industrial use. Examples: Phosgene used for manufacturing plastics.

Then it is evident how sensitive and selective detectors for such compounds are required mainly for industrial safety and civil protection, while detectors for military applications can be considered not interesting within the scope of this work.

Among the compounds belonging to the above schedules, DMMP (Dimethylmethylphosphonate) plays a relevant role.

DMMP is not classified as toxic, but becomes harmful if inhaled, swallowed or absorbed through the skin.

Yearly USA production of DMMP is between 91000 and 910000 kg.

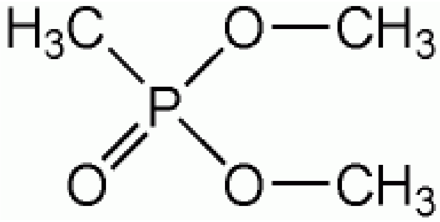
The importance of measuring DMMP can be easily explained by just looking at its possible applications:

- flame retardant;
- additive for gasoline;
- anti-foaming agent (food or drug ingredient);
- plasticizer;
- stabilizer;
- textile conditioner;
- antistatic agent;
- additive for solvents;
- additive for low temperature hydraulic fluids;
- catalyst and reagent in organic synthesis;
- Sarin precursor (military);
- Sarin simulant (military).

3.2 DMMP properties [2]

Dimethyl methylphosphonate, or methylphosphonic acid dimethyl ester (DMMP), is a colourless liquid or gas with chemical formula $CH_3PO(OCH_3)_2$.

The structure formula of DMMP is reported in the following picture.



Its melting point is -50 °C and its boiling point is 181 °C.

DMMP is a combustible compound that emits a distinct odour and slowly undergoes hydrolysis when in contact with water.

Moreover DMMP may soften some plastics and rubbers and it is a suspected carcinogen.

3.3 DMMP detectors [3-16]

There are only four approaches to analytical measurement of lethal toxic compounds:

(1) one-dimensional sensors, which rely on the selective detection of the analyte;

(2) two-dimensional sensors, in which a separation step is coupled with selective detection;

(3) three-dimensional sensors, in which a two-dimensional separation step is coupled with selective detection;

(4) four-dimensional sensors, in which a three-dimensional separation step is coupled with selective detection.

The 4 different configurations will be described in the following paragraphs.

3.3.1 One-dimensional sensors

The simplest approach for chemical detection is to target the specific compound of interest and selectively detect it in the presence of other background compounds and interferences.

One-dimensional detectors can be classified as in the following list:

- *Acoustic sensors*: SAW covered with selective membranes.
- *Optical sensors*: colorimetric indicators, luminescence based sensors.
- *Biosensors*: amperometric enzyme biosensor, highly selective protein antibodies.

3.3.2 Two-dimensional sensors

Due to the complex nature of the agents and their matrices, nonseparation-based analytical methods often experience interferences, which result in false positive or negative responses.

Thus, some type of separation method is often coupled to an analytical detector to provide more specificity of response and a broader range of application.

The most common separation devices are:

- Gas Chromatography;
- Liquid Chromatography;
- Capillary Electrophoresis;
- Ion Mobility Spectroscopy;
- Mass Spectrometry.

3.3.3 Three-dimensional sensors

Even with high-resolution, two-dimensional sensors, mistakes can be made with respect to identification of unknown analytes.

Thus, for absolute identification, data obtained using three-dimensional sensors are normally recommended.

In these devices a two-dimensional separation step is coupled with selective detection

Because of the complexity of these instruments, they are difficult to operate in the field without the support of a full mobile laboratory.

The most common three-dimensional sensors are:

- GC/MS: Gas Chromatography/Mass Spectrometry;
- LC/MS: Liquid Chromatography/Mass Spectrometry;
- IM/MS: Ion Mobility/Mass Spectrometry;
- CE/MS: Capillary Electrophoresis/ Mass Spectrometry;
- GC/GC: Gas Chromatography/Gas Chromatography;
- LC/GC: Liquid Chromatography/Gas Chromatography.

3.3.4 Four-dimensional sensors

Given that chromatographic separations occur on the order of minutes, ion mobility separations on the order of milliseconds, and mass separations on the order of microseconds, four-dimensional sensors are possible when these separation techniques are coupled in series.

3.4 Approaching DMMP detection

The approach followed within this study was aimed at verifying our capabilities for developing DMMP sensors based on the mass changes transduction technique.

The transduction elements were surface acoustic wave devices, provided by the IDAC Institute of CNR, whose characteristic frequency was about 430MHz.

Fig. 33 reports one of the SAW devices.

Fig. 33: transduction element for DMMP detection.

3.4.1 Chemically Interactive Material [17-32]

Recent experiments demonstrated that the luminescence of Terbium and Europium complexes (both in liquid and solid phase) is greatly influenced by the presence of compounds like ammines and alcohols.

Since lanthanide ions also have a strong affinity for the P=O group, then it is reasonable envisaging a higher sensitivity for organophosphorous compounds with respect to ammines and alcohols.

Then the CIM selected for this study was an erbium porphyrin, being erbium a lanthanide.

Fig. 34 reports the structure of the sensitive layer.

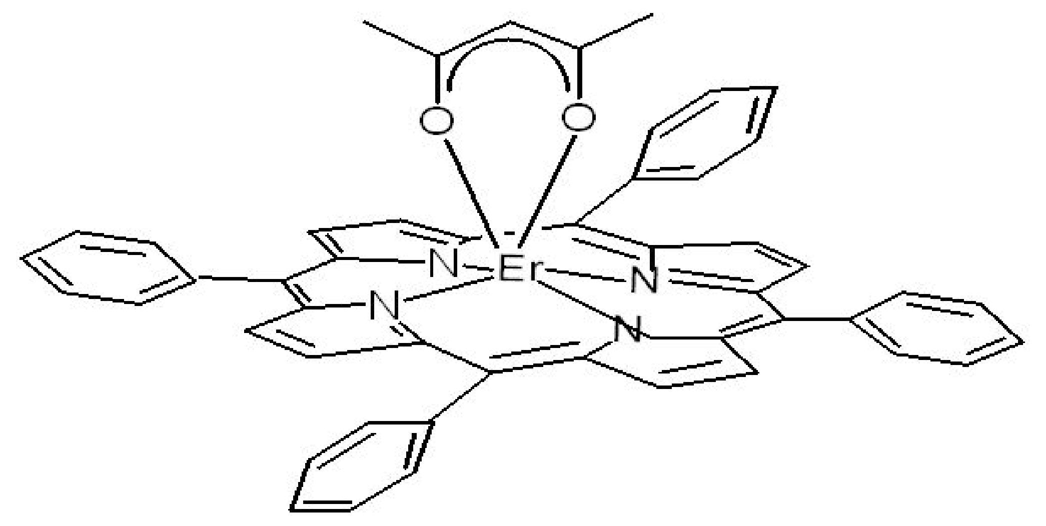


Fig. 34: Er-porphyrin used for the study.

The sensitive layer has been deposed on to the transduction element surface by the spray casting technique, using a deposition time between 12 and 16 seconds.

Fig. 35 and Fig. 36 report the transduction element covered with the chemical interactive material.

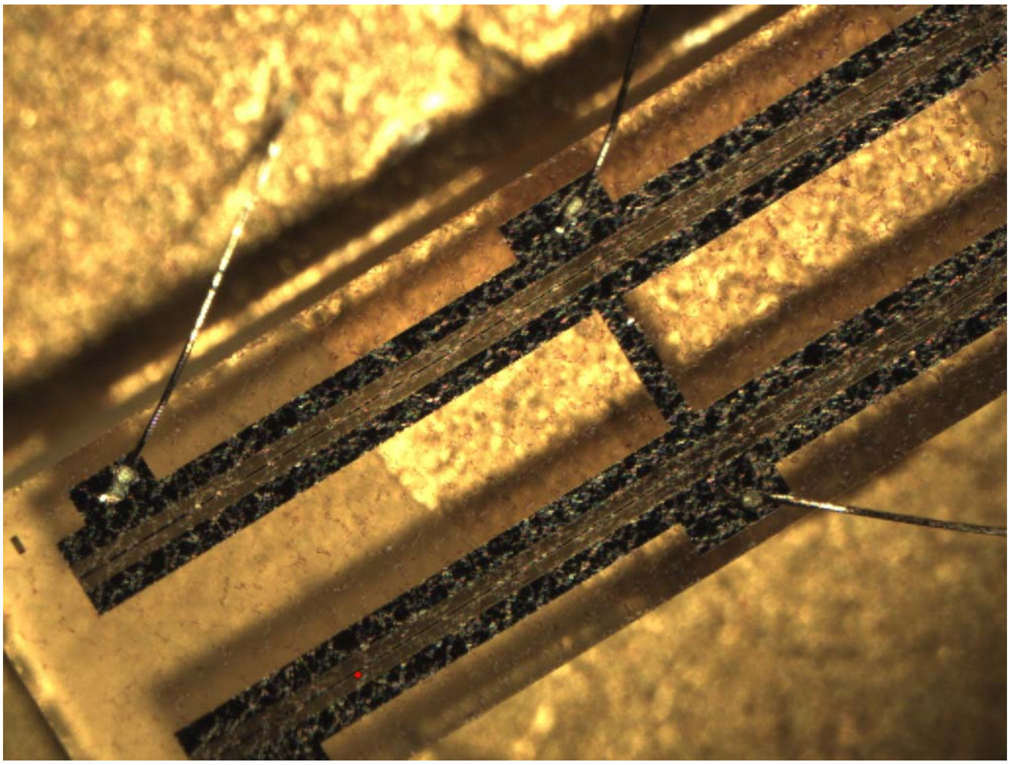


Fig. 35: transduction element covered with the sensitive layer.

