

## Cross-sensitivity compensation in electrochemical gas sensors.



### Introduction

The reliability and accuracy of Testo emission measurement technology has earned it a very good reputation among customers worldwide. Typical applications are the adjustment and monitoring of heating systems as well as measurements on combined heat and power plants, engines or turbines. Depending on the fuel and the plant settings, the gas matrix in these jobs is fairly well known.

In addition to this however, emission measuring instruments from Testo are used for monitoring the most diverse processes in which the gas composition can vary considerably. This white paper concerns itself with the issue of the possible cross-sensitivity of gases occurring here, and how to deal with it.



Fig. 1: Electrochemical gas sensors in the measuring instrument testo 340

### Cross-sensitivities in gas sensors

The term cross-sensitivity describes the fact that a sensor reacts not only to the target parameter, but also to other influencing parameters. To put it another way: A sensor with cross-sensitivity does not possess perfect selectivity. This is especially challenging for gas sensors, as the measurement of a specific gas concentration should ideally be possible in a gas matrix of any complexity – with hundreds of gases and vapours potentially interfering with the selectivity. It is therefore not surprising that almost all measurement principles used in gas sensors show a cross-sensitivity to accompanying gases. For example, paramagnetic measuring instruments for oxygen also react to nitrogen dioxide, and ammonia and carbon dioxide act as interfering parameters in chemiluminescent methods for the determination of nitrogen oxides. The electrochemical gas sensors as used in Testo measuring instruments are also not free from cross-sensitivities.

### Cross-sensitivities in electrochemical gas sensors and compensation strategies

The functional principle of an electrochemical gas sensor is explained in the diagram in Fig. 2.

The gas to be measured, for example carbon monoxide (CO), must pass through a diffusion barrier (a capillary or membrane), and in the case of some sensor types a chemical filter, and then reaches the so-called working electrode. This “floats” in an electrolyte, i. e. in an acidic or alkaline, aqueous solution. The gas molecule triggers a chemical reaction at the working electrode and ions, for example protons ( $H^+$ ), are formed, which reach the counter-electrode, where they react with the oxygen present as a solution in the electrolyte. At the same time, an electrical current is created which is diverted to an external circuit and serves as a measure of the gas concentration present. The third electrode (reference electrode) is used to stabilize the sensor signal.

In order for these chemical reactions to take place at the electrodes, they must contain a noble metal (e.g. platinum) as a catalyst. The choice of suitable catalyst materials for electrodes is limited, and the corresponding materials demonstrate their catalytic effects with different gases. By mixing different catalysts, the selectivity over a specific gas can be increased. However, it is unavoidable that electrochemical gas sensors show cross-sensitivities. A platinum electrode, for example, possesses a high catalytic activity and in a gas sensor for CO filled with aqueous, diluted sulphuric acid, will also demonstrate the cross-gases NO, NO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>.

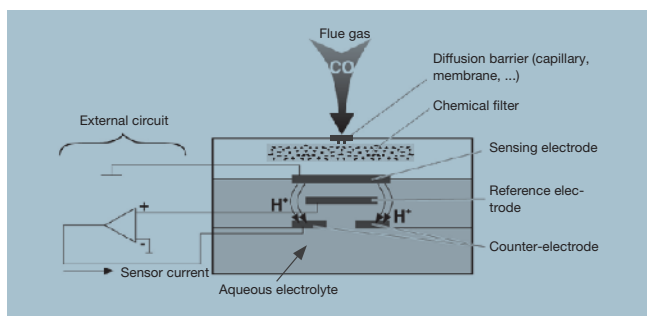


Fig. 2: Electrochemical sensor for CO and other gases (schematic representation)

So how then can these undesired cross-sensitivities in gas sensors and gas measuring instruments be minimized, in order to achieve a reliable and accurate display of gas concentration even in unknown and complex gas mixtures? Various strategies come into play:

### Catalyst materials

The most important approach is, as already mentioned, a targeted selection of catalyst materials and mixtures for the electrode and of the correspondingly suitable electrolyte. All in all, the technology in commercially available electrochemical gas sensors has reached a well developed level. In detail however, further progress can be achieved. As an example, a newly available, CO-insensitive SO<sub>2</sub> sensor is described on page 5.

