

Review of Small Commercial Sensors for Indicative Monitoring of Ambient Gas

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The traditional ambient gases monitor stations are expensive, big and of complex operation. So they are not suitable for a network of sensors that cover large areas. To cover large areas these traditional systems algorithms usually interpolates the measurements to calculate the gas concentrations in points far away of the physical sensors. Small commercial sensors represent a big opportunity for making sensor networks that monitor the ambient gases within large areas without the necessity of interpolation. There have been some successful previous works on these sensor networks with custom sensors and with commercial sensors but the information and characteristics of these sensors is difficult to compile and compare. In this work we review the literature on commercial sensors for ambient gas measurements over a hundred commercial sensors and compare their performance with the specifications of the European Directive on air quality 2008/50/EC.

1. Sensor technologies

Almost the totality of the small commercial sensor available belong to four different technologies, resistive sensors, electrochemical sensors, dispersive infrared radiation absorption (NDIR) and photo ionization detector sensor. We review each one and their characteristics in the following sub sections.

1.1 Resistive sensors

The transducer sensor mechanism of these devices consists in a metal oxide that changes its resistance or conductivity when exposed to different ambient gases. Tin oxide is the most used metal oxide used because it reacts with a big number of gases and has strong changes on its resistance. The model widely accepted is that tin oxide form grains and the boundary of those grains dominate the conductivity. In presence of an oxidizing gas, oxygen in ambient air, the molecules of this gas react with the tin oxide trapping electrons of the surface. This accumulation of electrons creates a negative charge space that act as a barrier for the electrons and thus increases the conductivity.

The sensors are usually small with a size around a dozen millimeters and a weight about a few grams. The sensors need high temperature to increase the rate of the reactions so a heater is usually incorporated into the sensor. The resistive sensors respond to a wide range of concentrations of the gases, from a few ppb (Kida et al., 2009) to several thousand of ppm (Katulski et al., 2009). The sensors signal to noise ratio provided by the manufacturers is usually not very clear. Desorption tends to be slow but in most of the cases their response time is around a few minutes (Katulski et al., 2009). These sensors present the more cross sensitivity of all the reviewed sensors, reacting to nearly any volatile compound (reducing or oxidizing), toxic gases like NO_x, or volatile organic compounds. Manufacturer methods to deal with cross sensitivity are providing short tables of equivalent responses, incorporate different dopants or placing filters. The temperature and humidity are magnitudes that

interfere in the responses and have to be controlled or measured with precision in order of provide a model of their influence. The stability is probably the worst problem of this kind of sensors. The response changes over time and the sensors needs to be recalibrated. Manufactures do no provide much information about the drift or stability.

Several authors model the response as:

$$G - G_0 = a \cdot p^b \quad (1)$$

Where G is the conductivity, G_0 is the conductivity at zero gas concentration, p is the gas concentration and a and b are constants (Kohler et al., 1999). Other methods use the Schotty expression for the conductivity to describe the response (Barsan, 1994). There is also the possibility to extract temporal parameters from the response curves, points taken at different times (Aleixandre, 2004), integral of the response curve (Jerger et al., 2002), coefficients of curve decomposition (Vergara et al., 2011) or other methods like extracting parameters from the curves of resistance after changing temperature (Kohler et al., 1999). Other authors use non parametric methods such as neural networks, (Katulski et al., 2009) linear partial least squares (PLS) and spline fitting of the data (Kohler et al., 1999).

1.2 Electrochemical sensors

The mechanisms of this kind of sensor are electrochemical reactions that happen within the sensor between the gas present and the some electrolyte. These reactions produce a current that is measured outside giving a electric current that depends on the gas concentrations (Jacquinot et al., 1999) following the well know Nerst Law for electrochemical reactions (Kumar et al., 1988).

The usual size of these sensors is about 20 mm and the consumption is very low because the signal generated is a low level electrical current so the main power requirement is its amplification. Some manufacturers uses liquid or gaseous electrolytes as e2V while others use solid ones (Kumar et al., 2000), organic gel electrolytes as Citytech or porous PTFE with catalytic materials as e2V. These different compositions determine the selectivity and sensitivity to target gases such as VOCs (Nagai et al., 2010), toxic gases: O₃ (Knake et al., 2002), NO₂ (Ono et al., 2001), NO (Miura et al., 1999). The traditional electrolytic sensors have a very high range of detection of gas concentration (Saponara et al., 2011) but new sensors can achieve low detection limits (Katulski et al., 2009). The usual detection limits for O₃ and NO₂ are 10-20 ppm and in some cases the rage can be even as low as 2 ppm, for other gases it is usually higher for example 100 ppm to NH₃ of Synkera sensors. The error tends to be similar in all sensors and they show a deviation from linearity of about 2-5 %, but in some cases the error can rise up to 10 %. The cross sensitivity to other gases can be fine-tuned by the selection of different electrode materials but cannot be eliminated completely.

