DEFINITION

Pellistor poisoning is the process by which the response of the sensor to the target gas is reduced because of the presence of certain gases/vapours. These species react with the catalyst surface and reduce its capacity to oxidise the target gas, also known as its catalytic activity. These species can be categorised depending on the degree of reversibility of the effect.

Poisons

Compounds in which the effect is irreversible are known as poisons. Typical poisons are organic silicon compounds, organo-metallic compounds and organic phosphate esters. Pellistor sensors which are not designed to have some resistance to poisons (these are usually non-porous) can lose over 90% of their response to methane within a few minutes when exposed to as little as 10 ppm of an organic silicon compound.

Inhibitors

Compounds are classed as Inhibitors if the pellistor response recovers when the compound is removed. Typical inhibitors are halogen-containing hydrocarbons. Compounds containing sulfur, e.g. H_2S, can show both tendencies depending on the concentration and the exposure time. The degree of poison resistance and the rate of recovery have been found to increase with the operating temperature of the sensor.

MECHANISM OF POISONING

The difference between the two compound types is related to the way in which they adsorb on the catalyst surface and what compounds are then produced. For both types, the catalytic activity is reduced because the poison or inhibitor adsorbs more strongly onto the catalyst surface than the target gas, this adsorption stage being critical to the overall reaction. The number of available catalytic sites are therefore reduced or covered, causing a decrease in the rate of the reaction with the target gas.

In the case of the inhibitor, the process reaches equilibrium, which is dependent on a function of the temperature and the concentration of inhibitor concentration. Once the inhibitor is removed, the molecules of inhibitor adsorbed on the surface are desorbed and the sites are then available for reaction with the target gas and the catalytic activity and signal are restored.

In the case of a poison, no equilibrium is set up and the reaction with the catalytic site is not reversible. Coverage of the sites increases and in theory the response can be reduced to zero irrespective of the concentration of the poisoning species. The time taken for this to happen will depend on the concentration.

It should be noted that the degree of signal loss is also dependant on the target gas. For methane, the oxidation reaction can only take place on the catalytic sites with the highest activity. Therefore it is the methane signal that is most affected by poisoning and inhibition. Organic silicon compounds in particular can react on these sites to form a layer of silica-type compounds. The effect of the presence of poisons on the response to gases that are easier to oxidise, e.g. butane, is much less than that for methane. It is not unknown for pellistors that have lost nearly all of their response to methane due to silicon poisoning to have a virtually unchanged response to butane.

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METHODS TO REDUCE POISONING EFFECTS

1) Limitation of Diffusion Rate

The rate of poisoning is related to the rate of diffusion of the poisoning species to the detecting element. Thus if the rate of diffusion is slowed down, the effect will decrease. This can be achieved by either fitting a fine sinter or mesh in front of the detecting element, or by fitting a can with a small hole above the detecting element. This will improve the degree of resistance to poisons, but the target gas signal itself will fall as its rate of diffusion to the detecting element is reduced. However, any improvement will not be substantial.

2) Filters

There are several commercial types of filter capable of removing pellistor poisons. The majority are types of activated carbon. These compounds have a large absorption capacity but have the drawback that if the structure is too fine, the flow of gas into the sensor is reduced and the time of response to the target gas will increase. Open-weave carbon cloths offer a compromise between absorption capacity and response time. One significant problem with this type of filter is that hydrocarbons above C_4 are partially or totally absorbed, thereby limiting the use of the sensor to applications such as coal mining, where these types of compounds are not likely to be present.

3) Detecting Bead Design

A major method of increasing the resistance to poisons is to increase the intrinsic catalytic of the bead by increasing the number of sites. This is most easily done by simply increasing the size of the detecting element and it is noticeable, even in the case of pellistors which are not designed to be resistant to poisons, that larger beads have much more resistance than smaller beads. However, solely increasing the bead size is not an option for low power sensors for portable instruments. In this case the increase in the number of catalytic sites is brought about by making the bead porous and diffusing the catalyst site throughout the pores. The overall size and power requirements of the small bead are retained. The porous structure has another property of restricting the access of high molecular weight poisons to the catalytic sites whilst still allowing the reactant and product gases to diffuse in and out of the pores.

Low power pellistors made using these techniques improve the time taken to lose 10% of the sensor output in 20 ppm of silicon from several seconds to approximately an hour. In the case of larger high power sensors, this can be increased to over 10 hours.

NOTES FOR INSTRUMENT MANUFACTURERS

A large number of pellistor sensors are used in portable gas detection instruments. In this application, the sensor is located in intimate contact with components of the instrument. Care must be taken in the choice of materials used in the instrument in that they must not contain compounds that can desorb and act as pellistor poisons. Problems have been found in the past with parts such as seals, conformal coatings and displays. It is recommended that all parts of the design be tested prior to the instrument being put into production.