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Factorial Experimental Design to Optimize a Methodology to Analyze Odorous Chemical Mixtures: Effect on a Sensors Array and on Odour Concentration

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The aim of this study is to check the influence of the chemical composition of odorous and non-odorous gases on the odour concentration and on the sensor responses. Design of experiments (DOE) is used to plan mixtures composition for 5 compounds with different levels of concentrations. The synthetic gas experiments consist of preparation of samples based on the factorial design consisting of five compounds i.e., Trimethyl Amine, Hydrogen Sulphide, Methane, Limonene and n-Butanol. Pareto plots are examined to evaluate the main effects of each sensor on the odour concentration. In addition, the response of each individual gas sensor is examined as a function of the chemical composition as well as the odour concentration. The response surface methodology analysis (Peris et al, 2009) is carried out on the experimental design of the synthetic gases. The stepwise procedure was used to analyse the results which is an automated tool used in the exploratory stages of model building to identify a useful subset of predictors. All the combinations are carried out with step wise regression and without stepwise regression. Also BOX-COX transformations with different values of alpha are also considered during the development of the regression model. Afterwards, multivariate analysis is performed to check the performances of a sensors array regarding the fluctuation of chemicals concentration. Finally, real odorous samples from a municipal solid waste site are measured with the same array and the results are compared with the ones obtained with the synthetic odorous gases.
Index terms– Experimental design, synthetic odorous gases, sensors array, odour concentrations

1. Introduction

Trimethyl Amine, Hydrogen Sulphide, Methane, Limonene and n-Butanol are major compounds found in outdoor air pollution especially industrial sites like pulp and paper industry, tanneries, distilleries, municipal solid waste sites etc. These compounds have consequences on environment and health and comfort of the population exposed to it (Peris et al, 2009; Deshmukh et al, 2014). As such it is necessary to measure and monitor these compounds at regular basis. The foremost requirement is the installation of online rapid monitoring tools and techniques. Chemical analysers are widely installed onsite for the continuous measurement of the odorants responsible for the odors. However, analysers are costly tools. Further, chemical analysers when installed for onsite measurement respond only to the specific compounds (Deshmukh et al, 2017). Dynamic sites like municipal solid waste dumping sites have huge number of compounds and no matter how many analysers are deployed some odor causing compound remains unrecognized (Romain, 2015).
Another alternative can be the use of instrumental odor monitoring systems (IOMS) equipped with low cost sensors (electronic nose systems) which has found various applications from aerospace industries to medical applications. Electronic nose system developed three decades ago has also been used for measurement of odours from various industries and dumping sites etc.

In the present work, five compounds are used to prepare synthetic gas mixtures in the laboratory and exposed to instrumental odor monitoring system consisting of metal oxide sensors and to olfactometer. The combinations of mixtures are prepared using factorial design of experiments.

In addition, air samples from municipal solid waste site have also been collected and exposed to the same set of sensors and to olfactometer. The results of the two studies i.e synthetic gas mixtures prepared in lab and MSW site samples are presented.

2. Materials and method

2.1 Gas mixtures preparation

The synthetic gas experiments consist of preparation of samples based on the factorial design. The five compounds are Trimethyl Amine, Hydrogen Sulphide, Methane, Limonene and n-Butanol.

The samples are prepared in 35 L nalophan bags. The volume of the bag is chosen to enable simultaneous exposure to sensors array and olfactometer. The gas volume is check with a gas counter (RITTER Drum-type gas meter-type TG05/5) and with the flow value of the mass flowmeter during a determined time. A humidifier designed by the lab is used. Based on calculations, a known volume of the liquid samples of limonene, n-butanol and TMA (pure or prediluted) is injected by a gas tight syringe in bags filled with wet synthetic air. For hydrogen sulfide and methane, dilutions from gas cylinder (Air Liquide) are applied. A dilution device with different mass flow controllers (BROOKS trademark) is used to introduce determined gas volume of H_2S and CH_4 in a known volume of wet air. Two 500 mL/Liter mass flow controllers are used to prepare the humidified air of 25 % and 50 %. The output of one mass flow controller is passed through humidifier; the flow rate through humidifier was kept at 125 ml and 250 mL to achieve 25 % and 50 % humidity respectively. The rest part was filled with dry air passed through mass flow controller. Correction factors of the mass flow are applied in function of the gas. The samples are prepared in the morning and measured in the afternoon.