The temperature has also an influence on the response of the sensor, but it can be modeled. Some studies have shown dependence on wind velocity on ambient applications probably influencing the chemical equilibrium on the surface (Gerboles and Buzica, 2009). The sensors show long term stability, for Nemoto and e2V ones around 2 % per year or up to 15 % per year. Some problems of stability can arise from the lack of oxygen or humidity. While the consumption of oxygen is very low and the sensor can operate long times without being exposed to oxygen, a constant exposure to oxygen should be supplied. Some electrolytic sensor need humidity to function correctly and a very low value can cause problems while others sensors based on solid materials are not so dependent on the ambient humidity.

The calibration of these sensors follows the Nerst law and are well calibrated for the gases to measure and are either linear or logarithmic.

1.3 Infrared radiation absorption sensors

Another technology of sensors is the optical transducing mechanisms based on the Infrared Gas Absorption Spectra. In these sensors an infrared light illuminates the gas to be measured. The asymmetric molecules present on the gas adsorb the radiation at determined narrow bands of adsorption characteristic of each molecule. The intensity of this adsorption follows the Beer-Lambert equation (Pandey et al., 2007).

$$A = \text{Log}_{10} \left(\frac{I_0}{I_t} \right) = a \cdot l \cdot c \quad (2)$$

Where A is the absorption, I_t is the light intensity measured, I_0 the light intensity emitted, a a factor of absorption that depends on the gas and the frequency, l the length of the path of the light and finally c is the concentration of the gas.

These sensors have a size of a few millimeters and a power consumption of a few hundred mW. The detection range of these sensors goes from 5 % vol to 3,000 ppm for hydrocarbon gases and CO₂. Their response is well characterized and follows closely the model equations. The noise is high reaching up to 500 ppm of hydrocarbons or 50 ppm of CO₂ and they have very fast response times, around tenths of seconds. All the hydrocarbons share a similar absorption band, originating on the carbon hydrogen bond, what makes all them cross sensitive. The CO₂ in the other hand has a very characteristic absorption band which makes the sensors very selective to it, being a very good CO₂ sensor candidate (Kumar et al., 2000).

The method of calibration consist on calculate the parameters that fit the model of the sensor from reference gas.

1.4 Photo Ionization Detector Sensor

In the photo ionization measurement process the molecules of the target gas are illuminated by high energy UV light. The absorbed of a photon by a molecule can break this molecule and generate electrical charged ions. These ions are exposed to an external electrical field and generate a current. This electrical current is proportional to the gas concentration.

The usual size of these sensors is around 20.2 mm x 16.5 mm, with a weight of 8 g and a power consumption of 110 mW. Several enterprises sell these sensors (Alfasense and CityTech) but all seems to share same manufacturer: Baseline-MOCON, Inc.

This sensor is able to detect VOCs with ionization potentials bellow 10.6 eV, that means VOCs whose molecules break with energies bellow 10.6eV. For the benzene, the detection limit is up to 100 ppm. And the limit of detection is very low reaching 3 ppb of Benzene.

The responses show a 3 % deviation of the linearity. Above 10 ppm the linearity of the sensor decreases but also does the noise. The sensors are fast with times of response of less than 3 seconds. Any VOCs with ionization potentials less than the ionizing potential of the lamp used can and will be measured, decreasing the selectivity of this sensor. The different responses are well calibrated and provided in tables for more than fifty gases. For benzene a Xenon lamp (9.6 eV) is advised. There is small temperature dependence and the humidity sensitivity is below an equivalent response of 0.2 ppm for changes of 90 % r.h. Although the sensor is very stable it requires frequent calibration. The manufacturer recommends a recalibration once a month in clean environments with low particle count and low VOCs present.

The response is very well calibrated fitting the measurements to linear equations. But since the lamps vary one from each other, each lamp replacement requires a new calibration.

