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Exploratory data analysis for industrial safety application

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Abstract

We tested the detection properties of four MOX sensors toward different ozone mixtures to identify sets of sensing layers and interfering compounds concentrations most suitable for a reliable detection of ozone. The measurement campaign lasted 1 year divided in four sessions. We collected a substantial amount of measurements (more than 500) with diverse interfering gases: ammonia, ethanol, ethylene, carbon monoxide and humidity. Due to the dimension of the data set it could not be analyzed using the conventional methods generally applied for characterizing gas sensors: evaluating the sensor performance by visual inspection of the sensors responses is unfeasible. For this reason we systematically applied the exploratory data analysis methodology. We used some simple but effective statistical techniques to insight the data. This approach allows us to draw sound conclusions about the causes of variation in the data, e.g. time (sensors' long-term stability) or interfering effects of different chemical compounds. All the analysis techniques employed in this work are implemented in a software package developed at our laboratory.

We concluded that the two best stable and sensitive sensors are based on WO_3 and SnO_2 (Au catalyzed). We ranked the contributions of different gases on sensor responses, deducing that out sensors are suitable to detect steps of 50 ppb of ozone when ethylene is less than 10 ppm. Carbon monoxide does not affect the measurements still, the strongest interfering compound is humidity that needs to be controlled or parallely measured also in a preliminary stage.

Keywords: Exploratory data analysis; Industrial application; Ozone detection; Sensors array

1. Introduction

Ozone detection is not only an environmental priority but also an industrial requirement to keep workplaces healthy. Catalytic ozonation is widely used in industrial processes and the trend is proceeding upwards. Typical applications include water and wastewater disinfection (wastewater plants, hospitals) and food sterilizing (approved in 2001 in the US) where ozonation systems are used, e.g. in modified air packaging lines and fruit storages.

Ambient ozone level in workplaces where ozonation is used has to be monitored. The US Occupational Safety and Health Association (OSHA) has set strict exposure limits to assure workplace safety [1]. OSHA has defined the ozone exposure limits as follows: threshold limit value (TLV) is 100 ppb, short-term exposure limit is 300 ppb The normal background level of ozone in workplaces is 30 ppb [2]; thus for indoor applications it is important to investigate and characterize sensitive layers for ozone concentration higher than 30 ppb. For the industrial application envisaged, the effect of interfering gases can have a relevant importance due to its presence in the environment as will be shown in this paper.

Up to now, the only solution for ozone monitoring is given by ozone analyzers that are highly selective and sensitive, but also quite expensive (about € 10,000o). Gas sensors arrays (or electronic nose) offer a cheaper alternative approach.

The need to get portable, user friendly, cheap and low power consumption devices for gas detecting drives the market trend. The technological improvements occurred in the last decade in system miniaturization is leading towards small and smart devices containing a reduced number of sensitive gas sensors coupled to pattern recognition software implemented in a microprocessor. Our paper shows that this trend might be followed also for ozone monitoring. Portable devices can be proposed to the final user for a dedicated application with reduced price and more specific sensing capability with respect to electronic noses.

During the last years different metal oxide sensors such as tungsten oxide, indium oxide, mixed indium and iron oxide, revealed suitable for ozone sensing ([3–8]).

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This work is motivated by the lack of exhaustive studies in monitoring ozone in realistic conditions: long measurements time, diverse interfering gases and different humidity levels. These operative conditions are not generally used in the preliminary sensor testing stage but they are the most indicative about the actual sensor working capabilities.

We tested an array composed of four metal oxide gas sensors toward mixtures of ozone and four interfering compounds, carbon monoxide, ethylene, ammonia and ethanol at different concentrations. Also two different humidity levels are monitored to evaluate the influence of that parameter on sensing properties. We carried out four measurement sessions, lasting from 2 to 4 days each, over a 1 year period in order to evaluate sensor stability. Testing different interfering species at different humidity concentrations over a long period of time permits to determine critical parameters for a possible industrial application of such sensors.