2.2. Factorial design

A two level Plackett-Burman factorial design is used to design the mixtures of synthetic gases. The design consists of two levels, high level and low level, for all the five compounds (Table 1). Factorial designs permit the simultaneous study of the various effects such as interaction, squared effect and linear effect of the variable under study on the response of the experiment. Without the use of such design of experiments the interaction effects of the variables on the response remains undetected.

Table 1. Design of experiments using factorial design

	Limonene (ppmv)	n-Butanol (ppmv)	H_2S (ppmv)	CH_4 (ppmv)	TMA (ppmv)
Low Level	2	20	0.25	0	0.25
High level	6	80	1	3	6

2.3. MOS array, olfactometer

The sensors array is composed of 6 metal oxide sensors TGS 800, TGS 823, TGS 2444, TGS 2602, TGS 2620, GGS 1330. The sensors are placed inside a cylindrical chamber in PTFE (200 ml) and linked to a pump with a flow rate regulated at 200 ml/min. The chamber temperature is kept at 50°C by a heating resistor and natural cooling. RH is recorded. The stabilised resistance (kOhm) is recorded. The sensors array is exposed to humidified synthetic air (25% or 50%) before and after each cycle of exposure of sample. Specific software controls the hardware and allows the acquisition of the sensor signals.

Odile Olfactometer (Odotech cie) is used for the analysis of the samples according the EN 13725 standard. The odor concentration varied from 1202 – 40102 ou_E/m^3.

2.4. Data treatment: response surface methodology

The response surface methodology analysis is carried out on the experimental design of the synthetic gases in Minitab software. The stepwise procedure is selected to analyse the results which is an automated tool used in the exploratory stages of model building to identify a useful subset of predictors. The process systematically adds the most significant variable or removes the least significant variable during each step. Standard stepwise regression both adds and removes predictors as needed for each step. The process stops when all variables not in the model have *p-values* that are greater than the specified Alpha-to-Enter value and when all variables in the model have *p-values* that are less than or equal to the specified Alpha-to-Remove value. Due to use of standard stepwise both backward and forward selection is included for analysis of the

model. During the analysis the terms of the six individual sensors or the single compounds are included in each step regardless of *p-value*.
All the combinations with stepwise regression and without stepwise regression are carried out. Also BOX-COX transformations with different values of alpha are also considered during the development of the regression model. In each approach, full quadratic terms are considered. BOX-COX transformation is normalization technique which normalizes the data according to the following equation

$$T(\lambda) = \frac{(Y^{\lambda} - 1)}{\lambda} \qquad (1)$$

where Y = response variable
$\boldsymbol{\lambda}$ = transformation parameter (value between – 5 to 5)
Based on the observations stepwise regression that included all individual factors at each step of regression analysis results in maximum prediction capability.
The relationship between the independent factors (sensors response or single compounds) and the dependent variable (odour) is calculated using the following second order polynomial equation