2. Target Gases

In the following section we present the compiled data of the reviewed sensors from the manufacturing companies listed in Table 1 and the comparison to the required ranges for the different gases of interest in the European directive on Air Quality 2008/50/EC (EC, 2012). The results are summarized in the Figure 1.

The resistive metal oxide and electrochemical sensors perform well and have a good sensitivity to NO₂. But very few reach the 0.15 - 0.01 ppm mentioned in the European directives. Among the interference gases present in ambient gases only O₃ should be considered. SO₂ in some sensors (Sensoric 3ENO) shows a small sensitivity that can go up to 2 ppb NO₂ indetermination in the usual ambient concentrations extracted from the European Air quality database AirBase (AirBase, 2012). Other common interference gases such as Cl₂ and H₂S should not be taken into consideration because of the low concentrations expected in ambient air, 1 ppb to 0.05 ppt and 0 to 3.6 ppb respectively (AirBase, 2012).

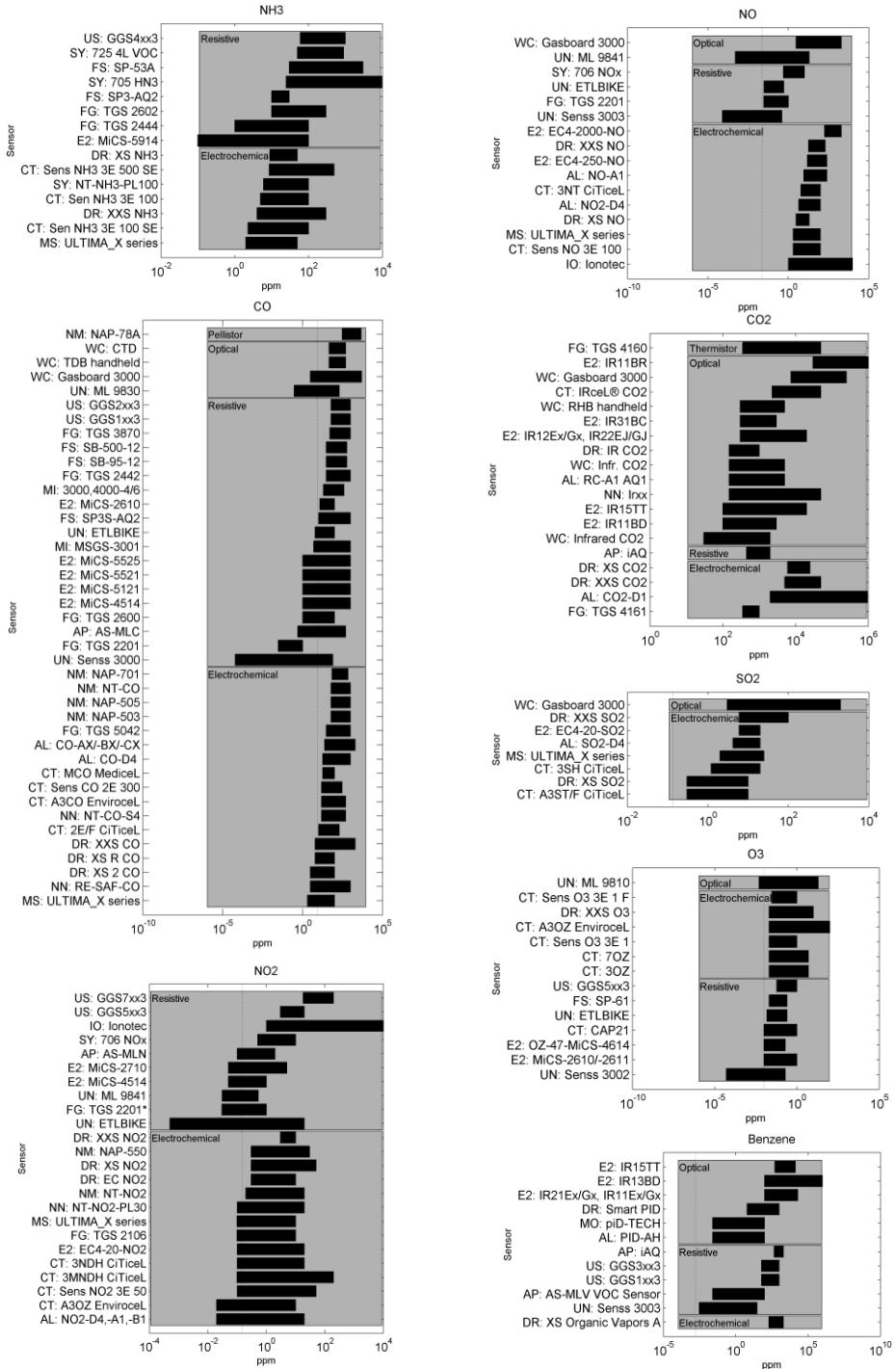


Figure 1: The concentration ranges of detection of the different sensors evaluated in the review. The dotted line represents the typical concentration of the European directives when available. The sensor that belongs to the same sensor technologies are grouped in the named grey areas.

Table 1: List of manufacturers of the gas sensors reviewed, accessed December 2011

Company name	Abbreviation	Web address
Alfasense	AL	www.alphasense.com
Appliedsensor	AP	www.appliedsensor.com
Citytech	CT	www.citytech.com
Draeger	DR	www.draeger.com
e2V	E2	www.e2v.com
Figaro	FG	www.figarosensor.com
FIS	FS	www.fisinc.co.jp
Ionotec	IO	www.ionotec.com
Microsens	MI	www.microsens.ch
Mocon	MO	www.mocon.com
MSA	MS	www.msanet.com
Nemoto	NM	www.nemoto.eu
Nenvitech	NN	www.nenvitech.com
Synkera	SY	www.synkera.com
Unitec	UN	www.unitec-srl.com
UST	US	www.ust-india.com
UST	US	www.umweltsensortechnik.de
Wuhan Cubic	WC	www.gassensor.com.cn

Resistive and electrochemical sensor measure well the O₃ because it is also very reactive. O₃ is unstable at high temperatures, and some sensors use it to implement filters. O₃ can be measured by resistive and electrochemical sensors at low concentrations of 10 ppb. Of the reported cross sensitivities, only NO₂ should be relevant. Chlorine dioxide will only be of interest in indoor monitoring since is used for disinfection and cleaning. Hydrazine and ozone should not simultaneously exist in the atmosphere as Hydrazine reacts fast with ozone with a life time of 17-25 min. The NO is a reducing gas and the resistive sensors that measure NO usually are selective to