Détecteurs de gaz pour le contrôle des atmosphères toxiques et explosives dans l'industrie du gaz

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GAS SENSORS FOR CONTROLLING TOXIC AND EXPLOSIVE ATMOSPHERES

IN THE GAS INDUSTRY

DETECTEURS DE GAZ POUR LE CONTROLE DES ATMOSPHERES TOXIQUES

ET EXPLOSIVES DANS L'INDUSTRIE DU GAZ

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SUMMARY

Nowadays continuous survey of explosive and/or toxic atmospheres is easier thanks to sensors which are more reliable than before and less expensive than industrial analyzers. New technologies developments, like microprocessors, thin layers deposits and integrated optics will lead in the future to miniaturized instruments with high performances.

This text will introduce the state of the art in commercially available detectors and trends in new technology developments.

RESUME

La surveillance continue des atmosphères explosives et/ou toxiques est facilitée de nos jours par l'existence de capteurs fiables et d'un coût moins élevé que les analyseurs industriels. Les développements technologiques comme la micro-informatique, les dépôts en couches minces et l'optique intégrée vont permettre dans le futur d'obtenir des appareils miniaturisés très performants.

Le texte ici présent est une introduction à l'état de l'art en détecteurs du commerce, et aux tendances des nouveaux développements technologiques.

18e Congrès Mondial du Gaz, Berlin, 8-12 juillet 1991

INTRODUCTION

A gas sensor is a transducer which gives directly an information on gaseous composition of the surrounding atmosphere. It uses a selective chemical layer and a physical transducer. Originally well different from an analyzer which gives an information on gaseous composition trough a specific treatment, i.e. indirectly, the sensor becomes more and more similar to the analyzer due to its integration into a computerized multisensor system. The difference between those two elements remains then in the smaller size and the present lower precision of the sensor.
The qualities requested from the sensors are sensitivity, precision and reproducibility, specificity, immunity to interfering factors, short response time.
This review paper is a short description of sensors presently used for atmosphere control and of developments including new technologies and new materials.
Following subjects are developed : reactive tubes, reaction heat sensors, thermal conductivity sensors, semiconductors, electrochemical sensors, then new orientations, first ones yet commercially available (miniaturization, electronics addition), second ones still under development (new materials, new principles, new technologies).

1. COMMERCIAL SENSORS

1.1 Reactive Tubes

These detectors are now more than thirty years old, but they are still in use. They give a semi-quantitative measurement without any delay.
A holder, silica for example, is impregnated with a product. This product reacts irreversibly with the gas to be detected and gives a coloration. This holder is setted in a graduated glass tube : the sampling of a quantity of air to be analyzed is made with a pump, through the reactive tube. The coloured length depends on the gas concentration.
This method is quite selective, but some reactions may be interfered by components, like air humidity : so the tubes have a dessicating powder at the air inlet.
Because of temperature influence, precision is estimated to be 30 % relative. Response time is short because the reactions are fast : it depends on pumping rate. Storage life is limited ; high temperatures must be avoided. Easy maintenance and use, small cost make this method very convenient. It is used especially for gas leaks, pollutants emissions control and individual or collective survey of toxic gases like CO, CO_2, NO_x, SO_2, H_2S, O_2 deficiency.
Many accessories have improved their use : prolongator tubes for sampling, electrical pumps, automated reading ... Diffusion tubes allow survey of inhaled gas quantities, that is very useful for work hygiene.

1.2 Catalytic combustion sensors

These sensors are dedicated to combustible gases measurements ; all types of explosimeters are using them, wether portable instruments for the survey of gas leaks, or fixed instruments for plants watching.
Two types have been available on the market for thirty years : either a simple catalytic wire is used as a heater, reactor and measuring device, or a catalytic pellet is used as the reactor, a metallic wire heats it and is used as measuring device.
When the combustible gas oxidation takes place on the sensor, it causes a temperature rise of the sensor, which is measured by the rising of wire resistance.
Most used catalytic wire is a 80 microns diameter platinum wire. It was not very often used in gas industry until now because it had a short life time ; now it becomes a new interest thanks to the use of a new measuring method which gives it more than one year lifetime without important decrease in sensitivity. Its temperature (900 to 1 000 °C) gives it a good resistance to catalysts poisons like sulfur compounds.
Catalytic pellets have invaded the explosimetry market. They consist of a ceramic holder which is impregnated with a catalyst (platinum, palladium, rhodium ...) and heated by a platinum wire, up to 450-500 °C.