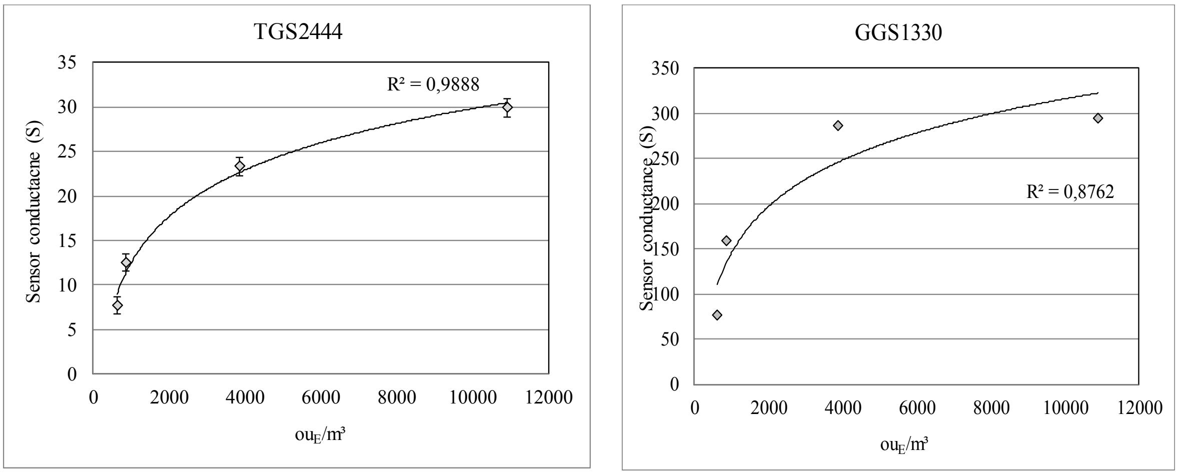
$$y = \beta_0 + \sum_{i=1}^{i=n} \beta_i x_i + \sum_{i=1}^{i=n} \beta_{ii} x_i^{\,2} + \sum_{i<j}\sum \beta_{ij} x_i x_j \qquad (2)$$

where y is the predicted response;.β_0 a constant; β_i the linear coefficient; β_{ii} the squared coefficient; and β_{ij} the product-coefficient, n is the number of factors (Deshmukh, et al., 2014; Montgomery, 2011). The analysis of variance is used to determine the significant terms for the response. Whereas, the p-values are used as tool to check the significance of each of the coefficients. The smaller the magnitude of p, more significant is the corresponding coefficient. The model adequacies are checked by R^2 and predictive error sum of squares (PRESS). A model with large R^2 and low PRESS values is considered to be a good model. The same approach is applied for the relationship between the single compounds (independent factors) and the odour concentration (dependent variable).

3. Results and discussions

3.1 Sensor conductance versus odour concentration of samples with same chemical composition

One of the sets from the factorial design is selected from the design of 14 sets. Each set has different chemical composition and generates diverse odour concentrations. For example a composition set consisting of Limonene 2 ppm, TMS 6 ppm n-Butanol 0.5 ppm, H_2S 20 ppm and CH_4 100 ppb resulted in 31 907 ou_E/m^3 whereas other set consisting of Limonene 2 ppm, TMS 1 ppm n-Butanol 80 ppm, H_2S 1 ppm and CH_4 0 ppb odour was 4065 ou_E/m^3.



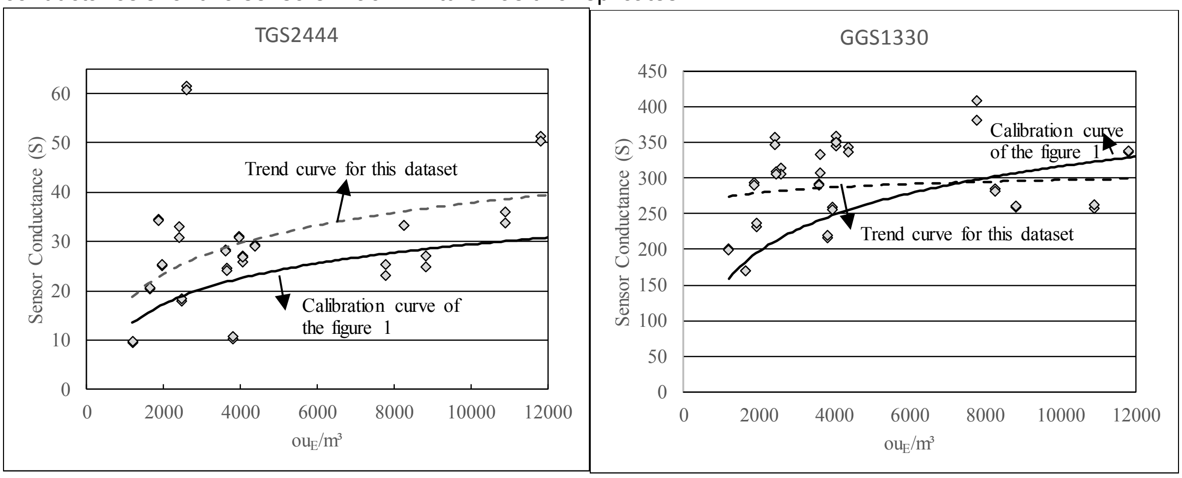
(a) (b)