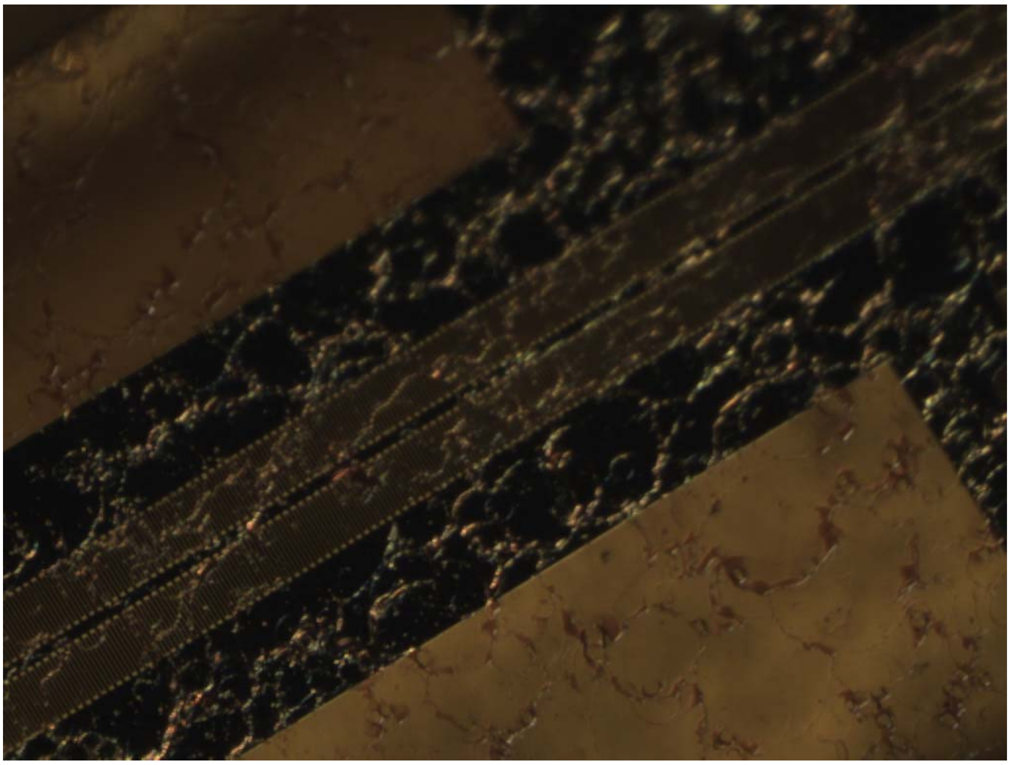


Fig. 36: detail of the transduction element covered with the CIM.

The pictures demonstrate that the deposition technique is still too rough and a homogeneous layer cannot be obtained yet.

3.5 Prototype design and development

Prototype devices have been mounted inside an ad-hoc designed chamber, and the experimental set-up was as described in the following:

N2 tank (carrier and cleaning gas);

Mass Flow Controllers set;

DMMP bubbler;

Measurement chamber;

HP frequency counter;

NI-GPIB-USB board;

ad-hoc developed acquisition SW;

Power Supply unit.

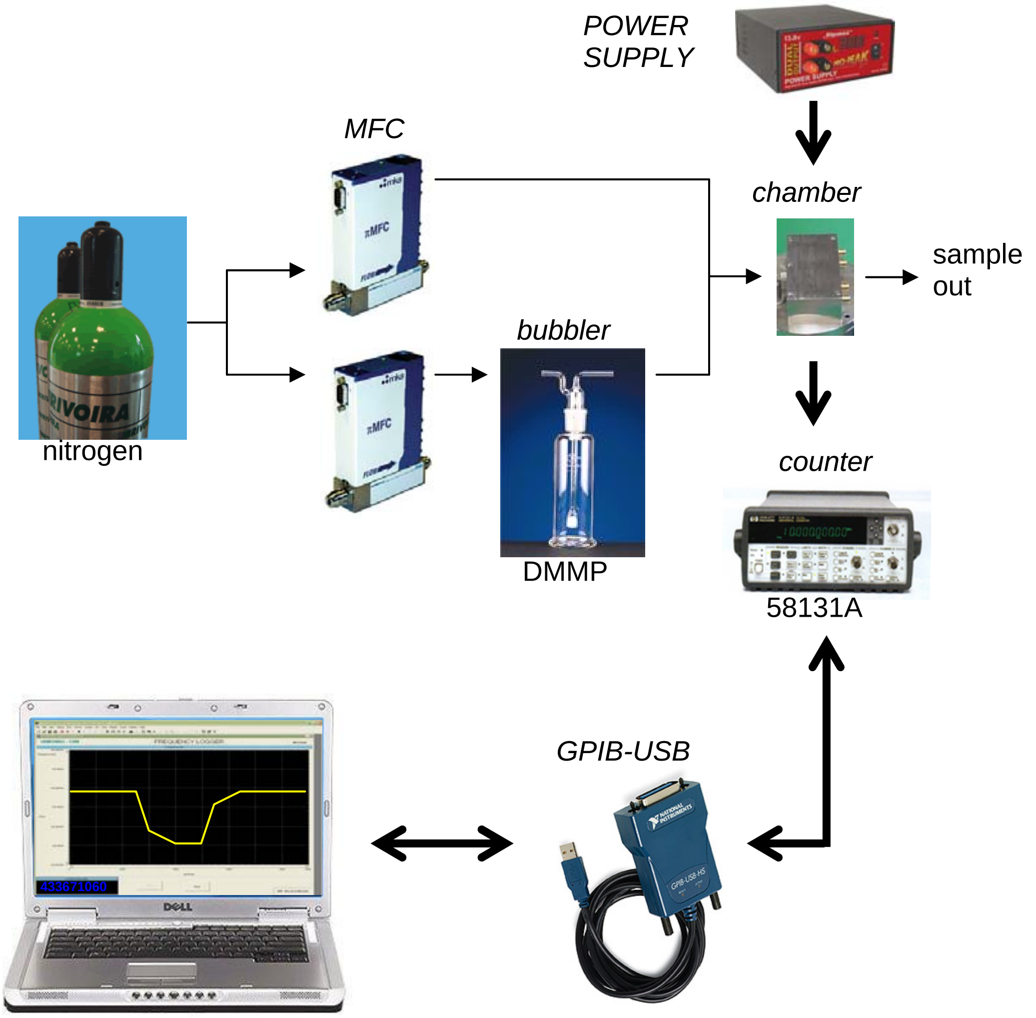


Fig. 37: measurement set-up.

3.5.1 Data acquisition software

During the screening phase the readout device was a commercial frequency counter (Agilent 58131A) interfaced with the PC through a GPIB-USB board.

The user interface (see also Fig. 38) was an ad-hoc tool, developed within the VEE (Agilent) programming software.

The designed user available functions are:

- Counter setting;
- Data displaying both in numerical and graphical modes;
- Data storage (text format).