The sensitivity may be decreased by catalyst poisons like silicium, sulfur, lead, halogens ... That's why many studies have been made, especially in Great-Britain, about the pellet structure and resistance to poisoning has been well increased.
Metrological quality of explosimeters may be verified trough conformity to the new existing european standards, EN 50-054 to EN 50-055. The instruments have to be constructed in conformity with electrical security standards. Nowadays electrical consumption and working temperature are too high to permit an entirely intrinsically safe instrument.
Two drawbacks have to be mentioned : one is the response error in low oxygen concentrations (< 12 % v/v) ; another is the response ambiguity in high combustible gas concentrations : oxygen in not sufficient enough to ensure the complete combustion and so the reaction heat is equivalent to the one obtained in low gas concentrations.
This ambiguity can be avoided by different means, one is the use of a thermal conductivity sensor, as described in the next section.

1.3 Thermal conductivity sensors

To avoid the ambiguity of measurements previously mentioned, portable instruments are equipped with small non reactive heated beads ; their equilibrium temperature depends on thermal conductivity of the ambiant atmosphere. As before, this temperature is measured by a thermal heater resistance variation. Precision of these sensors is a few per cent of gas volume. The most precise measurements are for gases which have a very different thermal conductivity from air, for example hydrogen.
As before these sensors are calibrated for the gas which has to be measured. When more than two gases are present measurement is false.
These sensors are used for combustible gas leaks detection above LEL, for measurements of binary components, as chromatography detectors for example, and for some particular gases, like hydrogen, not measured by infrared technique, or carbon dioxide, if an infrared technique is too expensive for the application.

1.4 Semiconductor sensors

These sensors have been on the market for about 10 years, principally in Japan where they are used as gas leaks detectors in domestic appliances.
Made of a semiconductor metallic oxide, mostly SnO_2, they work on this simple way : a gas with oxygen, or a reducing gas is absorbed on the surface of the semiconductor and modifies the O_2-O_2 vacancies equilibrium. That changes the electrical resistance of the sensor ; this change depends on the gas concentration. The semiconductor is heated to obtain a reversible reaction. The choice of temperature is governed by the gas to be measured, this allows some selectivity : an H_2S sensor will work at 150 °C, a methane sensor at 500 °C.
Thanks to this sort of reaction, the sensors are adapted to many applications, from a few ppm of toxic gases to combustion surveillance, through fire detection or CO monitoring ... Drawbacks are the interferences of gases or vapors not to be detected, or humidity, from which false alarms occur. Studies are still necessary to get a better selectivity, reproducibility, especially for all the applications in security, for which reliability is the first criterion.

1.5 Electrochemical sensors

These sensors can be splitted into two types : those with solid electrolyte, those with a liquid one.
Solid electrolyte sensors now available on the market work at a very high temperature (> 600 °C). They use the change of the electrochemical potential at the solid-gas interface on a logarithmic way with gas concentrations : two different concentrations of gas face the two ends of the electrolyte, that gives a potential difference between them.
To get a better precision in high gas concentrations a current is forced to pass through the electrolyte, a linear response is then obtained. The best known sensor is the zirconia sensor to measure O_2 concentrations. There exist SO_2 sensors, but these use a O_2 sensor too, for taking into account the SO_2/SO_3 equilibrium.
Precision is good, lifetime too. To have a better response time a catalyst metal is placed at the gas-electrolyte interface, but it can create some errors in presence of reducing gases.

The sensors are used in combustion control, and in surveying the pollutants emissions of furnaces. Liquid electrolyte sensors grew very rapidly during the last years and are now currently used in individual or collective security, especially for monitoring CO, H_2S or O_2 deficiency.
O_2 sensors exist for about 15 years : a lead electrode is consumed by O_2 in air, through a liquid electrolyte before which a semipermeable membrane is placed. Oxidizing current is a direct measurement of O_2 concentration.
These sensors have a limited lifetime, depending on the consumption rate of the electrode. The temperature variations are easily compensated. Precision is about 1 % relative. Some gases can interfere, either modifying diffusion phenomena, or changing the electrolyte acidity ; CO_2 is such an interfering gas. Then other sensors were developped, which use O_2 as an oxidising agent, and the gas to be measured as a reducing agent. They allow measurement of 1 to 1 000 ppm gases, like CO, H_2S, NOx, SO_2 ... At the working electrode the gas diffuses trough the membrane and reduces the electrolyte ; the electrolyte is renewed through oxidation at the auxiliary electrode. Oxidoreduction current is a linear measurement of gas concentration.
To get better performances, specially to avoid the decrease of current through electrodes polarization, many sensors have 3 electrodes : a third electrode, the reference electrode, keeps the working electrode potential constant ; the current needed is then related to gas concentrations.
Lifetime is theoretically not limited, because of the use of oxygen present in air. In practice, they can live 1 to 3 years, depending on the ambiant conditions.
Electrical current is about 0.1 microamps per ppm gas : the sensors are intrinsically safe. Because of high impedances of electrolytes and membranes, manufacturers have to pay attention to electromagnetic immunity.
Response time depends on gas : 20 to 30 seconds for CO, it can be one and a half minute for H_2S, because these molecule diffuse slowly through the semipermeable membrane.