Figure 1. TGS 2444 conductance (a) and GGS 1330 (b) in relation to the sample concentration at RH 50%. Each diluted sample contains the same compounds and has the same ratio between each compounds. The non diluted sample contains: Limonene 2 ppm, H2S 1 ppm, TMA 250 ppb and n-Butanol 20 ppm and has an odour concentration of 10 904 ou_E/m^3

The composition of the selected set for observation of dilution is Limonene 2 ppm, H_2S 1 ppm, TMA 250 ppb and n-Butanol 20 ppm. The odour concentration of this original composition has a value of **10 904 ou/m^3**. Three dilution ratio is applied on the original sample. The diluted samples are then exposed to the sensors array and to the olfactometer. The Figure 1 illustrates the conductance's of two of the six sensors (mean value of 3 measurements) to the set of odour concentration with same composition but different dilutions.
According to their respective technical datasheets, TGS 2444 has good selectivity for ammonia and GGS1330 is developed for the leak detection of combustible gases like CH_4. The mixture exposed to the sensors array does not contain any CH_4. However the sensitivity of the GGS 1330 to the mixture is rather high.
In the range from 627 to 4000 ou_E/m^3,the conductance are linearly correlated to the odour concentration and could be correctly calibrated by this way. At higher concentration, a saturation effect appears and forces to use a logarithm model. The four others sensors have a linear response for the full range of odour concentration.

3.2. Sensor conductance versus odour concentration of samples with same compounds but different compounds ratios

A number of 12 odour concentrations are prepared according the factorial design results. This mixtures contain the same compounds but in various ratios. As for the Figure 1, Figure 2 shows the stabilized conductance's for two sensors. Each mixture has two replicates.



(a) (b)

Figure 2. TGS 2444 conductance (a) and GGS 1330 (b) in relation to the sample concentration (RH 50%). Each sample contains different ratio of compounds

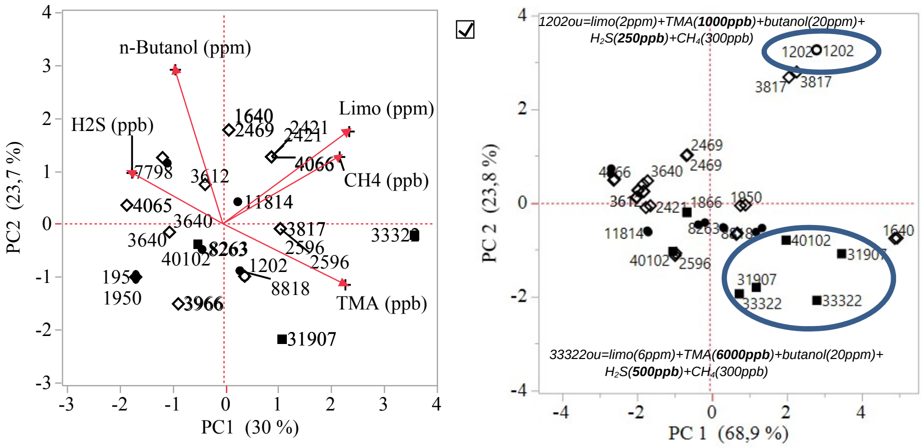
An obvious higher dispersion of the data set than the one of the calibration experiment (Fig1) is observed. It is explained by the difference in the chemicals ratio of the samples. The calibration curve obtained after dilutions of an original sample (Figure 1) does not fit well with this dataset. A worst result is obtained for the GGS1330 and is explained by the addition of CH_4, which was not in the mixture used for the calibration.
The odour value is partially dependent of the TMA content (Figure 3a). The selectivity of TGS 2444 for NH_3 could explain the relative good behaviour of this sensor for the odour concentration even for different ratios.