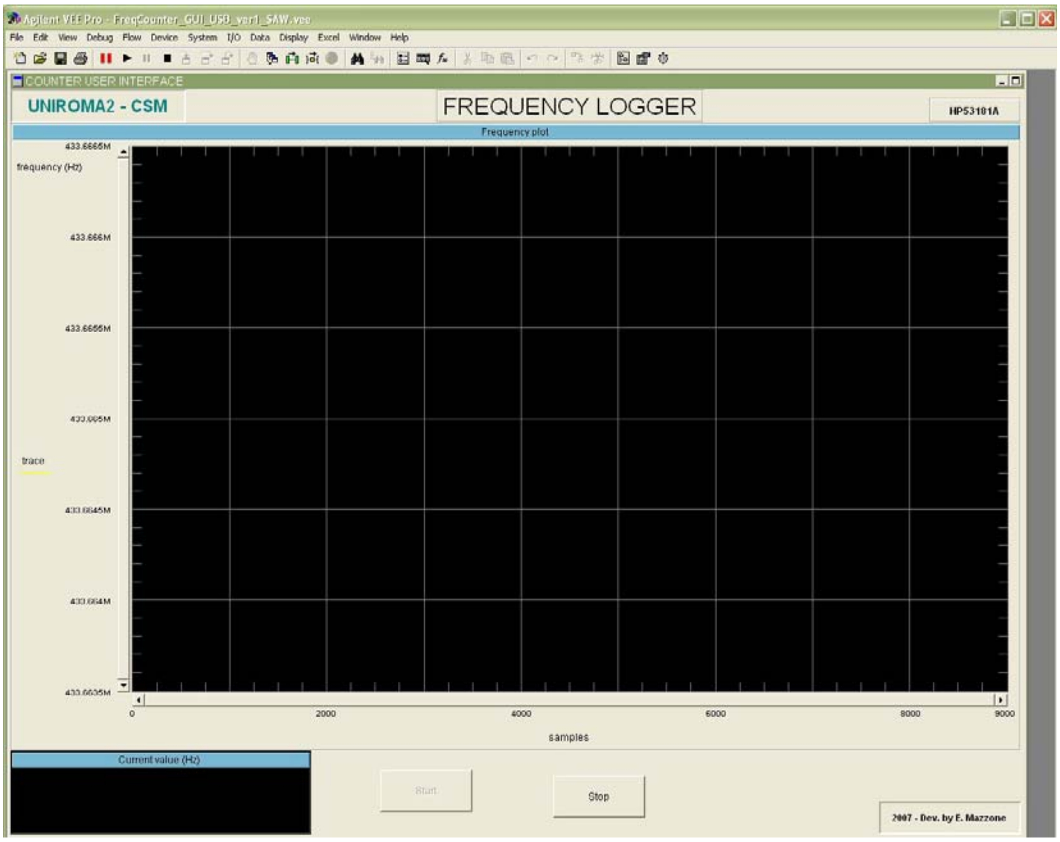
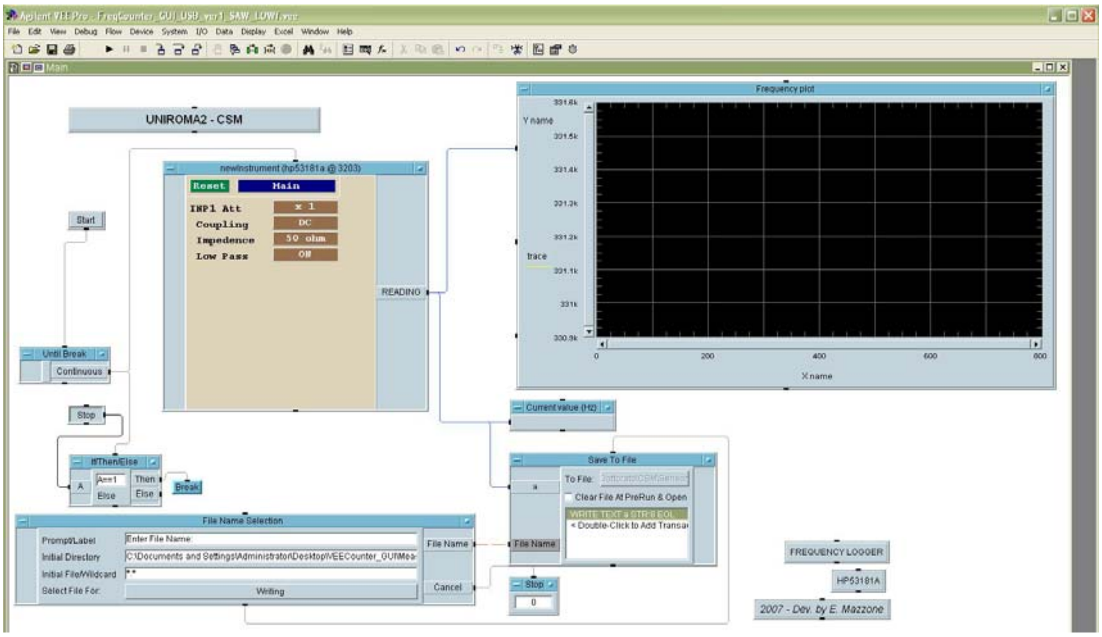


Fig. 38: user interface.

Fig. 39 reports the object oriented design of the user interface.



INP1 Att x 1
Coupling DC
Impedence 50 ohm
Low Pass Off

Prompt/Label: Enter File Name:
Initial Directory: C:\Documents and Settings\Administrator\Desktop\VEECounter_GUI\Mea
Initial File/Wildcard: *.*
Select File For: Writing

Fig. 39: object oriented code of the GUI.

3.6 Measurements

Test measurements have been performed on two prototype sensors, with deposition times of 12 and 6 seconds respectively, plus an empty transduction element to be used as a reference.

The devices were enclosed in gas chamber provided by the IDAC-CNR institute.

According to the test protocol, the sensors have been exposed to various DMMP concentrations, i.e.: 5%, 10%, 15% and 20%.

Fig. 40 reports a typical output of one of the sensors to the above concentrations.

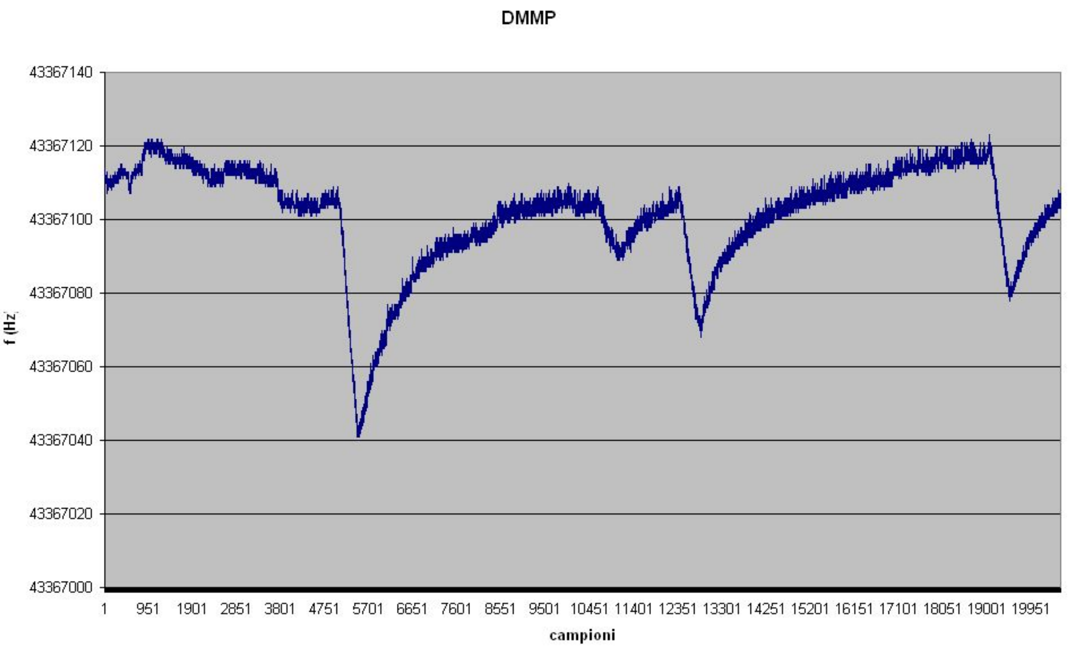


Fig. 40: typical sensor response to DMMP @ 5%, 10%, 15% and 20%.

The responses at each concentration range were:

- Δf = 120 Hz @ 10% DMMP;
- Δf = 385 Hz @ 15% DMMP;
- Δf = 650 Hz @ 20% DMMP.

Since the DMMP is a very dense compound and since the target mixture was obtained using a bubbler, it has been necessary applying a correction on the gas concentration value.

Using the Antoine equation it can be estimated that the resolution level of tested sensors is well under 5ppm.

3.7 Demo system assembly

As in the case of carbon monoxide, also this feasibility study demonstrated that the selected approach is very promising for developing low cost, selective DMMP sensors.

The next step consisted in developing a multichannel acquisition system that allows for measuring up to four sensors simultaneously.

That architecture, besides speeding up the feasibility study, could be used as a demo system and could represent the starting point for further industrialization.

Fig. 41 reports a blocks schematic of the demo set-up, which includes the following modules:

- conditioning electronics (transduction electronics);
- NI PCI-6601 acquisition board;
- user interface and data logger software (LabView).