### Bias voltage

The selection of a suitable bias voltage for the working electrode can also lead to an improvement of the selectivity. This method is used, for example, in NO sensors. The working electrode uses graphite as a catalyst material, and an additional bias voltage of 300 mV over the reference electrode, which is also integrated into the sensor. Here too, aqueous sulphuric acid is used as an electrolyte. The electrochemical potential of this system allows it to demonstrate NO – however not, or at least hardly, the accompanying gases NO<sub>2</sub> and CO, which gives electrochemical gas sensors a comparatively high level of selectivity.

### Filters

Many electrochemical gas sensors use chemical filters against cross-influences. In order to fulfil the filter function, the filter material must retain the the interfering accompanying gases while allowing the target gas to permeate unhindered. This can be achieved when the target gas tends to be slow to react and the interfering accompanying gases tend to be reactive. The electrochemical gas sensor for CO is used here as an example. A filter material based on potassium permanganate absorbs and binds the cross-gases NO, NO<sub>2</sub> and SO<sub>2</sub> and allows CO as well as the cross-gas H<sub>2</sub> to permeate unhindered. In doing so, the material is used up. For this reason, the filter component is usually positioned after the diffusion barrier which controls and limits the access of gas to the sensor. This means that only a small part of the gas which surrounds the sensor or is transported to it for the measurement must be filtered. The advantage of this absorbent filter is its high level of effec-

tiveness. The disadvantage that not only capacity but also lifetime are limited, should be noted.

The challenge increases when the target gas tends to be reactive and the interfering accompanying gases tend to be slow to react. There are only a few effective filter media for this combination. In SO<sub>2</sub> sensors, silver sulphate is used as a filter medium for H<sub>2</sub>S and HCl. In NO sensors, silver oxide is used, which retains SO<sub>2</sub>. In this case, the mechanism is a little different to the absorbent filters described above: The cross-gas is adsorbed onto the filter medium, i.e. deposited on its surface. This is a physical process which depends on the ambient temperature and the concentration of the cross-gas in relation to the available surface area of the filter material. A sudden increase in the ambient temperature, for example, can dissolve the adsorption adhesion, allowing the cross-gas to separate from the filter and trigger an interference signal at the working electrode. A positive effect of this adsorptive procedure is the possibility of filter regeneration when a cross-gas is no longer present in the surroundings, and is slowly released again from the filter due to the concentration gradient. The filter capacity is therefore more variable than in the case of the absorbent chemical filters.

### CO sensor with H<sub>2</sub> compensation

As a special case among electrochemical gas sensors, the CO sensor with H<sub>2</sub> compensation should also be described: Hydrogen is demonstrated similarly well at platinum electrodes in aqueous sulphuric acid as carbon monoxide and, just like CO, it cannot be chemically or physically retained in a filter. However, one can utilize the high level of mobility of this very small molecule by installing a further auxiliary electrode of the same design as the working electrode and positioned behind it in a CO sensor. Due to the differing mobilities of the two molecules, a meaningful quantity reaches this electrode only for H<sub>2</sub> and triggers a signal, while CO is already almost completely transferred at the working electrode. The differing sensitivities of these two electrodes to the two gases make it possible to distinguish which of the two gases is present in which concentration, allowing compensation for the influence of H<sub>2</sub> in the CO measurement.

In contrast to the classical cross-sensitivity described above, a different effect is to be observed in electrochemical O<sub>2</sub> sensors: Carbon dioxide as an accompanying gas does not trigger a chemical reaction at the working electrode, however as an acidic gas it is drawn by the alkaline electrolytes, thus influencing the controlled access of O<sub>2</sub> into the sensor. This interference in the detection of the target gas by a cross-gas is also known from other measurement principles, and is referred to as quenching.