NO₂ and O₃. Unfortunately they are not very selective to other reducing gases so the manufactures incorporate filters. This gas is also well measured by resistive and electrochemical sensors. The CO gas is fairly common and presents a persistent threat to health in a good number of environments. So manufactures have developed a wide range of sensors that detect this gas. The CO can be detected by resistive, electrochemical and optical sensors. The requirements are about 10 ppm. The CO₂ is another problematic gas that has been heavily regulated. This gas is usually measured in high concentrations and the NDIR shows a very good sensitivity and selectivity in that range so it is a sensor well suited for most of the applications. The Benzene is a hydrocarbon and while several sensors can detect it, they have very low selectivity to other hydrocarbon gases. For this gas the Photo Ionization sensors shows a very good response but they require a lot of maintenance. The NDIR sensors show a too high limit of detection, but some calibrations could be used to lower those limits. The Unitec Sens 3003 seems to achieve a much higher sensitivity to benzene than the rest of sensors putting it well inside the range of desired concentration (a few ppbs). The SO₂ is an emission regulated gas in European directive 1999/32/EC and 2001/81/EC (EC, 2012). This gas presents a problem for resistive metal oxide sensors leading to a poison of the surface that makes sensing this gas very difficult with that kind of sensors. The requirement of high sensitivity (0.03 - 0.15 ppm) puts the NDIR sensors in a very bad position, so the only sensors available to measure this gas are electrochemical. NH₃ is a gas regulated by the European directive 2001/81/EC. It is detected by electrochemical and resistive sensors, showing a good sensitivity, but as usual they have poor selectivity to other gases.

3. Conclusions

The resistive sensors tend to have the higher sensitivity, but have serious problems with reproducibility and stability making them unreliable on most of the applications. The electrochemical sensors are in general second on sensitivity and present better stability characteristics. The Infrared Gas Absorption

Spectra sensors are less sensitive and are not available for each target gas, but if they are able to detect the target gas in the range of interest, they are a very good option due to its stability and deterministic calibration. The photo ionization sensors are really sensitive, selective and reproducible, but they are only available to few gases and require a higher maintenance.

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