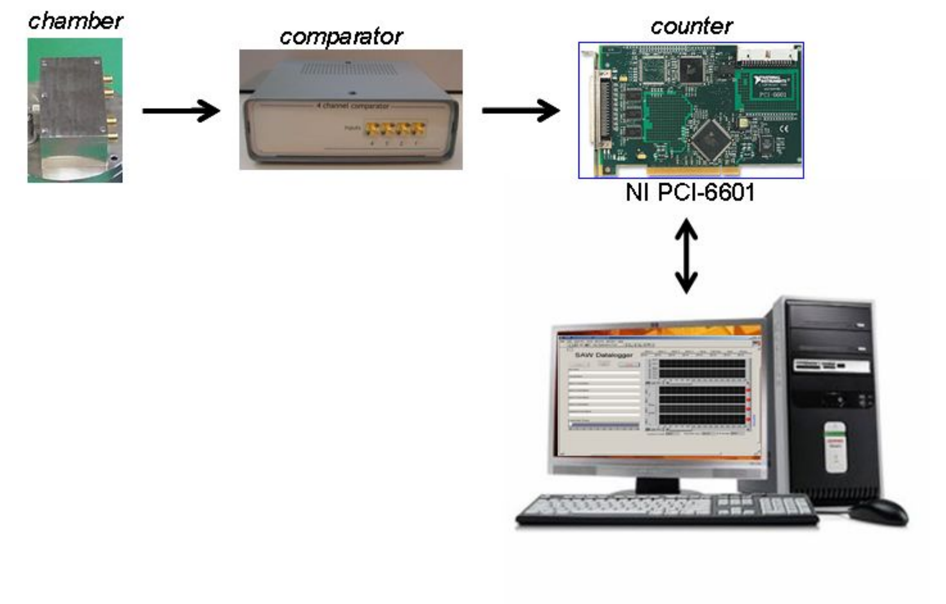


Fig. 41: representation of the multichannel acquisition system.

The single modules will be described in the next subparagraphs.

3.7.1 Conditioning electronics

The conditioning circuit was designed and developed adapt the sensors' output signals so as to maximize the performances of the acquisition system.

The main characteristics of the conditioning electronics were:

- TTL compatibility of the output levels;
- 0-2MHz bandwidth.

The architecture is based on a commercial integrated TTL comparator (MAX909), whose main features are:

- Propagation Delay = 40 ns;
- Supply Current = 700 uA (3.5 mW);
- Wide Input Range (Icludes V-);
- Low Offset Voltage (500 uV);
- Internal Hysteresis (Provides Clean Switching);
- Input and Output Short – Circuit Protection.

The system has been designed to support a differential measurement strategy: the outputs represent the frequency shifts of each sensor with respect to a reference device.

That solution ensured that the output signals were within the bandwidth of the comparators.

Fig. 42 reports the I/O characteristics of the MAX909, for a sinusoidal input of 10MHz.

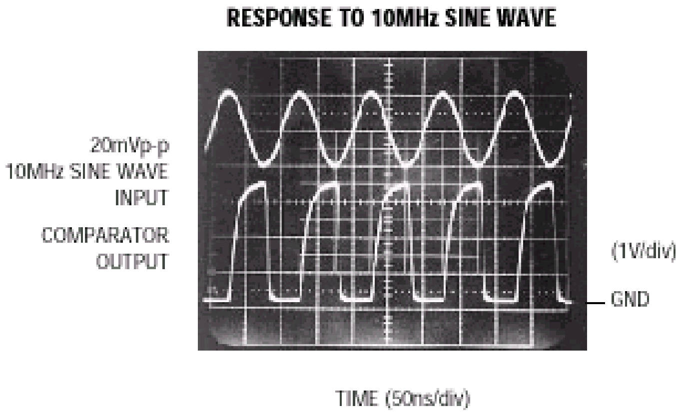


Fig. 42: designed I/O performances of the MAX909.

The board is composed by four identical channels, whose schematic is reported in Fig. 43.

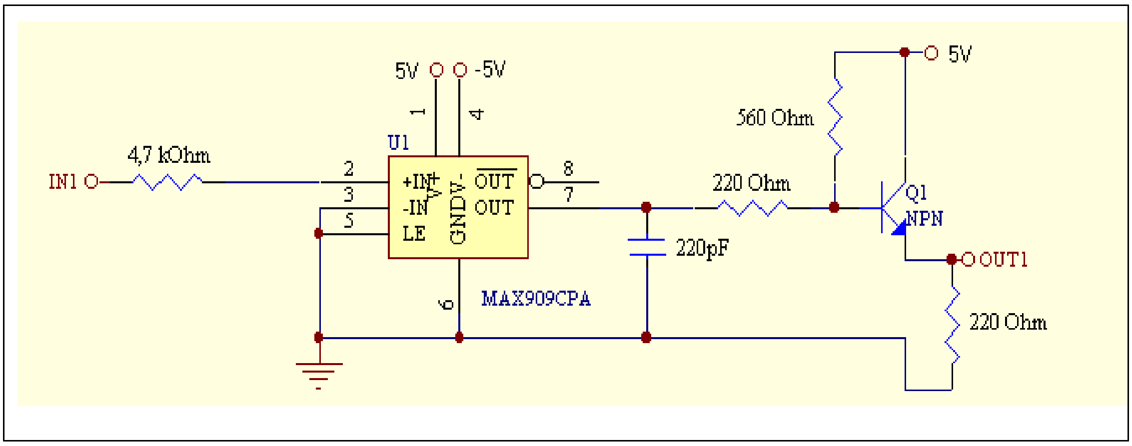


Fig. 43: schematic of comparator circuit.

As shown in Fig. 44 and Fig. 45 , the MAX909 is followed by a low-pass filter and by a transistor stage that provides the right amount of current for the National Instrument board to function properly.

Fig. 44 and Fig. 45 report the 3D board simulation and a picture of the realized device respectively.

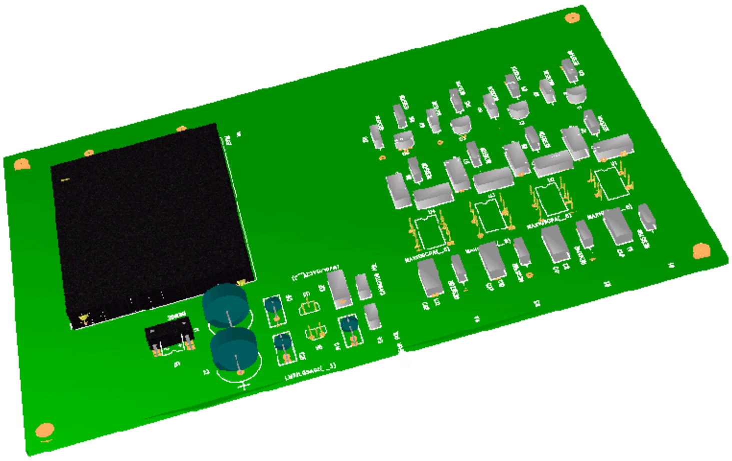


Fig. 44: 3D representation of the mother board.

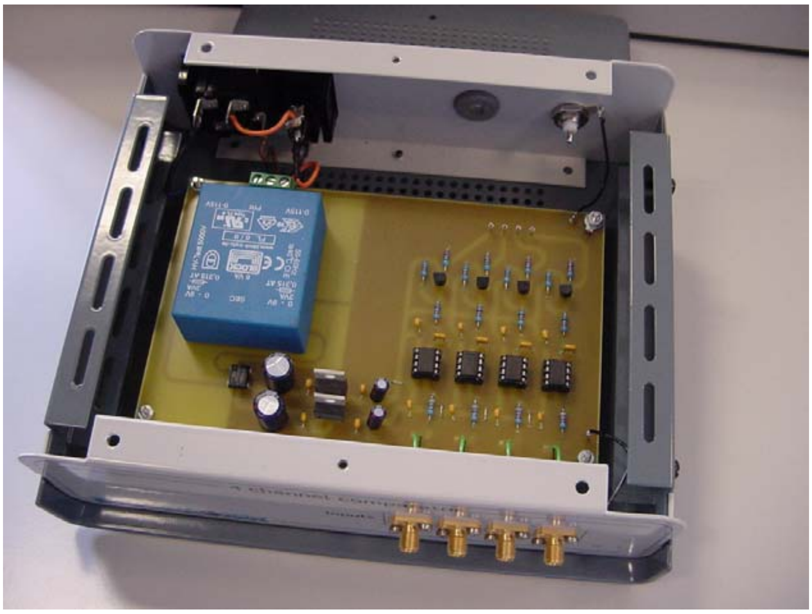


Fig. 45: digital picture of the prototype comparator.

3.7.2 Acquisition board

The demo system is equipped with a National Instruments data acquisition board, NI-PCI6601, which is responsible for counting the frequency outputs of up to four sensors.

The board is mounted on the PCI slot of a desktop computer, thus incrementing the overall dimensions, a trade-off compromise which should be taken into account to obtain the required flexibility during the feasibility study.

The board provides the following features:

- Internal 20MHz timebase;
- 4 32-bit counters (1 DMA, 3 IRQ)
- 32 I/O digital lines.

3.7.3 Data logging software

The data logging software, developed within the LabView programming environment, stores data from the 4 sensors using the single DMA counter, thus to achieve a high acquisition bandwidth.

This solution was adopted since the IRQ counters do not allow the transmission rate required for the real time simultaneous acquisition of the 4 channels.

Fig. 46 reports the flow diagram of the acquisition routine.