In summary, one can establish that cross-sensitivities can be avoided or minimized by various strategies (choice of electrode material, selection of bias voltage, filters, compensation using auxiliary electrode). In some types of sensor, a residual cross-sensitivity remains. Its potential influence must be taken into account when a gas matrix with an unknown composition is to be analyzed.

#### Compensation of cross-sensitivities

The cross-sensitivity can be compensated for display in a measuring instrument. The prerequisite for this is that the concentration of the interfering gas is measured separately. And for a precise compensation, the exact cross-sensitivity value should be known and used.

For example, a typical electrochemical NO sensor also reacts to NO<sub>2</sub> with a cross-sensitivity of approximately 5 %. This means that the signal response to NO<sub>2</sub> is only approximately 5 % or one twentieth as large as to NO. If, for example, 100 ppm NO and 100 ppm NO<sub>2</sub> are equally present, the sensor produces the same signal as for 105 ppm NO. If NO<sub>2</sub> is measured separately at 100 ppm, the calculated 5 ppm can be subtracted for the NO reading, so that the correct value of 100 ppm is shown.

Similarly, the quenching influence of CO<sub>2</sub> described above can be subsequently compensated against the O<sub>2</sub> reading, as long as the CO<sub>2</sub> concentration is known. In the Testo flue gas measuring instruments without separate CO<sub>2</sub> measurement, this compensation works with a CO<sub>2</sub> value calculated from the fuel selection.

As a leading manufacturer of portable measuring instruments for gas analysis, Testo states in the instruments' instruction manuals the cross-sensitivities of the installed electrochemical gas sensors to numerous potential interfering gases, as well as the cross-sensitivities between the individual sensor types implemented in the measuring

instruments. This allows the Testo customer to estimate for his special application whether, and for which measurement parameter, a cross-influence must be taken into account.

#### Peculiarities of gas measuring instruments and gas sensors from Testo

Characteristic for Testo gas measuring instruments are the electrochemical gas sensors in exclusive Testo design installed in them (see Fig. 1). They were developed specially for the applications and requirements of Testo's customers. In addition to other unique features, the Testo sensors have excellent working lifetimes with regard to their component filters, and some also have the option of exchanging filter elements. This reduces or eliminates the risk that a complete sensor, in which only the filter is used up, needs to be replaced (see Fig. 3).

With regard to the compensation of cross-sensitivities, a great deal of effort is invested in the correct adjustment of the cross-sensitivity values during the works adjustment of the exclusive Testo sensors. Apart from this, the testo EasyEmission software can be used to allow the user to re-adjust the cross-sensitivities himself.



Fig. 3: Exclusive Testo sensor with exchangeable filter

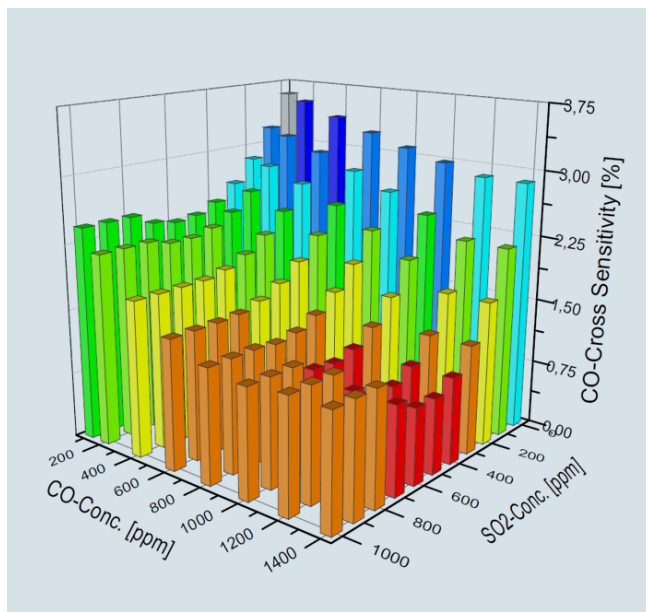


Fig. 4: CO cross-sensitivity of an SO<sub>2</sub> sensor dependent on the CO and SO<sub>2</sub> concentration

