SENSORIAL AND INSTRUMENTAL APPROACHES TO INDOOR AIR MONITORING

Livio de Santoli[1], Gino Moncada lo Giudice[1], Angelo Milone[2]

[1]Dipartimento di Fisica Tecnica, Università La Sapienza, Roma
[2]Dipartimento di Energetica e Applicazioni di Fisica, Università di Palermo

ABSTRACT

The paper deals with a research about analytical techniques for meaningful, reliable, cost-effective, in-situ, real-time and continuos determination of airborne chemicals, by means of a new electrochemical sensor; the research aims to develop objective instrumental sensing systems able to substitute the subjective human responses.

Sensor detection capability could regard a series of analytes: carbon dioxide, carbon monoxide, inorganic pollutants, ammonia and other metabolic gases, irritants, odours. The behaviour of a single analyte as well as of their mixtures, allows to obtain both specific and overall responses in chemical indoor air quality IAQ control: a procedure which employs mainly carbon dioxide concentration as oxidant and ammonia as reducing element able to evaluate Indoor Air Quality is described.

KEYWORS

Air Quality, Measuring Techniques, Carbon Dioxide

INTRODUCTION

The development of analytical techniques for recognition, evaluation and measurements of airborne chemical species has been planning since a couple of years by using :

- electrochemical flow through potentiometric sensors (EFS),
- sampling devices and procedures,
- gaseous standards (or gaseous reference materials, *GRM*) for calibration of both sensors and analytical methods, (Scarano et al., 1995; Moncada et al., 1995).

Sensor detection capability could regard a series of analyses: carbon dioxide, carbon monoxide, volatile organic compounds (VOC), inorganic pollutants (such as NOx, SOx, O_3), ammonia and other metabolic gases, irritants, hazards and odours. The behaviour of a single analyte as well as of their mixtures, will be the matter of the research, in order to obtain both specific and overall responses in chemical indoor air quality IAQ control.

The gaseous concentration of an analyte A is reported as molar fraction y_A (mol mol^{-1}), or as gaseous partial pressure P_A (ppm). A *GRM* is defined as a gaseous matrix (usually air) with y_A known, and reported as A-*GRM*; in many cases more than one A should be considered ($A_1, A_2, ..., A_n$).

Indoor air pollution load is caused by emission of small amounts of a great number of chemicals from human and material sources (Baughman et al., 1993); it can be expressed as sensory load or chemical load, and can be quantified both as emission rate and gaseous concentration by means of instruments which integrate the effect of chemicals as perceived by human nose.

The research aims to realise meaningful, reliable, cost-effective, in-situ, real-time, continuos determinations of chemicals at low concentrations, to substitute subjective human responses (i.e., olfactive sensations and disease); therefore it is related to the subjective approach (Fanger, 1988).

The IAQ case here reported refers to an indoor air composition mainly dependent on human presence and, to a minor extent, on

the nearby outdoor air; CO_2 is therefore the major analyte, NH_3, metabolic gases and inorganic pollutants being the minor ones.

Experiments have been carried out in two laboratories of the University La Sapienza, Rome: the Chemistry Department Lab and the Fisica Tecnica Department Lab.

The electrochemical sensor has several version, each suited for single analytes or mixture of them; it has been used a version able to detect all together CO_2, inorganic pollutants and metabolic gases: therefore its response y_Σ, can be considered as an integral index of indoor pollution.

Due to the predominant presence of CO_2, sensor and analytical method calibrations were carried out by using CO_2-$GRMs$, i.e. atmospheric air with known y_{CO2} values: thus, y_Σ values are reported as CO_2 equivalent gaseous concentrations.

Preliminary experiments concerned the signals characteristics of the sensor and the precision and accuracy of the measurements; then systematic measurements of y_Σ with calibrated sensors were carried on related to the sampling zone, the number of people, the time, the room ventilation rate and the constraint conditions.

EXPERIMENTAL PART
Experimental set-up

The electro-chemical sensors are based on:

a. measurements of the electromotive force E (mV) of the potentiometric electrochemical cell:

IE / WS /RE

(IE = indicator electrode; WS = flowing working or electrolyte solution; RE = reference electrode);

b. the dependence of E as a function of WS composition;

c. the dependence of the latter as a function of air composition.

A membrane (the tubular sensor membrane, SEM) separates WS from the environment; the unknown or the standard air sample is carried, with a known gaseous flow-rate, F_g, $0.1\div1$ mLs^{-1}, against the SEM, through which the analytes permeate, dissolve in WS and give E variations.

The IE and RE nature, F_g, the WS basic composition, its flow rate, F_l, $10\div100$ µLs^{-1}, SEM properties, sensor geometry and structure constitute degrees of freedom which permit several designs for the sensor to be realised and employed, each suited for one or more analytes and for specific problems.