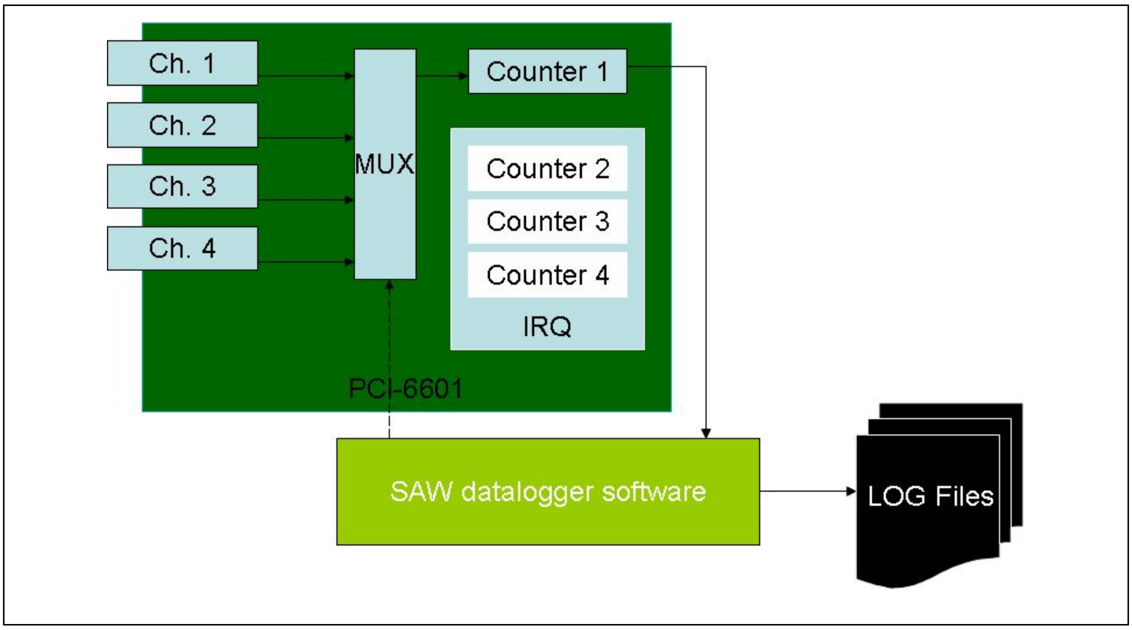


Fig. 46: flow diagram of the acquisition routine.

The user interface is very simple and allows setting the measurement session, editing custom information (e.g.: sensitive layers composition) and displaying the data plots.

Fig. 47 reports the control panel of the user interface.

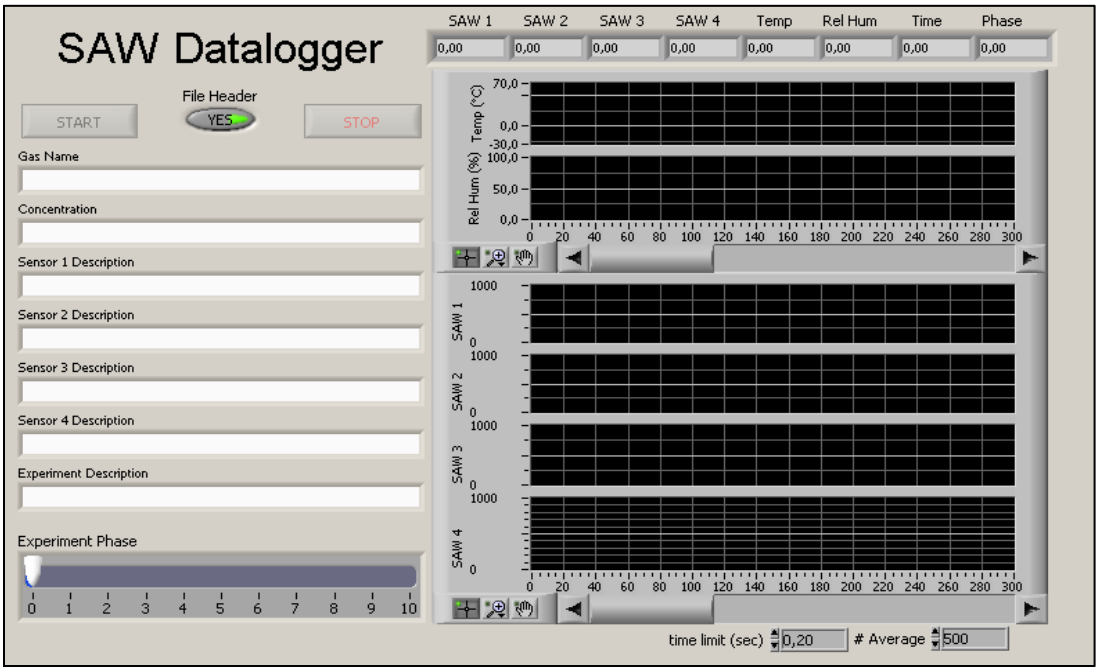

SAW 1: 0,00
SAW 2: 0,00
SAW 3: 0,00
SAW 4: 0,00
Temp: 0,00
Rel Hum: 0,00
Time: 0,00
Phase: 0,00
File Header: YES
time limit (sec): 0,20
Average: 500

Fig. 47: user interface of the demo system.

3.8 Comparison with the state of the art [17-31]

The results obtained during this feasibility study show that lanthanide-porphyrin complexes can be exploited as sensitive layers in SAW transduction elements for developing DMMP sensors based on mass changes.

This approach is aimed at obtaining compact, low cost, selective and highly sensitive toxic gas sensors, and it is being attempted since many years.

Nowadays it represents the leading solution adopted by researchers worldwide.

The resolution level obtained within this study has been estimated in 5ppm and as been compared with some results published during the same period.

Sensor type	**Performances**	**Reference**
QMB	Range = 5-60ppm DMMP Sensitivity = 3,14Hz/ppm DMMP LOD = 0,94ppm DMMP	[35]
SAW	Range = 1-5ppm	[36]
MOX	Range = 0,02-0,8ppm	[37]
MOX	LOD = 50ppb	[33]
OPTICAL	Range = ppq to ppb	[38]

Though the literature data are not expressed according to a standard, it is evident that most of the claimed performances are better then those here presented.

It is worth pointing out that the guidelines for improving the sensitivity and resolution levels have already been identified in the following:

Selection/development of a controlled deposition technique;

Selection of a more sensitive transduction element;

Accurate temperature control;

Accurate flow control;

Proper shielding (also at layout level).

Thus, it is reasonable envisaging that better performances can be achieved during industrialization.

3.9 Discussion

This chapter reported about the feasibility study concerning the possibility of developing a toxic gas sensor based on Surface Acoustic Wave devices.

The selected target was chosen due to its large scale industrial use and due to its potential use as a nerve agent precursor (DMMP is a Sarin stimulant).

For the above reasons, highly sensitive and selective DMMP sensors may be required in a large field of applications, from industrial security to civil protection and also to military use.

The scope of this study was the investigation of a development strategy for toxic gas sensors, which could possibly provide the following features:

- high sensitivity;
- high resolution;
- high selectivity;
- low cost;
- low power consumption;
- low dimensions;
- low complexity.

The last characteristic should be intended as a comparison with the standard analytical tools usually adopted for such analytes: GC, LC, CE, MS, IMS (and their use in series).

The sensitive layer, a lanthanide-porphyrin complex, was chosen according to the results of preliminary studies that showed a high affinity versus organophosphorous compounds such as DMMP, thus allowing the expectation of state-of-art comparable performances of the sensor.

Prototypes have been tested at various concentration levels and compared with the results published by other authors.

The comparison shows that the performances are much lower with respect to MOX and OPTICAL sensors which, on the other hand, are characterized by higher power consumption (MOX) and higher cost (OPTICAL).

It is worth pointing out that the performances are comparable with respect to analogous devices based on QMB and SAW.

The above successful results lead to the decision of designing and developing a demo system to be used as a starting point for a future industrialization of the sensor.

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Chapter 4

Development of QMB biosensors for CO and DMMP detection: a feasibility study

4.1 Introduction

This last chapter of the Thesis reports the activities related to a preliminary study on the applicability of sensing layers made of biological compounds for detecting CO and DMMP.

The reason why this investigation was made is in that up to date no papers have been published on this topic, being it really innovative.

This study has been carried out in cooperation with Prof. Compagnone and Dr. Mascini of the University of Teramo, Food Science Department.

The importance of measuring CO and the importance of measuring DMMP have already been discussed in the previous chapters, for the same reasons the target gas have not been changed.

Also the transduction technique was not modified and great attention has been paid on acoustical transduction elements such as TSMR resonators.

The prototype measurement system was set up using an electronic nose, thus allowing testing an array of 8 sensors simultaneously.

What is worth pointing out is the selection of the sensing material, in that it was of biological type: a set of amino acids whose properties will be discussed in the next section.

- Glutamic acid;
- Leucine;
- Histidine;
- Phenylalanine;
- Tyrosine;
- Lisine.

