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Method for increasing reliability in gas detection based on indicator gradient in a sensor array

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ABSTRACT

We present a method for analyte detection using an optical sensor array. The method is implemented in an ammonia gas detector, using a pH sensitive dye. The array is composed of four sensors, each coated with a different concentration of the dye. The resulting signal vector is collected by measuring the absorption at a single wavelength, at each sensor. Simple correlation of the signal vector with an expected gradient-like response enables detection of ammonia. Moreover, it improves immunity to false signals created by changes in illumination intensity and the humidity of the environment. The method of detection is generic and applicable to sensor arrays where the probe concentration can be controlled.

1. Introduction

Reliable detection of chemical and biological materials depends on the selectivity and sensitivity of the system. Although both properties are desirable in any sensing scheme, they often contradict each other. This can be seen as the trade-off between probability of false detection and probability of misdetection [1]. Prioritizing these properties is a matter of the specific implementation conditions. In the following, we present a data analysis method for improving the detection reliability for a given chemical, in the presence of other chemical agents and perturbations that generate spurious signals. Furthermore the method provides a thresholding parameter which can be tuned by the user according to his priority considerations between sensitivity and selectivity. We demonstrate the method in a sensitized porous silicon optical detector array aimed at identifying ammonia gas at varying humidity conditions and unstable illumination.

Monitoring gaseous ammonia is of great importance in environmental, automotive and industrial applications. Much effort has been invested in the production of ammonia sensors with various sensitivities and detection limits [2,3]. Such gas sensors may be based on pH sensitive dyes [4–7] or polymers [8], where the detection is based on the color change of the material when in contact with ammonia. Immobilization of sensitive dyes onto porous silicon for ammonia detection has been studied [9–11] due to its high surface area and easy fabrication. One of the major drawbacks of dye-based ammonia sensors is their sensitivity towards other gases, such as air humidity, which affects their performance [7,12,13]. The response of such sensors depends on the relative humidity (RH) and therefore various sensors have been developed with multi analysis capability, i.e. simultaneous detection of ammonia and humidity [13–15]. However, the gas selectivity remains a critical limitation in practical applications. A previous study proposed a method in which the working temperature of an array of three tin oxide gas sensors was periodically varied in order to achieve improved gas discrimination [16]. For such systems, the need for hotplates with suitable mechanical strength at elevated temperatures and power consumption is a drawback. Another study demonstrated discrimination of organic vapors using an array of porous silicon sensors of different porosity and pore morphology. Sensitivity of PSi sensors for different vapors varied significantly with the variations of pore dimensions, and thus facilitated discrimination through the analysis of the array collective output, using artificial neural networks [17]. Other studies have demonstrated discrimination based on Principal Component Analysis (PCA) and supervised machine learning techniques [18], which require system training and calibration.

In the case of porous silicon sensors, water vapor creates a shift in the absorption spectrum [19], therefore altering the absorption

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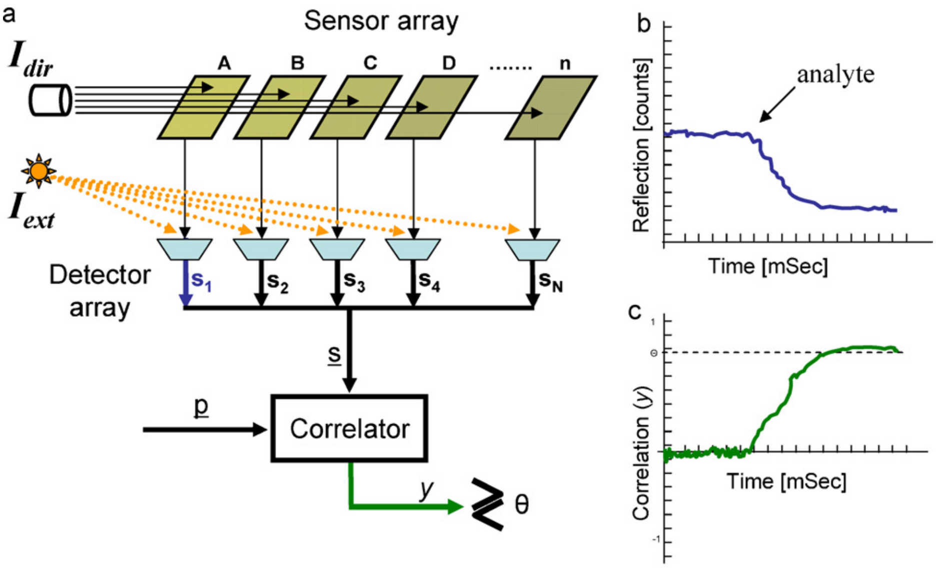