The set-up of sensor, sampling device, data logger related to a specific IAQ problem, is referred as a sensor system (Figure 1).
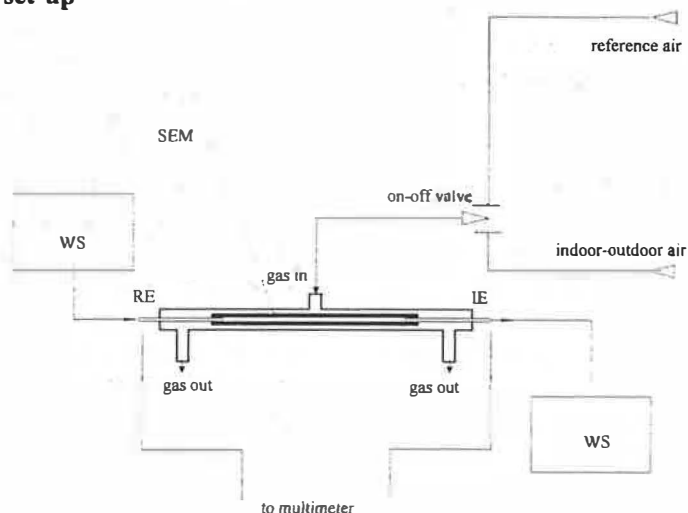

Figure 1 - Sensor system.

Sampling Devices and Procedures

Two are the driving force utilised for realising the unknown or standard samples impact against the SEM: compression, by means of a carrier gas from a cylinder, or depression, by means of a peristaltic pump.

The peristaltic pump is able to withdraw known volume samples in defined points of the room (single point investigation), while the cylinder is conveniently used as carrier gas for sampling air defined volume, representative of a larger zone.

Reference Gases

Two CO_2-GRMs in commercial standard cylinders were used as primary standards; their certified y_{CO2} values were respectively: 0 ppm and 812 ppm. A third calibration point (300 ppm) was gravimetrically prepared from synthetic air by adding CO_2.

RESULTS

Sensor Signal Characteristics: Noises, Drifts and Sensitivity.

In defined environmental and experimental conditions, sensor signal noises ranged from 0.1 μV to 1 μV, and drifted from 0.1 μV/min to 1 μV/min, depending on atmospheric pressure and room temperature. Sensitivity, according to experimental conditions, ranged from 10 to 40 μV ppm^{-1} (up to 70% of the values calculated by a physical-math models, Scarano et al., 1978). Figure 2 shows the signals obtained in the calibration phase.

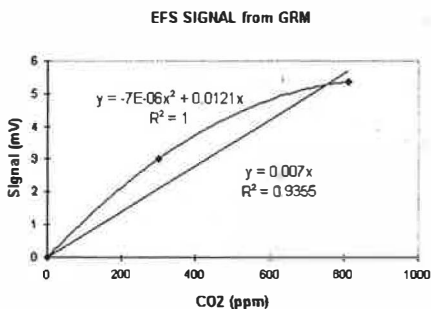**EFS SIGNAL from GRM**

$y = -7E-06x^2 + 0.0121x$
$R^2 = 1$

$y = 0.007x$
$R^2 = 0.9355$

Figure 2- EFS signals vs CO_2 certified values

Calibration

Reference samples were driven by means of a carrier gas prepared alternatively from the above mentioned cylinders or atmospheric air flowing through water and soda-lime traps, in order to eliminate CO_2 and other acid-base and redox components.

The air was let to flow with a total flow rate F_1; a part of it F_2 was diverted through water and soda-lime traps, then rejoined to the main stream, obtaining gaseous mixtures with y_{CO2} values corresponding to different removal factors $F_D = \dfrac{F_1 - F_2}{F_1}$.

In the investigated range, a straight line (r=0.990; slope=20μV ppm^{-1}) was obtained. The linear behaviour was tested also for y_{CO2} values up to 800 ppm.

Precision and Accuracy

The repeatability from coherent calibration experiments was 0.5÷2% in both the laboratories; therefore, the same figures can be considered for reproducibility and precision. Measurements accuracy rests on the existing primary standards and their reliability, which is yet a debated argument and a field of researches.

Single-Point Investigation and Zone Investigation

Random sampling points gave poor results, depending on drifts and human presence.

The meaningfulness of sampling and reliability of analytical results have been obtained by means of two experimental approaches, as reported below.

When sampling point was placed into an exhaust hood, the y_Σ measured values resulted representative of the balance between emission rates from human beings and fresh air rate.

