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Qualitative and quantitative substance discrimination using a CMOS compatible non-specific NDIR microarray

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ABSTRACT

A non-specific non dispersive infrared (NDIR) micro-optical gas detection system is presented. The system is based on a monolithic filter microarray (up to 16 non substance oriented elements) that is attached by flip-chip onto a matching microarray of thermopiles, configuring a compact CMOS compatible optical detector. The system aims to combine the stability of infrared optical devices and the versatility of electronic-nose approaches. The transmission spectra of the filters, multi-peaked and of broad band nature, are not oriented to any specific substance detection, and multivariate regression techniques are used to predict gas type and concentrations from the voltage pattern generated by the thermopile array. The ability of the system for substance discrimination has been proved by means of qualitative volatile identification (ethanol, isopropanol and acetone) and quantitative tests have been performed with CH_4 and CO_2 mixtures.

1. Introduction

Lots of large impact applications (industrial process control, environment monitoring, homeland security, health...) will benefit from gas sensing systems that are deployable, or at least portable, meaning by this, robust, small size and low cost systems.

Infrared (IR) based systems are usually considered high-end benchtop systems [1], and certainly an effort for miniaturising them will be most welcome as has been the case for non dispersive infrared systems (NDIR) [2]. In those systems a broadband thermal source illuminates a gas cell, and a set of filters and infrared detectors collects and measures the transmitted light at particular wavelengths. The working principle relies in an intrinsic light-matter interaction that renders them quite selective. This is because most gases exhibit distinct absorption features in the infrared region of the electromagnetic spectrum. Ideally, this makes possible choosing a narrowband pass filter that collects exclusively information at that characteristic wavelength and consequently allows the extraction of quantitative information about the concentration of a given species (through the Lambert-Beer equation) without interference from any other species that could be present. Some other advantages of these systems are their immunity to false alarms and poisoning (there is usually no contact between sample and detector), and their great stability (because as a rule they include a reference channel free of any absorption for compensation of external conditions and aging of optical elements). They have disadvantages as well when compared to electrochemical, catalytic and metal oxide sensors. They are 'systems', not point-like sensors. As such they are complex, needing the combination of different elements (IR source, gas cell, detectors, specific filters...), and the more substances that are to be detected the more complex the system becomes. The specific filters, although extremely precise, are expensive and difficult to integrate in the detector and into the whole system. They are usually manually attached to the detector lid or integrated as a filter roulette, which is a moving element compromising both robustness and size of the system. NDIR appliances are often used in situations where those disadvantages are not a serious drawback and can be kept simple. For instance when different gases are present but they group in a family and it is their simultaneous detection that is needed (e.g. detection of explosive level of hydrocarbons), or when monitoring the concentration of a particular gas in a very well controlled atmosphere (anaesthetics, for instance).

There are situations where a multichannel system is a must because several gases are to be detected, or one specific gas is the target but interfering species cannot be ignored because the blocking capacity of the specific filter is not enough. For instance, ethylene is a gas whose detection and control is very interesting in large climacteric fruit store-houses (such as the ones used for long term storage of apples and pears) since it signals and trig-

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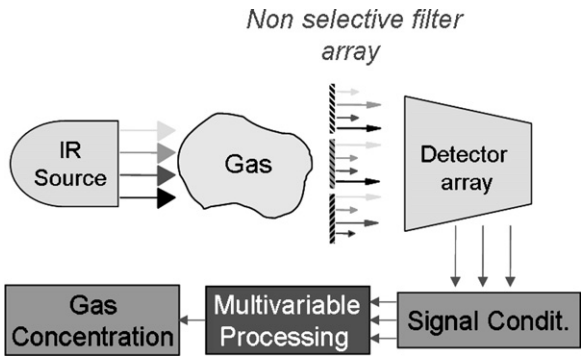

Fig. 1. Diagram of the presented new NDIR system based on the collective response of an array of non-selective filters.

gers ripening. This gas has its main absorption band centred at 10.6 μ, which overlaps partially with that of ammonia. Ammonia is used as a refrigerant in those chambers so a leak event would mislead the ethylene sensor. An ammonia channel can be added centred at 9.7 μ where ethylene signal is weak but not null. At that wavelength ethanol, whose presence is also likely because it is produced by fruit under stress, has a very strong absorption. Fortunately ethanol exhibits another absorption band at 3.5 μ in which no ethylene or ammonia absorption exists. Therefore, a third channel has to be added in order to tell apart ethanol from ammonia. The point here is that because of the interfering species present in a given atmosphere a multichannel system is needed for a single species determination [3]. Even in that case the channels may not be completely independent because of the finite width of the absorption peaks and of the tails of the bandpass filters, so some degree of data processing may be needed.