1.6 Conclusion

A great diversity of sensors exist on the market. Drawbacks depend on use. Advantage is always the lower price than analyzers. Through the years they improve on reliability and reproducibility thanks to quality monitoring in manufactures.

2. NEW ORIENTATIONS

2.1 New developments to be commercialized

Miniaturization of electronics and optics, microprocessors invention make the sensors extra rising and permit new sensors types to appear :
used for a long time only in analyzing field, optical sensors now enter in the sensor field. So are optical explosimeters, which are miniaturized open path infrared analyzers. Their response time, with mechanical protective parts, is still long ; their precision is not as high as that of catalytic combustion sensors, but they don't suffer from poisoning.
Microprocessors allow real time correlation of different sensors signals, and interferences corrections. So are portable combustion controllers using electrochemical sensors for O_2, CO, NO_x and SO_2 measurements. Precision is now not sufficient enough because interfering coefficients are changing for one sensor to another, creating about 20 % deviation between the real and calculated values.

2.2 New developments in laboratories

New technologies, new materials, new principles are the ferments of a great diversity of research in gas sensors field.
New materials are for example semiconductors like metallic phtalocyanines, solid electrolytes working at the ambiant temperature.
New principles are field effect transistors, piezoelectricity, surface acoustic devices. For all these principles a membrane adsorbs, with some selectivity, a gas which modifies the properties of the microelectronic device on which it is deposited.

To get those sensors being commercially acceptable, the membranes have to make progresses in selectivity and humidity immunity.
New technologies are integrated optics and optical fibers, microelectronics and thin layers, which allow great decrease in electrical consumption and mass production at a reduced cost. Finally, the advent of microprocessor would make the developments moving towards the gas identification through real-time signals treatments.
Further, the miniaturization of electronics allow measurement and treatment technologies to merge through conditionning on a same sensor, signal processing and the sensor itself. Advantages are a better signal-to-noise ratio, thanks to on-site amplifiing, the increase of caracteristics performances (correction of linearity, pressure, temperature, increase of frequency response), signal conditionning well adapted to chosen digital transmission (AD conversion, in situ impedance change, output formating, mean values calculations).

Conclusion

This short review gives an idea of the multidisciplinarity of gas sensor science : solid physicists, mechanical, electrochemical, electronical, optical, spectroscopical, catalyst or membrane chemical engineers, all are working for sensors development.
In all the sciences for sensors, like electrochemistry with its rapid growth, optics with its youth as a sensors science, science of heat, nowadays underestimated, we are going in the direction of miniaturization and integration.

Sensor type	Main advantages	Drawbacks	Utilization
Reactive tubes	reduced cost low maintenance real time result	unique use - semi quantitative	gas leak detection - toxic atospheres surveillance
Catalytic Combustion	reduced price good accuracy	poisoning susceptibility - measurement ambiguity at high concentrations - need of a reference sensor	explosimetry
Thermal conductivity	reduced cost can be very precise	need of a reference sensor	gas leak detection - chromatography detector - binary component mixture analysis
Semiconductor	reduced cost long lifetime	false alarms because of interferences - sensitive to humidity	gas leak detection - fire detection combustion surveillance toxic and combustible gases detection
Solid Electrolyte	specificity - Good lifetime can be miniaturized precise to low concentrations	falses measurements in presence of combustible gases - need of a reference non-linear	combustion control (O_2 measurement)
Liquid Electrolyte	intrinsically safe no sensitivity to humidity	limited lifetime (2 years) not always specific	toxic gas detection - O_2 deficiency detection - individual or collective surveillance

Fig. Main sensors used in gas industry