Fig. 1. (a) Sensor array detector. The vector of output signals $\underline{s}$ is correlated with concentration gradient $\underline{p}$. The system's direct internal light source I_{dir} is used for all sensors; the detector array is exposed to additional undetermined external light I_{ext}. Typical output signal of a sensor s_i (vs time) is seen in inset (b); typical output of the correlator, Y, is seen in inset (c). y is compared to a threshold Θ; when it is exceeded, the analyte presence is inferred.

at the wavelengths of interest. This shift can be detected when the spectral band of interest is analyzable but might generate a false positive signal when only a single wavelength is observed. Since full or even partial band analysis of the spectrum is complex and expensive, detection based on the absorption signal from a single wavelength is desirable. Here we present a method for ammonia detection at a single wavelength with increased immunity to spurious signals by using different concentrations of sensitive dye. Such spurious signals might be generated by sensor aging, illumination changes, and environmental conditions such as humidity or contamination. It is important to note that the system and method presented here do not require extensive calibration or training techniques. Our method makes use of four sensors of similar structure coated with different quantities of the pH sensitive dye Bromocresol purple (BCP). This enables the use of simple correlation techniques to detect ammonia in the presence of changing humidity.

2. The detection principle

2.1. System model

In general, a chemical or biological sensor uses a probe to react with the analyte of interest. The reaction leads to a change in the analyte, probe or the environment such that a measurable signal is generated. Such signal can be the current in a semiconductor device or the fluorescence from a chemical sensitive polymer [20]. The signal depends on the number of probes available to react with the analyte, while the precise type of such dependency differs between different sensor types and working conditions. In the work presented here, the available probes are chosen in a manner such that sensors of the same type generate a signal approximately linear with respect to the probe concentration on their surface. In this manner, the resulting signal vector accommodates for sensitivity and selectivity towards the analyte, but does not require training or calibration for its detection. A schematic drawing of such a sensor array is depicted in Fig. 1.

The demonstrated array is comprised of n optical sensors that are similar in all physical parameters other than the probe concentration. A common light source is applied to all sensors. The reflected light from each sensor is measured at a single wavelength by a dedicated detector. The detector array output is a vector of signals $\underline{s}$, where each element response s_i is

$$s_i = I_{\mathrm{dir}} \cdot h_i \cdot x + b_i + \upsilon_i \tag{1}$$

where I_{dir} is the direct light source intensity, h_i is the sensitivity of the sensor, x the analyte concentration, b_i the constant offset and υ_i the sum of external light source intensity fluctuations at the detector (denoted I_{ext} as in Fig. 1a) and other time dependent noises. The offset of each sensor is canceled by using the baseline steady state signal as a reference (e.g., averaging s_i over time after initialization, when there is no analyte in the system). We henceforth assume that b_i equals zero. We note that the linearity assumption in Eq. (1) will not hold for analyte concentrations that either saturate the sensor or are below its minimum detectable limit.

Assuming linearity, the ratio of sensitivities between two sensors is determined by the ratio of probe concentration. We therefore assume for simplicity that the sensitivity vector $\underline{h}$ is given by the product of the probe concentration vector $\underline{p}$ with some unknown transduction factor T:

$$\underline{h} = T \cdot \underline{p} \tag{2}$$

The array output $\underline{s}$ is

$$\underline{s} = I_{\mathrm{dir}} \cdot \underline{h} \cdot x + \underline{\upsilon} \tag{3}$$

We note that T may incorporate many different effects such as aging or the presence of other chemicals that may enhance or degrade the sensor's signal. Since in most cases both T and x are unknown, and coupled in the presented model, their efficient estimation cannot be achieved without a thorough calibration process of the factor T which in many cases depends on a series of environmental conditions. We emphasize that the method developed here does not require the a-priori knowledge of T, while preserving the ability to infer the presence or absence of the analyte, which is sufficient in many practical situations.

We next define the coefficient of variance for sensor i:

$$c_{\sigma,i} = \frac{\sigma(\upsilon_i)}{T p_i x_i} \tag{4}$$

where $\sigma(\upsilon_i)$ is the standard deviation of υ_i. It can be seen that higher values of T will yield lower values of $c_{\sigma,i}$, therefore better signal to noise ratio (SNR).