Although not common in mid infrared (MIR) appliances, multivariate data processing is not strange to other infrared applications. For instance, chemometrics is a norm when using near infrared (NIR) [4], where overtone overlapping is significantly more severe than in mid infrared. Even whole FTIR spectra obtained with high class spectrometers are cycled through data processing routines when complex mixtures with built-in variability (wine, animal odour. . .) are to be characterised [5,6].

In view of this fact we present in this work an alternative approach to infrared gas sensing based on the replacement of the expensive and hard to integrate specific filters by a single filter die consisting of a monolithically integrated microarray of non-specific filters. When assembled to a complementary detector array each gas will generate a distinct voltage pattern, and those voltage patterns will be discriminated by means of multivariate processing techniques in order to identify and even quantify the present gases (see Fig. 1). In this approach the complexity of standard NDIR systems is moved from the (more constrained) hardware-end to the (more flexible) software-end. The obtained platform is totally generic and versatile, although it has to be trained for each particular application. In addition, we show how the filter and detector arrays can be fabricated using silicon compatible microtechnologies thus obtaining a non expensive, miniaturised and compact detector module.

This paper describes our work in this genuine 'optical nose' approach, preliminary results of which have been previously published with regard to its technological viability, functional simulation and qualitative discrimination ability [7,8]. In this paper we extend the description of the system and its advantages, prove the system capability for quantitative determination of mixtures and analyse the impact of the filter architecture and array size on the results.

2. Non-specific filter microarray

The filter microarray is composed of filter elements based on Fabry-Perot structures with oxide cores of thicknesses ranging from 2 to 8 μ sandwiched between silicon mirrors. As a result, each element presents many broad transmittance bands in the mid infrared region. Their number and their position depend on the thickness of the oxide: the thicker the oxide, the more numerous the bands since more wavelengths are able to meet the constructive interference condition. An example of the transmittance of those filter elements can be seen in [7]. As mentioned above, all elements of the same array share the same top and bottom mirror and only differ in the thickness of the oxide optical cavity. Nevertheless, two different types of filter arrays have been fabricated depending on the nature of those dielectric mirrors. In the simplest of the structures considered, the silicon wafer itself plays the role of the bottom mirror whereas the top mirror is a thin polysilicon layer. Antireflection oxide coatings complete the filter structure. Since the top and bottom mirrors are dissimilar, this structure will be referred to hereafter as asymmetric. A slightly more complex structure, yet very simple and cost effective, has been built as well, in which the bottom mirror is also a thin polysilicon layer optically separated from the underlying silicon wafer by an additional oxide layer similar to the antireflection ones. This structure will be referred as symmetric since both mirrors are of the same nature. As both mirrors are identical, the obtained transmittance bands are narrower than in the asymmetric case. Nevertheless the same number of peaks is registered in both cases. Nine and sixteen element versions of each array have been fabricated with the aim that the combined response of all the different elements covers the whole mid infrared region of (400–4000 cm^{-1}).

An example of the collective coverage of the infrared spectrum by the different arrays is shown in Fig. 2. Asymmetric arrays show *fewer* number of 'dents' in their combined spectra since the transmittance peaks summing up are *broader*, and 16 element arrays exhibit less *pronounced* 'dents' since *more* elements are being added up. All arrays perform adequately in this respect, especially the asymmetric ones for which the minimum transmittance value associated with the more distinct of the dents is always above the minimum value attained by the overall combined spectra envelope.

Two more points can be considered with regard to the useful combination of the element spectra. The first one is that the fabricated arrays are transparent in the whole infrared region, except for those wavelengths where the constituent materials of the filters themselves (silicon and silicon dioxide) absorb. Since all elements are composed of several micron thick oxide layers, the vicinity of the SiO_2 main absorption at 1100 cm^{-1}, (1000–1200 cm^{-1}), could be considered as an operative blind window since no light in this region will reach the detector. To improve this point in a future the oxide layer can be etched away with the help of surface micromachining: the oxide cores of the different filters will become air cores without inconvenient absorptions. The second point is that a high transmission region common to all filters is as inconvenient as a transmission gap shared by all elements. In both cases gas discrimination will be prevented in those regions. In this respect, it is worth noticing that a third symmetrical array version was initially envisaged in which the top and bottom mirrors consisted of a three layer stack of polysilicon-silicon nitride-polysilicon. This combination of layers with high and low refractive index gave rise to higher reflectivity mirrors and consequently to even better defined transmittance peaks. However, this structure also led to the presence of a pattern that was roughly reproduced in every filter in the same wavelength region rendering them useless as explained above.

Even though the structures themselves are quite simple, it is important to minimize their fabrication cost. The best way to ease the fabrication of arrays of up to 16 elements with different