Solvent detection in indoor air with a sensor array

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INTRODUCTION

It is recognized today that people receive the longest and greatest exposure to contaminants in the indoor environment. Health problems known as "building related illnesses" and "sick building syndrome" are related to this exposure. The indoor air quality is monitored in some countries (Germany, Luxembourg) by governmental organizations in order to evaluate the exposure of occupants to different pollutants and to identify eventual sources of health problems. The benzene and its alkyl-derivatives (BTX) are of a special interest due to the well-established toxicity and due to the frequency with which they are observed.

Gas chromatography - the standard method of the indoor air analysis - is a powerful technique, able to provide a complete image of the air composition. Nevertheless, it does not allow an immediate evaluation of the air quality since the analysis is usually carried out in the laboratory and needs a previous sampling. This is a serious drawback because the indoor air composition knows important time variations. A measuring system (even semi-quantitative) furnishing information quickly, able to work continuously and during extended periods of time would be very useful in order :

- to give a first appreciation of the state of rooms and to decide if a complete chemical analysis is necessary;
- to choose the optimal moment for taking of an air sample;
- to make a link between the concentrations of pollutants and the sources (activities);
- to furnish a more realistic image of occupants' exposition in the time;
- to react immediately on the pollution.

Gas sensors seem to suit well such application. They allow constructing a PC-driven small size measurement system, working without supervision during long periods of time. Sensors and complete modules for indoor air quality control are already proposed (for example IC-02-1 module based on SP-AQ or ST-AQ series sensors from FiS). Investigations of the perceived air quality with a gas sensor array were published as well (Schreiber, 2000; Wide et al, 1997). The present work intends to investigate the possibility of using commercial gas sensors to monitor organic pollutants like BTX, present in the indoor air at very low concentrations (typically ppb).

EXPERIMENTAL SECTION

Air composition in dwellings and public buildings is studied by means of gas chromatography and a sensor micro array 01D28 (MICROSENS, Swiss). The air temperature and relative humidity are measured as well. Chemicals contained in the air are sampled 10 min on CHROMOSORB® (airflow rate 200 ml/min) and analyzed. Only benzene and its alkyl-derivatives are quantified. The micro array 01D28 is composed of six metal oxide gas sensors (SnO_2 doped by Pd) equipped with standard (for two sensors in the array) or inter-digited electrodes. Isothermal working mode (500°C for all sensors) is applied. Conductivities after 10 minutes of signal acquisition in the studied air are considered as characterizing its chemical composition.

Discriminant Function Analysis (DFA) and different linear regression techniques (Inverse Least Squares, Principal Components Regression and Partial Least Squares) are applied to find a relation between the sensors signals and the indoor air composition as determined by the gas chromatography. Raw or pretreated (mean centered or auto-scaled) conductivities are used in the factorial regressions.

Stepwise rather that standard DFA and residuals analysis are carried out in order to appreciate the contribution of individual variables to the quality of the calibrated models. The root mean square error of calibration (rmsec) is calculated according to the relation :

$$rm\,\mathrm{sec} = \sqrt{\frac{\sum (C_P - C_M)^2}{n}}$$

where C_M (C_P) is measured (predicted) concentration and n is the number of observations.

Only variables improving the rmsec by at least 2% are retained for the regression.
Software packages STATISTICA™ and MATLAB 2.0 PLS_tool box are used for mathematical treatments.

RESULTS

Benzene (BE) and toluene (TO) are identified in all samples. They are accompanied usually by other aromatics : ethyl benzene (Et-BE), propyl benzene (Pr-BE) and xylenes (o, m, p-XY). The concentrations fluctuate in the range 3-40 $\mu g/m^3$ (1-12 ppb) for the benzene, and in the range 14-237 $\mu g/m^3$ (4-62 ppb) for the toluene. The concentrations of other aromatics are always lower (some tenths of the BE concentration). Temperature and relative humidity ranges are about 18-20 °C and 30-50% respectively.

