Humidity Extremes: Drying Out and Water Absorption

Alphasense electrochemical toxic gas sensors are low power devices with excellent resolution, dynamic range and selectivity. These electrochemical cells contain sulfuric acid electrolyte for ionic transport. See Application Note AAN 0104 for an explanation of their operation.

This aqueous acid electrolyte will lose water in low humidities and gain water in high humidities. This Application Note explains why Alphasense toxic gas sensors are specified to operate in the humidity range of 15 to 90% rh and describes sensor performance after drying out or absorbing water.

The Thermodynamics

Mixtures of water and sulfuric acid have been used for decades to generate a known water vapour pressure, also called the "equilibrium relative humidity" (erh). As the sulfuric acid concentration increases the water vapour pressure over the liquid mixture decreases, eventually reaching zero percent rh in concentrated sulfuric acid. Figure 1 below shows how the equilibrium relative humidity decreases as the sulfuric acid concentration increases. The erh is only slightly dependent on the temperature, as Figure 1 shows.

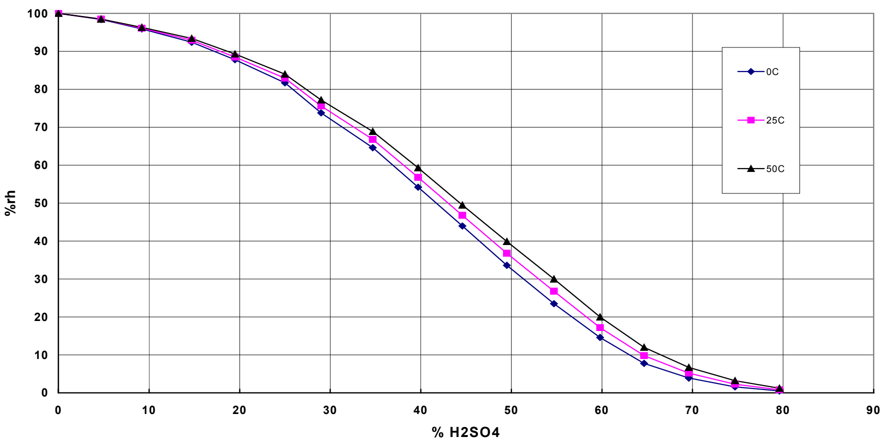

Figure 1. Equilibrium relative humidity (erh) of sulfuric acid and water mixtures.

Alphasense toxic gas sensors start out with a concentration of 5 M sulfuric acid corresponding to 60% equilibrium relative humidity at 20°C. If you expose a gas sensor to humidity less than 60% rh then this relative humidity difference will force the sensor to lose water by evaporation. Likewise, if you place the sensor in humidity above 60% rh then the sensor will absorb water.

In dry atmospheres the water/sulfuric acid electrolyte will lose water and become more concentrated so the electrolyte erh will decrease and eventually equal the relative humidity of its environment. The sensor stabilises to its local relative humidity environment.

Conversely, in very high humidities the electrolyte will absorb water and increase its erh. The danger is that if it absorbs too much water then the sensor cannot contain the extra electrolyte which can sometimes be two or three times the initial electrolyte volume, causing sensor leakage.

Figure 2 shows how an H2S-A1 sensor loses weight in low humidities and gains weight in high humidities at 20C.