4.2 Amino acids [1]

In chemistry an **amino acid** is a molecule that contains both amine and carboxyl functional groups.

In biochemistry, this term refers to alpha-amino acids with the general formula $H_2NCHRCOOH$, where R is an organic substituent.

In the alpha amino acids, the amino and carboxylate groups are attached to the same carbon, which is called the α-carbon.

The various alpha amino acids differ in which side chain (R group) is attached to their alpha carbon.

They can vary in size from just a hydrogen atom in glycine, through a methyl group in alanine, to a large heterocyclic group in tryptophan.

Beyond the amino acids that are found in all forms of life, many non-natural amino acids have vital roles in technology and industry.

For example, the chelating agents EDTA and nitriloacetic acid are alpha amino acids that are important in the chemical industry.

Alpha-amino acids are the building blocks of proteins.

A protein forms via the condensation of amino acids to form a chain of amino acid "residues" linked by peptide bonds.

Proteins are defined by their unique sequence of amino acid residues; this sequence is the primary structure of the protein.

Just as the letters of the alphabet can be combined to form an almost endless variety of words, amino acids can be linked in varying sequences to form a huge variety of proteins.

Twenty standard amino acids are used by cells in protein biosynthesis, and these are specified by the general genetic code.

These twenty amino acids are biosynthesized from other molecules, but organisms differ in which ones they can synthesize and which ones must be provided in their diet.

The ones that cannot be synthesized by an organism are called essential.

4.2.1 Properties of amino acids

The general structure of a α-amino acid contains the amino group on the left and the carboxyl group on the right, see Fig. 48, where *R* represents a side chain specific to each amino acid.

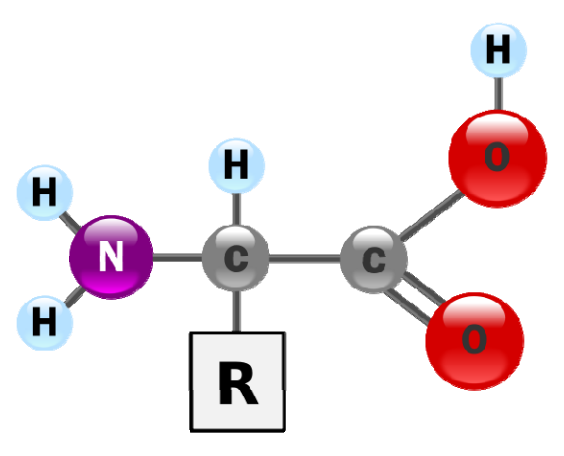


Fig. 48: amino acids structure.

The central carbon atom called C_α is a chiral central atom (with the exception of glycine) to which the two termini and the R-group are attached.

Amino acids are usually classified by the properties of the side chain that can make them behave like:

- A weak acid;
- A weak base;
- A hydrophile if they are polar;
- A hydrophobe if they are non-polar.

The 20 standard amino acids, along with their chemical properties, are catalogued in Tab. 11.

Amino Acid	**3-Letter**	**Side chain polarity**	**Side chain acidity or basicity**
Alanine	Ala	nonpolar	neutral
Arginine	Arg	polar	basic (strongly)
Asparagine	Asn	polar	neutral
Aspartic acid	Asp	polar	acidic
Cysteine	Cys	polar	neutral
Glutamic acid	Glu	polar	acidic
Glutamine	Gln	polar	neutral
Glycine	Gly	nonpolar	neutral
Histidine	His	polar	basic (weakly)
Isoleucine	Ile	nonpolar	neutral
Leucine	Leu	nonpolar	neutral
Lysine	Lys	polar	basic
Methionine	Met	nonpolar	neutral
Phenylalanine	Phe	nonpolar	neutral
Proline	Pro	nonpolar	neutral
Serine	Ser	polar	neutral
Threonine	Thr	polar	neutral
Tryptophan	Trp	nonpolar	neutral
Tyrosine	Tyr	nonpolar	neutral
Valine	Val	nonpolar	neutral

Tab. 11: list and properties of the 20 standard amino acids.

As amino acids have both a primary amine group and a primary carboxil group, these chemicals can undergo most of the reactions associated with these functional groups.

The multiple side chains of amino acids can also undergo chemical reactions.

4.2.2 Hydrophilic and hydrophobic amino acids

Depending on the polarity of the side chain, amino acids vary in their hydrophilic or hydrophobic character.

These properties are important in protein structure and protein-protein interactions.

The importance of the physical properties of the side chains comes from the influence this has on the amino acid residues' interactions with other structures, both within a single protein and between proteins.

The distribution of hydrophilic and hydrophobic amino acids determines the tertiary structure of the protein, and their physical location on the outside structure of the proteins influences their quaternary structure.

For example, soluble proteins have surfaces rich with polar amino acids like serine and threonine, while integral membrane proteins tend to have outer ring of hydrophobic amino acids that anchors them into the lipid bilayer, and proteins anchored to the membrane have a hydrophobic end that locks into the membrane.

Similarly, proteins that have to bind to positively-charged molecules have surfaces rich with negatively charged amino acids like glutamate and aspartate, while proteins binding to negatively-charged molecules have surfaces rich with positively charged chains like lysine and arginine.

4.3 Sensing layers [1]

The following subparagraphs describe briefly the amino acids selected for this feasibility study.

4.3.1 Glutamic acid

Glutamic acid (abbreviated as **Glu** or **E**; **Glx** or **Z** represents either glutamic acid or glutamate), is one of the 20 proteinogenic amino acids.

It is not among the human essential amino acids and the side chain is of polar type.

Fig. 49 reports the chemical structure of glutamic acid.

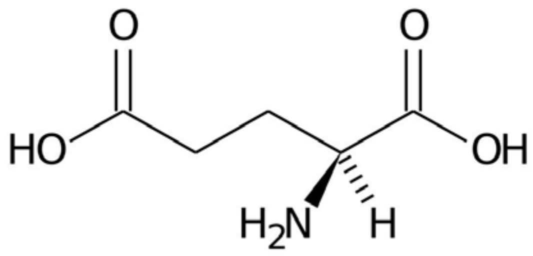


Fig. 49: chemical structure of glutamic acid.

4.3.2 Leucine

Leucine (abbreviated as **Leu** or **L**) is an α-amino acid with the chemical formula $HO_2CCH(NH_2)CH_2CH(CH_3)_2$.

It is an essential amino acid that has a hydrocarbon side chain.

Leucine is classified as a hydrophobic amino acid and its chemical structure is reported in Fig. 50.

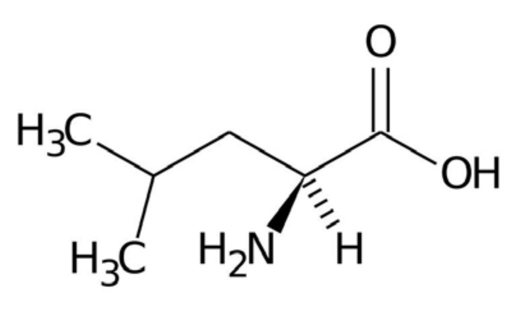


Fig. 50: chemical structure of leucine.

4.3.3 Histidine

Histidine (abbreviated as **His** or **H**) is one of the 20 most common natural amino acids present in proteins.

Its side chain is of polar type and its chemical structure is reported in Fig. 51.

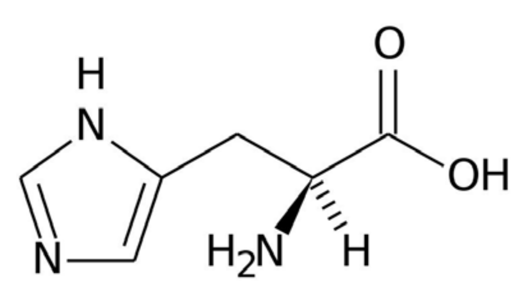


Fig. 51: chemical structure of histidine.

4.3.4 Phenylalanine

Phenylalanine (abbreviated as **Phe** or **F**) is an α-amino acid with the formula $HO_2CCH(NH_2)CH_2C_6H_5$.

This essential amino acid is classified as non-polar because of the hydrophobic nature of the benzyl side chain.

The chemical structure of phenylalanine is reported in Fig. 52.

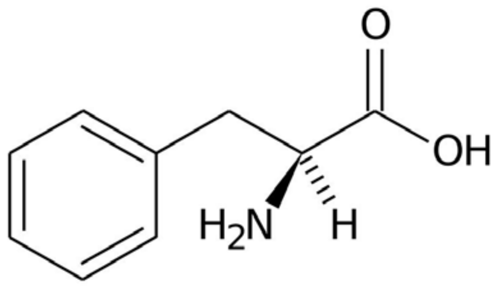


Fig. 52: chemical structure of phenylalanine.

4.3.5 Tyrosine

Tyrosine (abbreviated as **Tyr** or **Y**) is one of the 20 amino acids that are used by cells to synthesize proteins.