Two indoor air quality categories are defined according to the BE and TO content:
- *non-polluted air* : BE < 15 $\mu g/m^3$ and TO < 80 $\mu g/m^3$;
- *polluted air* : BE ≥ 15 $\mu g/m^3$ or TO ≥ 80 $\mu g/m^3$

and a model that distinguishes them on the basis of the sensors conductivities is constructed with Discriminant Function Analysis. All but two samples are used in the model construction;

the two remaining samples are kept for the model validation. However, further results should be considered only as preliminary results since they are only based on 13 observations.

The complete set of data produces a model, with a very low Wilks' *lambda* value (0.1353), that classes correctly all the observations. The two sensors working with standard electrodes are excluded first and their elimination scarcely diminishes the model quality (Wilks' *lambda* increases to 0.1355). The remaining four sensors are sufficient to distinguish readily the polluted and non-polluted air and to attribute both unknown samples to the correct category. The model performance is shown on figure 1 where the values of the root 1 for individual observations are plotted. For clarity reasons, rather than plotting the points on a single axis, the projections on the "root 1" axis have been split vertically Exclusion of additional sensors deteriorates the discrimination of air categories as well as the prediction capacity.

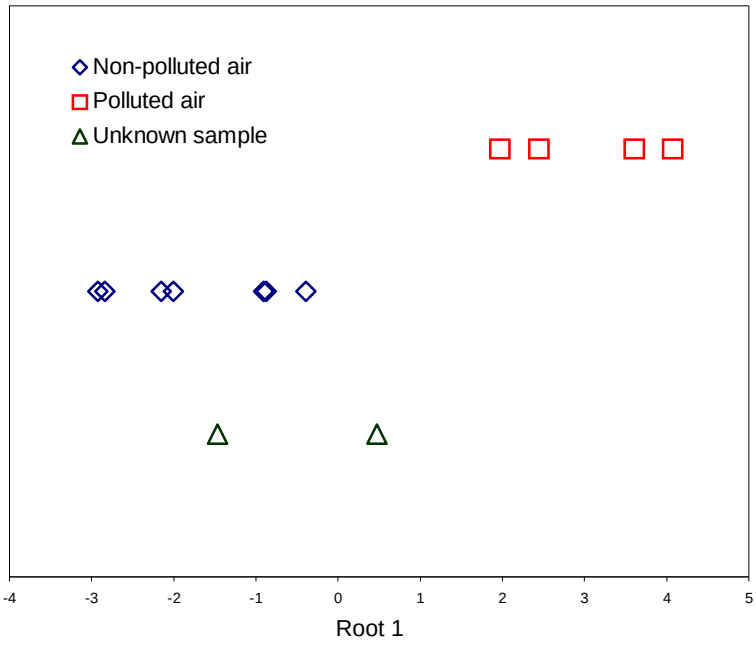

Figure 1: Results of a Discriminant Function Analysis on observations in the indoor air. Point projections on root 1 are split in the y direction. Non-polluted air: BE < 15 µg/m^3 and TO < 80 µg/m^3, polluted air: BE ≥ 15 µg/m^3 or TO ≥ 80 µg/m^3. Number of variables in the model: 4, Wilks' lambda: 0.1355.

Inverse Least Squares method provides a surprisingly good correlation between the conductivities of the six gas sensors and the benzene (resp. toluene) indoor air concentration (regression coefficient R^2 = 0.9554, respectively 0.7270). The analysis of residuals indicates that the sensor n° 3 contributes little to the benzene regression and can be discarded. The same sensor was also first discarded by the stepwise Discriminant Function Analysis.

Factorial regressions lead to comparable results. The variables number can be reduced to five in some cases without deterioration of the model quality. The best regression equation (R^2=0.9525 for the benzene, and 0.7232 for the toluene) is obtained with Principal Components Regression (conductivities auto-scaled). Figures 2 and 3 compare the measured concentrations and the ones predicted by this model.