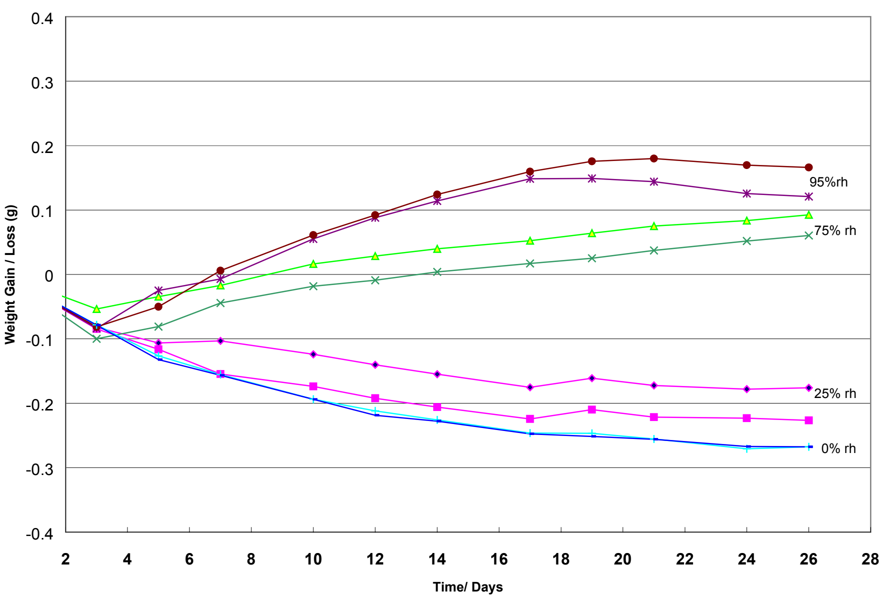

Figure 2. Sensor weight gain/ loss when subjected to humidity extremes.

The Kinetics

How fast does this happen? Figure 3 shows the rate of weight loss (i.e. water loss from the electrolyte) for an H2S-A1 sensor for 50 days when exposed to 0%rh air at 20°C. The sensor reaches a stable weight after 25 to 30 days. Note that sensors with larger gas diffusion holes reach their equilibrium weight in only 10 days while sensors with smaller holes take much longer. The rate of water loss is proportional to the hole area (not hole diameter). Note that sensors with large diffusion holes have high nA/ ppm sensitivity (i.e. are high resolution sensors) and sensors with small diffusion holes have lower nA/ppm sensitivity, with high range and lower sensitivity.

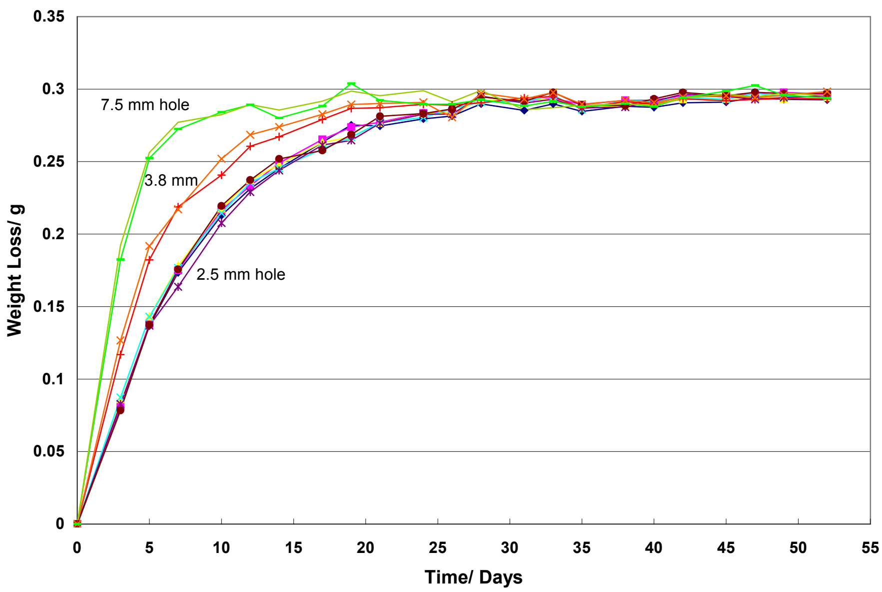

Figure 3. Weight loss for Alphasense H2S-A sensors in 0% rh. Increasing hole size speeds up water loss rate.

What else influences the rate of water loss or water absorption?