This is a non essential amino acid and it is found in large quantities in casein.

Tyrosine has a polar side chain and the chemical structure is reported in Fig. 53.

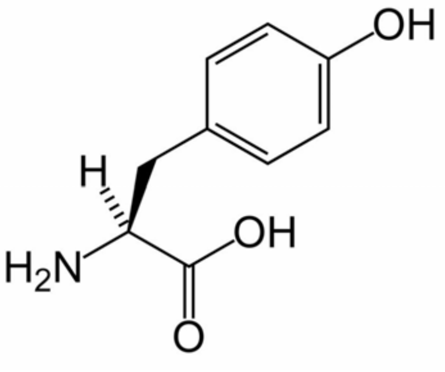


Fig. 53: chemical structure of tyrosine.

4.3.6 Lysine

Lysine (abbreviated as **Lys** or **K**) is an α-amino acid with the chemical formula $HO_2CCH(NH_2)(CH_2)_4NH_2$.

This amino acid is an essential amino acid, which means that humans cannot synthesize it.

Lysine has a polar side chain and the chemical structure is reported in Fig. 54. [1]

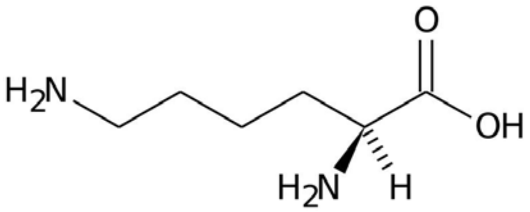


Fig. 54: chemical structure of lysine.

4.4 Self-assembly deposition of sensing layers [2-8]

The six amino acids described in the previous chapter have been deposed onto 10MHz TSMR resonators by the self assembly technique.

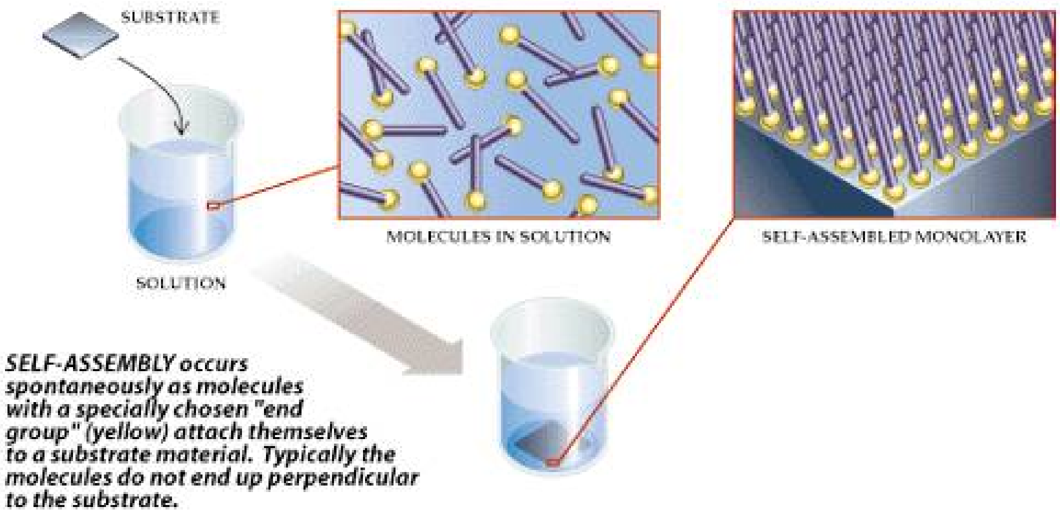
The self-assembling deposition consists in forming a covalent bond between the inorganic substrate and the organic layer.

That kind of interaction ensures a total and homogenous coverage.

This technique allows controlling the layers thickness with a monolayer resolution.

The self-assembling technique leads to the realization of extremely stable and reproducible layers and consists in repeatedly immersing the transduction element in a solution containing the sensitive molecule.

Fig. 55 Reports a schematic summary of the procedure.



***SELF-ASSEMBLY** occurs spontaneously as molecules with a specially chosen "end group" (yellow) attach themselves to a substrate material. Typically the molecules do not end up perpendicular to the substrate.*

Fig. 55: schematic representation of the self-assembling deposition technique.

Sensors used within this feasibility study have been realized by covering 10MHz TSMR resonators with a single monolayer of amino acid.

4.5 Measurement set-up

Tests have been performed on a set of 6 different sensors and 2 empty resonators as references, for compensating the environmental parameters such as temperature, relative humidity and flow rate.

Prototype devices have been mounted in an Electronic Nose measurement chamber and the complete set-up was as reported in the schematic Fig. 56.

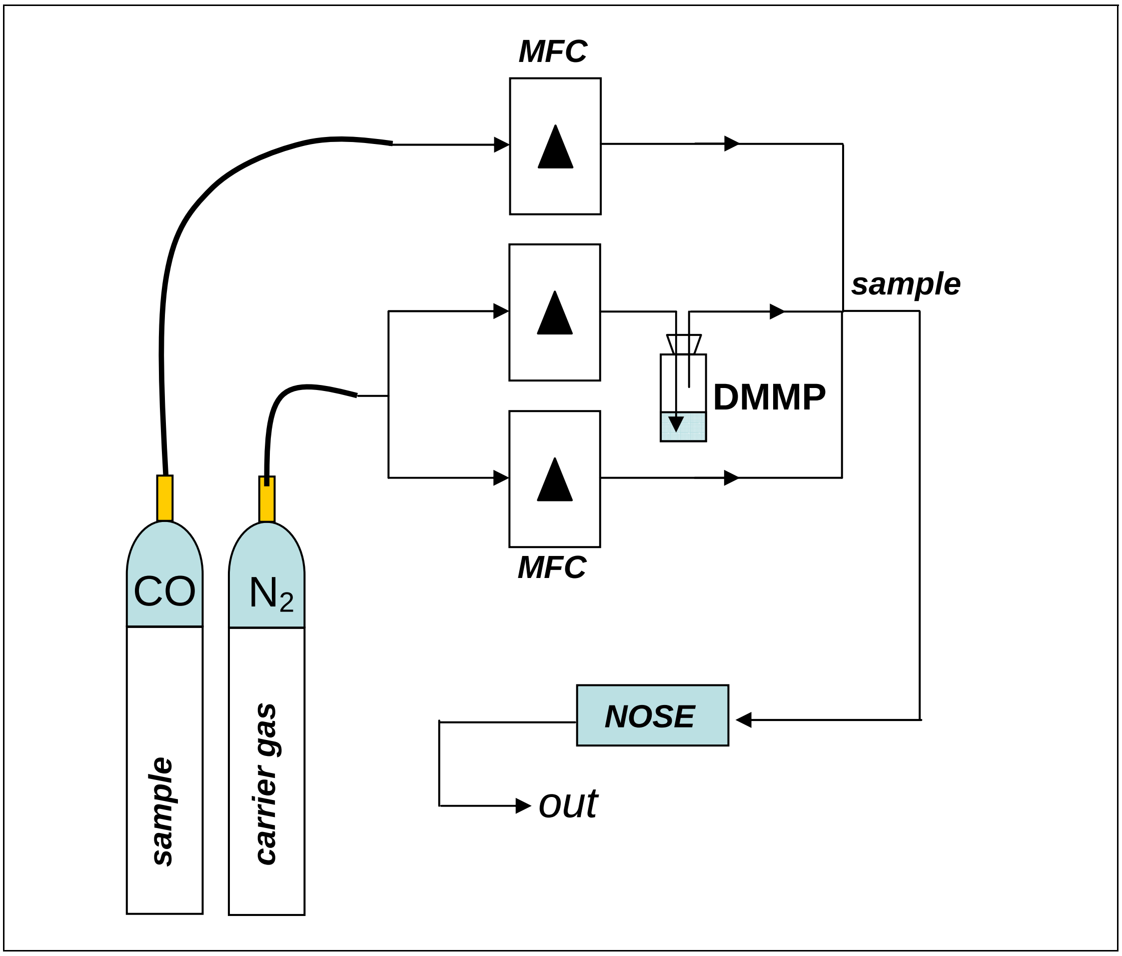


Fig. 56: schematic representation of the measurement set-up.

4.6 Results for CO

Preliminary tests with carbon monoxide have been performed at the following concentrations:

- 15ppm;
- 25ppm;
- 50ppm;
- 75ppm.

Fig. 57 reports the typical response of the sensors.