3.3 Sensors array response versus odour concentration of samples with same compounds but different compounds ratio

First, principal component analyses (JMP Pro 12.1.0 software from SAS) are performed on two data sets (44 data: chemical concentration and sensor signal) to highlight the relations between odour concentration/chemical compositions and sensors.

Table 2: sensor loadings

Sensors	Factor 1	Factor 2
R-TGS2602	**0.61**	**0.57**
R-TGS800	**0.97**	0.13
R-TGS823	**0.97**	0.04
R-TGS2620	**1.00**	0.00
R-GGS1330	**0.65**	**0.67**
R-TGS2444	0.06	**0.70**



(a) chemical concentration data (ppm) *(b) sensor signals (resistance kohm)*

Figure 3. PCA plots (score labels = odour concentrations in ouE/m³)

For the chemical data, the 2 first components explained only 57% of the data dispersion and it demonstrates that the odour concentration is not related to one or two compounds but to the relative ratio between the 5 compounds. However, high TMA value explains partially high odour concentration. There is no specific trend of the sensor array answer related to the odour concentration. The sensor 2444 has another behaviour and is strongly related to the PC2. It could again be explained by higher value of TMA (see composition of the mixture with odour concentration 1202 ou/m³ and 33322 ou/m³.

Box- Cox transformation with $\boldsymbol{\lambda}$ = 0 and stepwise regression a model is developed. The developed model results in the following polynomial equation:

$$\begin{aligned}\ln(Olfactometer) = 11.53 - 0.86*S_1 + 2{,}14*S_2 - 2.248*S_3 + 0.374*S_4 - 2.315*S_5 + 0.0237*S_6 \\ -1.360*S_1*S_1 - 0.326*S_2*S_2 + 0.001347*S_6*S_6 + 1.893*S_1*S_3 - 0.333*S_1*S_4 \\ +0.661*S_2*S_5 - 0.03193*S_2*S_6 - 0.01715*S_5*S_6\end{aligned} \quad (3)$$

where S1 to S6 are the resistance TGS 2602, TGS 800, TGS 823, TGS 2620, GGS 1330 and TGS 2444 respectively. The R^2 is found to be 96.61 %, R^2_{adj} is 95.21 % and R^2_{pred} is 93.88 % for the developed model.

3.4 Municipal solid waste odour sample collections and analysis

Samples are collected from different locations of municipal solid waste site. The samples bags are then analysed using the IOMS also used for the synthetic mixtures and olfactometer on the same day.

The results are then correlated using response surface methodology. The application of RSM with stepwise regression with no transformation resulted in the following polynomial equation

$$\begin{aligned}Olfactometer = -529 + 63.1*S_1 - 758*S_2 + 5*S_3 + 223.0*S_4 + 356.4*S_5 - 17.62*S_6 \\ -0.2070*S_6*S_6 + 63.4*S_1*S_2 - 48.1*S_1*S_3 - 12.06*S_2*S_6 - 9.461*S_3*S_4 \\ +14.97*S_3*S_6 - 3.969*S_5*S_6\end{aligned} \quad (4)$$

where S1 to S6 are TGS2602, TGS 800, TGS 823, TGS 2620,GGS 1330 and TGS 2444 respectively. The model summary consisting of R^2, R^2_{adj} and R^2_{pred} is as provided in Table 4.