The measurements' variability depends on a high number of variables: sensor type, ozone concentration, interfering species and their concentrations, humidity level and time progression. In order to visually understand how the variables affect the sensor response, we applied exploratory data analysis techniques. Exploratory data analysis (EDA) is a fundamental step in the data analysis cycle (the cycle consists of: data acquisition, data preprocessing, exploratory data analysis and classification) [12]. The aims of explorative analysis are manifold: maximize insight into a data set, uncover underlying structure, extract important features and detect outliers. A most valuable outcome of EDA is to check for prior assumptions and determine optimal experimental settings.

With EDA we identified the sensing layers and the interfering compounds' concentrations most suitable for our specific industrial target. We end up with a two-sensors array dedicated to ozone detection.

Finally, a quantitative evaluation of the ozone concentration in different mixtures with interfering gases is performed with the multi-linear regression (MLR) method.

2. Experimental and methods

Materials, deposition methods and working temperature are reported in Table 1 together with codes that will be used in the following to identify each sensor. The working temperature has been chosen as the best compromise between enhanced sensitivity (improved by decreasing the working temperature) and fast response/recovery times (improved by increasing the working temperature) [6].

Measurements were carried out with the flow-through technique in a temperature-stabilized sealed chamber (volume of 1 L) at 20 °C under controlled humidity, working with a constant flux of 0.2 standard litres per minute (s.l.m.). Gas mixtures were generated by certified dry air bottles with diluted target gases concentrations and a humidity control system. A multiple automatic mass flow controller system pilots the correct mixture composition before injection.

Ozone was generated through UV lamp discharge and the concentration was measured at the chamber outlet by a detector based on the wet chemical Brewer–Milford principle. A commercial readout electronic has been used to measure sensor resistance values.

We initially tested four interfering gases: ammonia, ethylene, ethanol and carbon monoxide. For three compounds, ammonia, ethanol and carbon monoxide, we observed a very low interfering behaviour with respect to ozone so, after some preliminary measurements, we decided to discard ammonia and ethanol. Carbon monoxide was chosen as representatives of this class of low-interfering gases. Ethylene showed a stronger interfering effect. Thus, we prepared samples mixing dry air and ozone or dry air, ozone and an interfering compound (ethylene or carbon monoxide). No ternary mixtures have been examined. The concentrations of the analytes employed are: ozone (0, 70, 140, 280, 560 ppb), carbon monoxide (0, 5, 10 ppm), ethylene (0, 5, 10, 30, 60 ppm). The measurements are performed at different humidity concentrations: 3 and 20% at 20 °C. Different humidity levels are considered to increase the system complexity and match more realistic industrial environments.

The detailed measurement table is reported in Table 2. We tested 581 samples divided in 30 different binary mixtures. We performed at least two repetitions for each gas mixture. Four blocks of measurements were carried out during an eleven months campaign with the same sensor array at two different humidity levels. During the last session we observed the poisoning of two sensors, CoO and InFe. As a consequence the measurements collected with such sensors were eliminated and were not considered for data analysis.

We designed the measurement protocol with up and down concentration ramps. The ramps are formed with increasing and decreasing steps of ozone concentrations. At each step (fixed ozone concentration) the concentration of a second component is changed (Fig. 1). The concentration of mixture constituents is kept constant for 30 min in order to stabilize the sensors response. The first measurement of each session measures the baseline (i.e. just air) which is than used to calculate the $(R_{ss} - R_0)$ feature as we described afterwards.

Table 1
Description of the sensors composing the array

Code	Material	Working T (°C)	Deposition method	Reference
WHT	WO_3	450	Thermal evaporation from metallic W source	[9]
SnAu	Au catalyzed SnO_2	450	RGTO SnO_2 layer + sputtered Au	[10]
InFe	Mixed In and Fe oxides	350	RGTO from sputtered In target with Fe insets	[6]
CoO	CoO	400	Reactive sputtering from Co target	[11]

The materials, the working temperatures, the deposition methods and the references for further synthesis details are reported in the table.