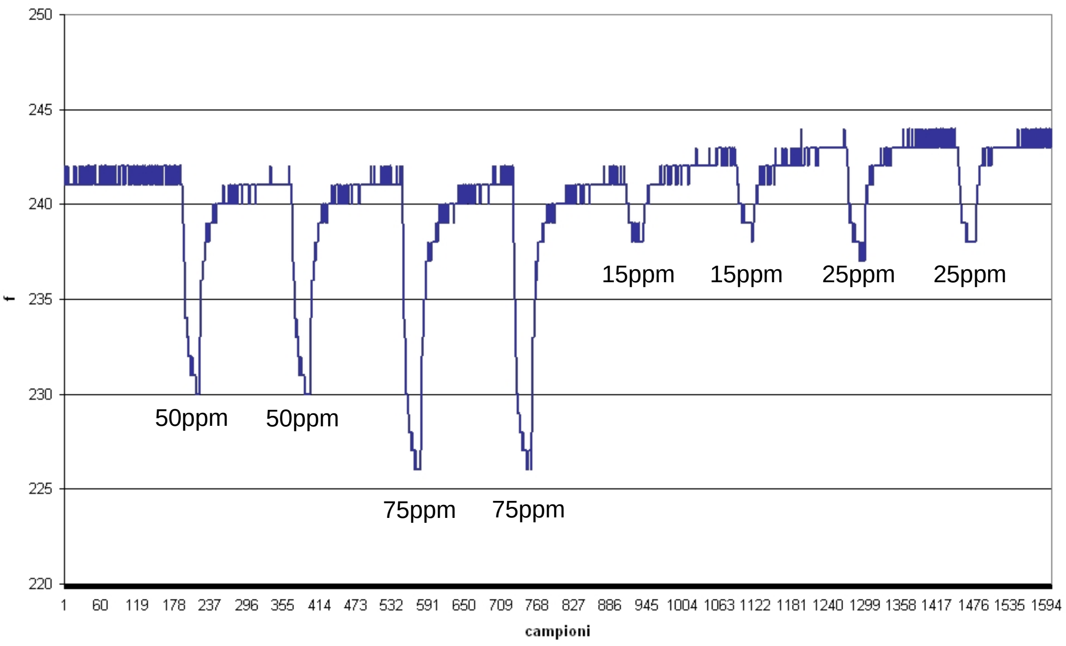


Fig. 57: response signal of the tyrosine covered sensor to CO.

An estimation of the tyrosine sensor’s performances is given in the list below:

- Response level @15ppm CO = 5Hz;
- Sensitivity @15ppm CO = 0.2Hz/ppm;
- Resolution @15ppm CO = 15ppm.

4.7 Results for DMMP

Tests with DMMP have been performed at the following concentrations:

- 55ppm
- 110ppm
- 165ppm

Fig. 58 reports the typical response of the sensors.

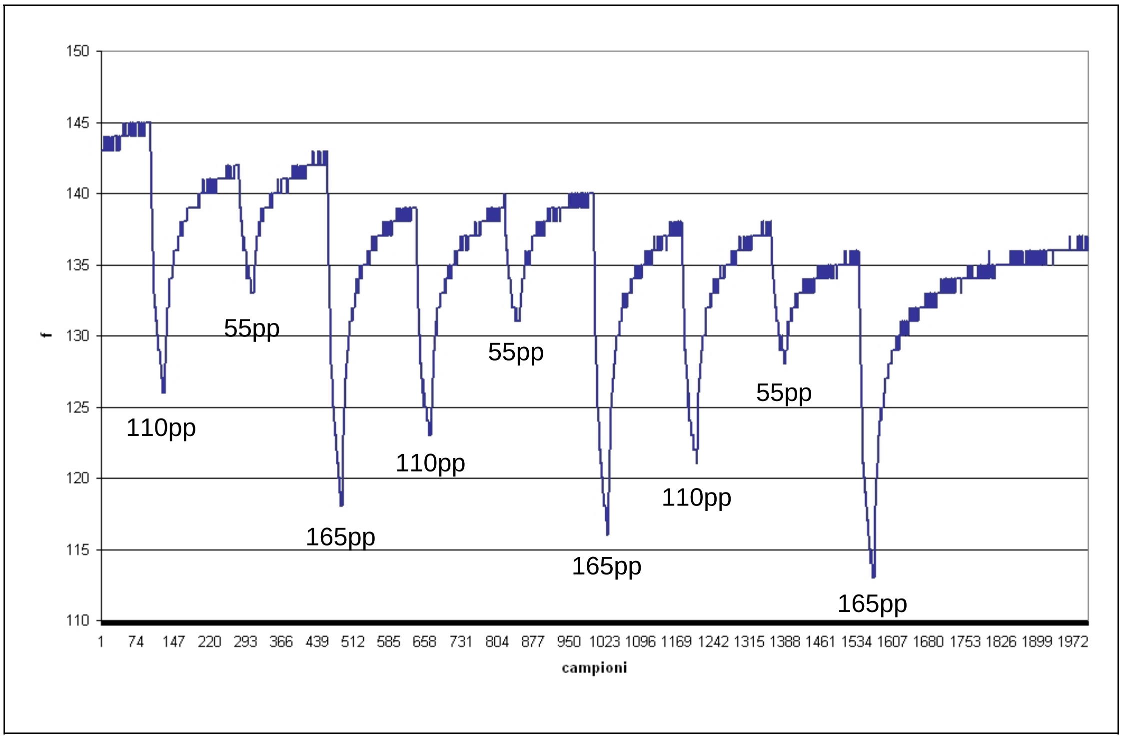


Fig. 58: response signal of the tyrosine covered sensor to DMMP.

An estimation of the tyrosine sensor’s performances is given in the list below:

- Response level @110ppm DMMP = 16Hz;
- Sensitivity @110ppm DMMP = 0.15Hz/ppm;
- Resolution @110ppm DMMP = 20ppm.

4.8 Discussion

The results obtained during this study demonstrated that amino acids can be used as sensing layers in QMB sensors for detecting CO and DMMP.

If compared with the analogous organic sensing layers described in the previous chapters, amino acids showed the differences listed below:

- Lower sensitivity;
- Improved resolution;
- Improved reversibility (if compare with Fe-porphyrins used for detecting CO).

The result about the sensitivity level is worth of additional considerations, in that the layer thickness was 1 monolayer.

It is reasonable foreseeing that increasing the sensing layer thickness, which can be easily done in a controlled way through the self-assembly technique, will result in an improved sensitivity.

The resolution levels and reversibility are already satisfactory.

For the above reasons it is possible to conclude that the mass change transduction technique, if implemented with biological sensing layers such as amino acids, could be in the future a valid alternative to the corresponding implementations with organic layers, such as Fe-porphyrins for CO and Er-porphyrins for DMMP.

References

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Chapter 5

Conclusions

The activities reported in this book have been carried out within the frame of the “*Innovative Materials and Technologies for Advanced Sectors*” Industrial innovation project, in cooperation within the Centro Sviluppo Materiali S.p.A.

The research project was split into two main lines:

- realization of a database on the state of the art of gas sensors;
- development of innovative sensors prototypes for carbon monoxide and DMMP detection.

The strategy behind the above separation was to perform a comprehensive approach to dangerous gases detection, starting from a profound analysis of the state-of-the-art to designing and testing prototypes which implement new transduction techniques for detecting the analytes with high sensibility.

Realization of the database required a huge effort, from the definition of the model of information to the implementation of the architecture.

Up to now, the database contains more that 1000 descriptive files concerning the most popular transduction techniques for gas analysis.

The database developed during the PhD course is an extremely valuable tool, which can be used as a knowledge base for researchers and technicians involved in sensors applications and is suitable for exploitation as a commercial product.

The second activities line was aimed at developing CO and DMMP sensors prototypes.

Carbon Monoxide was selected as a target mainly due to its high toxicity, which claims for better detecting systems.

The innovative approach to CO sensing was based on a biomimetic technology which uses the high affinity of iron ions towards CO molecules for enhancing the sensor’s sensitivity and selectivity.

The sensing layers were Fe-porphyrins, analogous the basic compounds of haemoglobin.

Then, the research line intended to use the biological effect of CO poisoning to develop a new kind of sensor.

The selected transduction technique is based on mass changes, using QMB devices for sensing.

Preliminary results where good enough that an industrial demo unit has been realized with the objective of becoming the starting point for further industrial development.

One of the main application areas of such a device can be envisaged in assessing the exposure to unknown amounts of CO during work activities.

The second target compound was chosen according to two main considerations: first of all because of its large industrial use, then because of its chemical properties as a simulant of the nerve agent Sarin.

The composition of the sensitive layers (complexes of lanthanide ions), was chosen as a consequence of preliminary studies of the interaction mechanisms between lanthanide complexes and chemical compounds containing a P=O group.

The transduction elements were Surface Acoustic Wave devices (SAW) that allowed implementing a mass change technique.

Also the results of this study were encouraging enough, even though some additional work on controlling the environmental parameters and experimental conditions should be done.

Then, great attention was devoted to studying the feasibility of biosensors based on amino acids and TSMR resonators, for detecting CO and DMMP.

These experiments, carried out using an electronic nose, showed that this approach is promising for obtaining highly sensitive, selective and stable sensors.

Finally, the goals have been reached with satisfactory results and a commercial exploitation of the prototypes, from the database to the biosensing devices, can be envisaged with a certain degree of confidence.