A sampling membrane, a silicone or PTFE tubing, 25 m length, 1 mm internal diameter, 1 mm thickness, 20 mL internal volume, was placed in the central part of the second laboratory. Through the membrane walls CO_2 and other chemicals permeate in amounts depending on their local

concentration values. Every 5 minutes (the sampling time) the carrier gas was diverted into the membrane for 60 s. The obtained y_x can be accepted as representative of the mean composition of the investigated zone. In Figure 3 is shown the EFS behaviour for an enviroment in which the only pollution source is that of human sedentary activity. In Figure 4 is represented the relationship of the EFS compared with a PAS (IR photoacoustic sensor) technique.
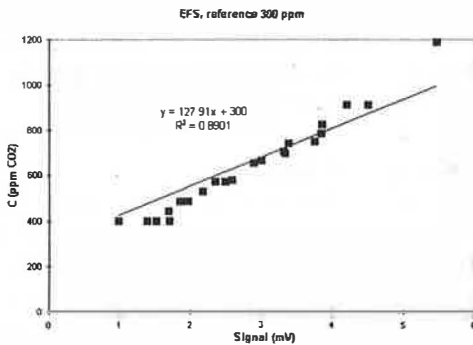

Figure 3 - EFS signals vs CO_2 produced by human indoor activity
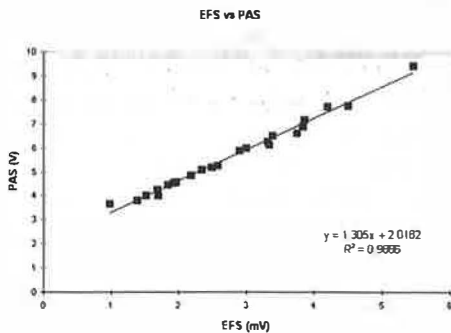

Figure 4 - EFS signals vs PAS signals.

Single-Point Investigation and Zone Investigation

A typical signal corresponding to a series of measurement samples is shown in Figure 5. Due to the more persistent reducing analytes charged into the SEM, after a positive increase, the signal goes down under the zero-line corresponding to the standard concentration value (Figure 5).
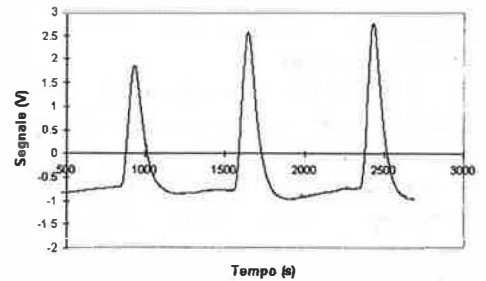

Figure 5 - EFS signals vs time

Combining the positive electromotive force $E+$ with the negative one $E-$ corresponding to each signal, it is possible to taking into account of the different nature of the input source. As an example, in Figure 6 are represented two experimental configurations:

- continue line - EFS response with 2 non-smoking persons in a sedentary activity;
- dash line - EFS response with 2 smoking persons (25%) in a sedentary activity.
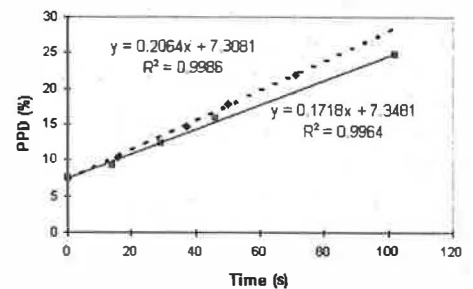

Figure 6 - EFS signals of mixed gas produced by smoking and non-smoking activity

The EFS global response in the latter Figure is represented in terms of PPD (predicted percentage of dissatisfated), calculated on the basis of the following expression:

$$PPD = k_1 E^+ + k_2 E^-$$

where k_1 and k_2 are appropriate constants of the instrument depending on his working and elecrtochemical conditions.

CONCLUSIONS

Encouraged by the results of this preliminary experiments, next steps for the research should be:

- y_{CO2} determination (by using interfering chemical traps and a suitable WS composition) and estimation of acid-base and redox state of air from the values: $(y_\Sigma - y_{CO2})$;
- $y_{CO+VOCs}$ determination as equivalent y_{CO2} after CO and VOCs oxidation to CO_2 by passage through a catalytic furnace;
- y_{NH3} determination, after suppression of CO_2 acid-base and redox CS from air.

Furthermore, odour determination in order to develop a IAQ sensor measuring the indoor air quality as the human nose will be investigated. Thus any source that emits substances which can be perceived by human nose, including odorants and irritants, are considered, in order to give an answer to the following :

- emission rate determination of pollutant by humans and materials;
- pollutant level determination (perceived air quality);
- influence of environmental tobacco smoke (ETS).

Further items should be: realisation of standard samples, i.e., of air samples with known and certified y_A values; miniaturisation and automation of the sensor systems; development of reliable sampling plans; development of experimental and theoretical models.

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