Table.3 Model Summary

S	R-sq	R-sq(adj)	R-sq(pred
68.15	92.98%	89.72%	88.18%

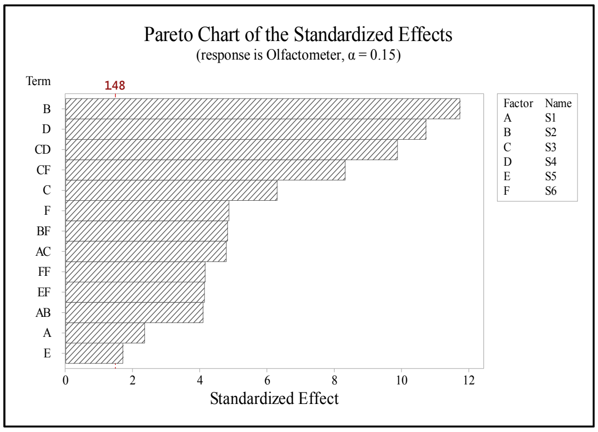
The R^2 value of the model represents how successfully the model fits the data. The high R^2 for the model shows that the developed model could explain the variations present in the independent variables. Whereas R^2_{pred} which represents the ability of the derived model to predict the output for unknown samples was also found to be high for the model. The pareto chart showing the standardized effects is as shown in Figure 5.

The performance evaluations of the prediction models developed are verified using RMSE (root mean square error) and MARE (mean absolute relative error) (Table 4).

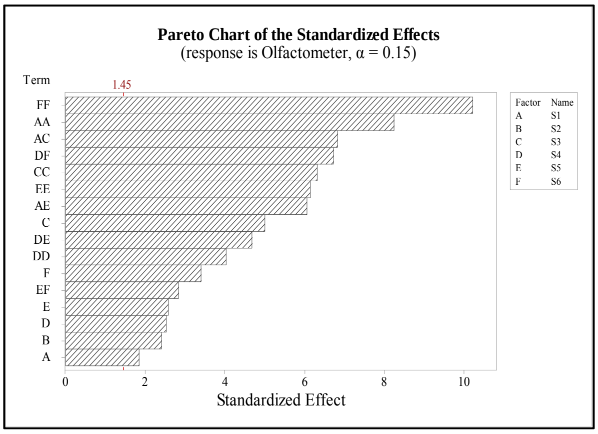
Table 4. Comparison of models developed for synthetic gas mixture and MSW site odours

	MSW Site	Synthetic gases
RMSE	0.1484	0.1850
MARE	0.0174	0.0156

The results are correct but it is needed to develop individual models specific to each application and not generalise models for IOMS.



(a)waste odour results



(b)synthetic gas mixtures

Figure 5. Pareto chart showing the standardized effect of sensors on the exposed odour

Conclusions

In this study, mixtures of five synthetic gases are exposed to a sensors array and to olfactometer. Different compounds concentrations ratios are prepared thanks to factorial experimental design Corresponding responses are studied. Further, the same sensors array is exposed to samples collected from MSW sites and corresponding odour concentration are measured. The results shows that it is not reliable to use synthetic gases to train an IOMS for further measurements of real MSW odours. Variations in their compounds ratios explain those bad results. The selectivity of MOS sensors used in this study do not allowed to apply the synthetic mixtures quantification model on MSW odours. A correlation model is developed (with response surface methodology) between sensor resistance and odour concentration for both MSW site samples and synthetic gas samples. For these selected gases and MSW odours, the models obtained with the response surface methodology are also unsatisfactory. However, factorial design experiment is an interesting tool to prepare synthetic mixtures in order to test the performances of each sensors but is not recommended to develop an odour prediction model. To train a MOS sensors array for odour quantification of complex odour composition, it is advised to work with the samples of the odour that will be considered and not with synthetic calibration gases.

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