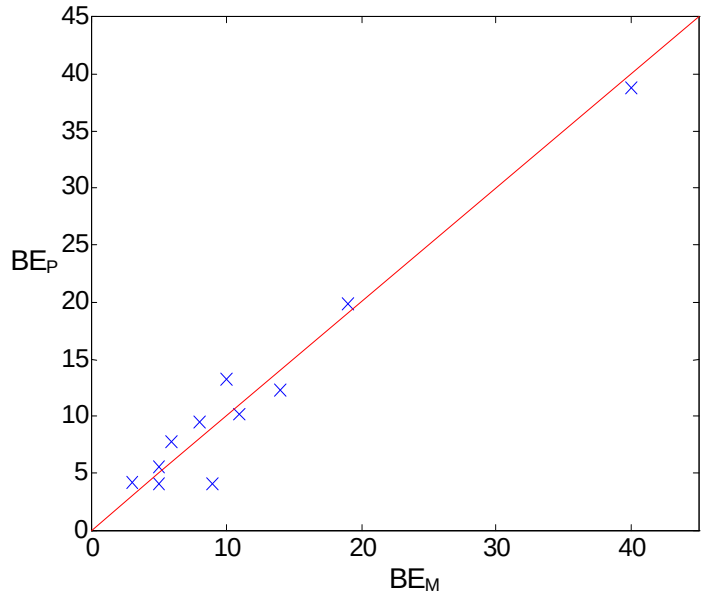

Figure 2: Comparison of the benzene concentration measured (BE_M) and predicted (BE_P) by the Principal Components Regression (sensors conductivities auto-scaled). Model based on five components, $R^2 = 0.9525$.

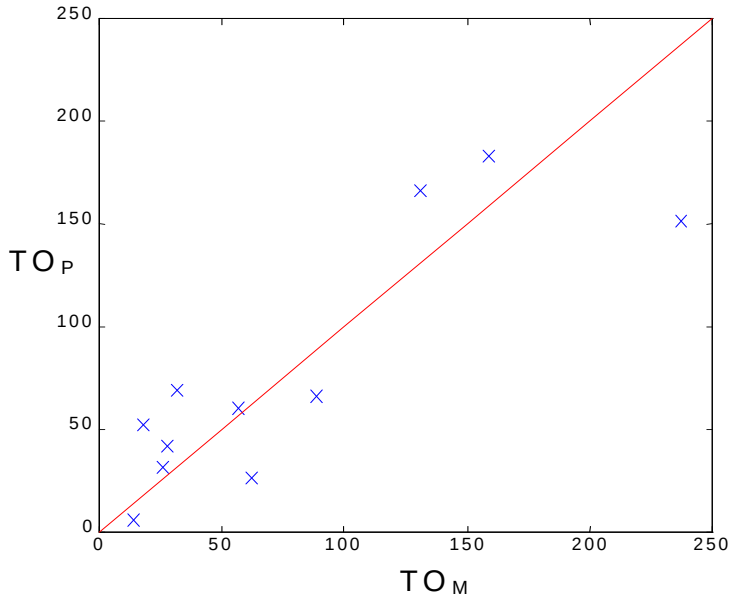

Figure 3: Comparison of the toluene concentration measured (TO_M) and predicted (TO_P) by the Principal Components Regression (sensors conductivities auto-scaled). Model based on five components, $R^2 = 0.7232$.

DISCUSSION

The data presented here suggest that the monitoring of aromatics substances in the indoor air by means of a micro-array of metal oxide gas sensors is possible. The array distinguishes polluted and non-polluted air and it can even evaluate the concentration of the benzene and the toluene. This is due most likely to a certain particularity of the indoor air composition,

rather than to an extremely high sensors sensibility (the company MICROSENS does not supply information on the detection limits).

It is observed in practice that the benzene is almost always accompanied by the toluene and by other alkyl-derivatives in the indoor air. Concentrations of individual substances vary, but their ratio stays quite constant and equal to :
BE : TO : Et-BE : Pr-BE : o-XY : m-XY : p-XY ≅ 1 : 3.2 : 0.4 : 0.1 : 0.4 : 0.8 : 0.3 (Daunderer 1991,Matenova 1999).
The metal oxide gas sensors are not selective and therefore, their conductivity increases proportionally to the total aromatics content. The concentration of individual substances can be estimated, as it represents a constant part of this total.

We consider our results as encouraging, but preliminary. Due to the well known variability of the indoor air composition, a large study in dwellings and public buildings should be undertaken in order to evaluate the array performance under different environmental conditions : temperature, relative humidity, and presence of other indoor air pollutants.

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