In the case of some cross-sensitivities, complex compensation algorithms are used which take concentration and temperature dependencies into consideration. As an example, Fig. 4 shows the cross-sensitivity of an SO<sub>2</sub> sensor to CO, and how it changes depending on the SO<sub>2</sub> and CO concentrations. The exclusive Testo SO<sub>2</sub> sensor compensates this complex '2-dimensional' influence with a set of 16 individual coefficients.

#### Limits to the compensation of cross-sensitivities

Electrochemical SO<sub>2</sub> and H<sub>2</sub>S sensors demonstrate cross-sensitivities to a comparatively high number of gases. Most of these influences can be subsequently compensated. If the gas matrix being analyzed is unknown as regards expected cross-concentrations, care should be taken in the evaluation of the measurement result, especially for these measurement parameters, and the possibility of an influence by a cross-gas should be checked.

A special challenge is when a comparatively small target gas concentration is to be measured in front of a very high background concentration of an interfering cross-gas – even if a subsequent compensation takes place. In addition to this, in very high cross-concentrations, the chemical filters described above can be overloaded, leading to a breakthrough of the cross-gas through the filter and to a sudden increase of the measurement value reading.

If a cross-compensation for a measurement parameter takes place in a Testo measuring instrument, its effectiveness can be experimentally checked by bridging the second sensor, which measures the cross-concentration, in the gas path. The first sensor now shows the concentration of its target gas and the uncompensated influence of the cross-gas.

Particular care is appropriate with electrochemical sensors when dealing with non-saturated hydrocarbon bonds. This class of substances includes many solvents and cleaning materials such as acetone and alcohols. If electrochemical gas sensors are exposed to these vapours over longer periods, in particular during storage, they can be irreversibly damaged. Their resting signal is drastically increased and their sensitivity and response time to the target gas considerably lowered. Sensors which have been damaged this way must be replaced.

#### Success in the further development of the SO<sub>2</sub> sensor.

In Fig. 4 one can see that a concentration-dependent cross-sensitivity of the SO<sub>2</sub> sensor to CO exists, and how it is compensated. However, there are gas analysis applications in which the CO concentration is several times higher than the SO<sub>2</sub> concentration. For example, in steel manufacturing, a typical SO<sub>2</sub> concentration of some 10 ppm must be measured in front of a CO background of 10,000 ppm and more. In spite of the actually small cross-sensitivity against CO, the signal of the electrochemical SO<sub>2</sub> sensor is dominated by the CO component in the gas matrix, and the compensation is pushed to its limit despite the complex compensation algorithm.

The Chinese environmental authority EPD has recognized this weakness and tightened the guideline for the approval of gas measuring instruments with electrochemical gas sensors for China. The norm HJ 57 states that instruments must prove their suitability by being exposed to a gas mixture of SO<sub>2</sub> and CO with respectively increasing concentrations, and the SO<sub>2</sub> reading must correspond to the applied SO<sub>2</sub> concentration within prescribed limits.

Testo is the first measuring instrument manufacturer to react to this changed normative situation in China. In collaboration with a worldwide leading manufacturer of electrochemical gas sensors, an SO<sub>2</sub> sensor has been developed whose CO cross-sensitivity is reduced to an absolute minimum of approx. 0.1 %, and therefore to around 1/20th of the previously typical value. This was achieved by adapting the catalyst mixture for the working electrode. In this SO<sub>2</sub> sensor with the type designation TSCi, the CO cross-sensitivity is no longer significant in most applications. In extreme applications with a very high CO background, a weak reaction to CO can still be observed, which for the SO<sub>2</sub> reading in the Testo measuring instrument is compensated to a value close to zero by the simultaneous measurement of the CO concentration and subsequent calculated compensation. The measurement accuracies required by the Chinese norm HJ 57 are complied with by the new exclusive Testo TSCi SO<sub>2</sub> sensor.

The performance capability of this sensor is demonstrated in Fig. 5a, 5b and 5c. They present the response of a typical TSCi sensor to SO<sub>2</sub> and to increasing CO concentrations up to over 20,000 ppm before and after the CO compensation. The SO<sub>2</sub> measurement is fast and accurate, the CO cross-sensitivity is present but so slight that it is only identifiable at closer inspection (Fig. 5b). The respectively applied very high CO concentration must be measured for the compensation of the CO influence. In this case, Testo is able to score specially with the measuring instrument testo 350 with the optional measuring range extension by controlled dilution in a separate gas path for the CO sensor. Fig. 5c presents the result of the CO compensation. The small peaks in the SO<sub>2</sub> reading just after the change in the applied CO value result from the slightly different response speeds of the two participant sensors. After approximately 30 seconds, a stationary status is reached in which the CO influence on the SO<sub>2</sub> reading is compensated with an accuracy of approximately ±1 ppm SO<sub>2</sub> – and this is in a influence range of over 20,000 ppm CO.

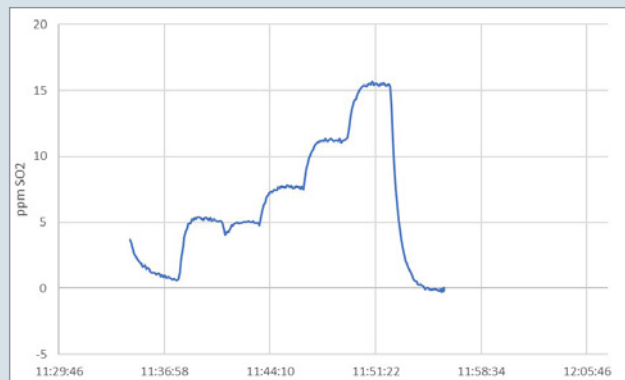
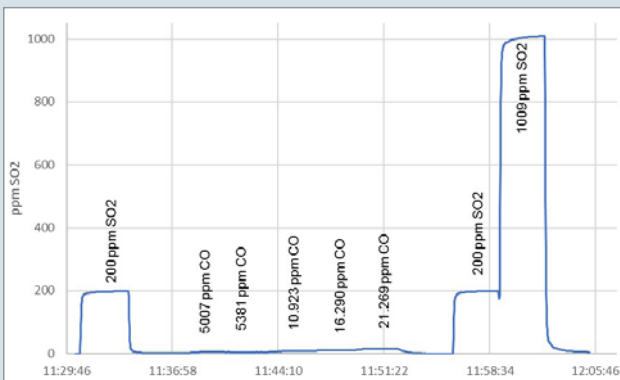


Fig. 5a/b: Response of a CO-insensitive SO<sub>2</sub> sensor TSCi to SO<sub>2</sub> and CO (uncompensated)



Fig. 5c: The SO<sub>2</sub> reading from the same measurement after CO compensation



**Conclusion**

The technology in electrochemical gas sensors has long reached a well-developed level. These sensors allow accurate and reliable measurements to be taken even in demanding applications. Influences from cross-sensitivities cannot be fully eliminated, and must be taken into account in particular in special circumstances such as the measurement of process gases or in the case of very high cross-concentrations.

Testo trusts in this sensor technology and ensures that the sensors in exclusive Testo design fitted in Testo gas measuring instruments are best equipped against cross-influences.

**More information:**

For more information on the topic of emission measurement from our experts at [www.testo.com](http://www.testo.com).

Subject to change, including technical modifications.

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