- Temperature affects the rate of water loss. At higher temperatures water evaporates or absorbs faster.
- Hole size influences the rate of water loss. Sensors with high range and low sensitivity will dry out slower because they have a smaller gas diffusion barrier hole.
- Rate of airflow across the sensor does not affect the rate of water/water gain.
- Sensors with chemical filters lose or gain water at the same rate as sensors without chemical filters.

Weight loss and weight gains are reversible: if you allow a sensor to stabilise in very dry air, then it will regain weight when you place it back in a moist environment.

Performance Changes

Alphasense Technical Group has studied the effects of water loss and gain on sensor performance.

Water Absorption

Sensor performance does not change as the sensor absorbs water. The sensor will appear to be normal with standard response time, sensitivity and zero current, but if it continues to absorb water above 90% rh then the sensor will leak – this is associated with either a large reduction in sensitivity or a very high zero current. In these cases the sensor has been used outside of warranted performance.

Performance Change During Dehydration

Dehydration is a more common problem. This complex problem has been modelled and the effects are mostly understood. During dehydration the sensor goes through two, possibly three mechanisms of water loss.

1. In the first 5 to 20 days the sensor rapidly loses water by evaporation.
2. Eventually the sensor has lost enough water that the equilibrium relative humdity approaches the ambient relative humidity and the sensor remains stable. If the sensor is used within rh specification then the sensor performance is stable and the instrument/ detector should be recalibrated at the ambient rh where it will remain stable.
3. If the sensor is used in atmospheres less than 15% rh (see Figure 7 below) the electrolyte cannot dehydrate to match the ambient relative humidity and will continue to lose water until there is inadequate electrolyte to transport ions between the electrodes– this sensor will fail, although it can be recovered by storing in a moist atmosphere (less than 90% rh).

Figures 4, 5, 6 and 7 show the response time (t_{90}) and sensitivity for CO and H_2S sensors.

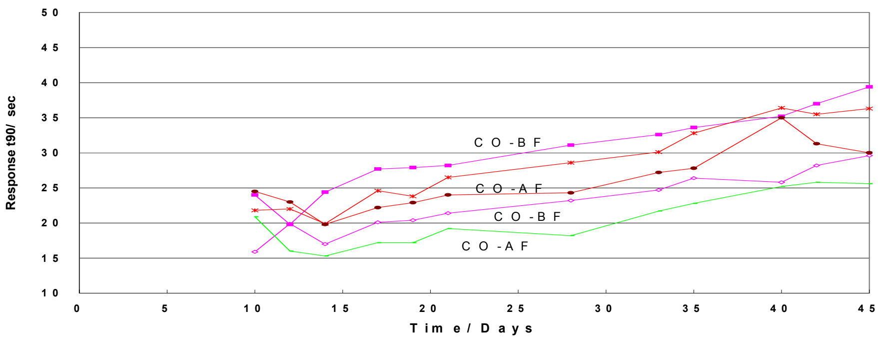

Figure 4. Increasing response time of CO sensors when losing water at low rh.

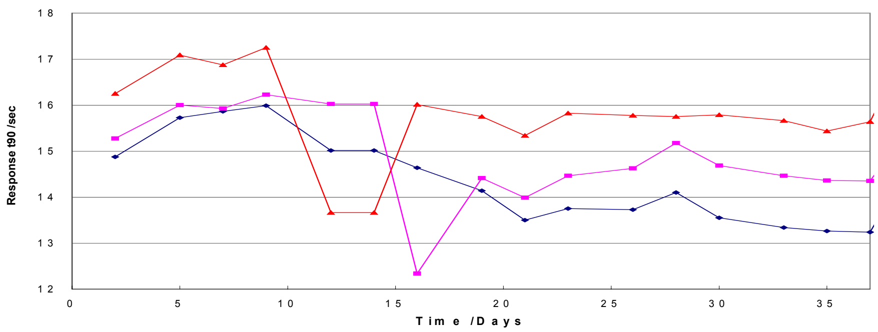

Figure 5. Response time (t_{90}) stays constant for H_2S sensors when losing water at 0% rh.

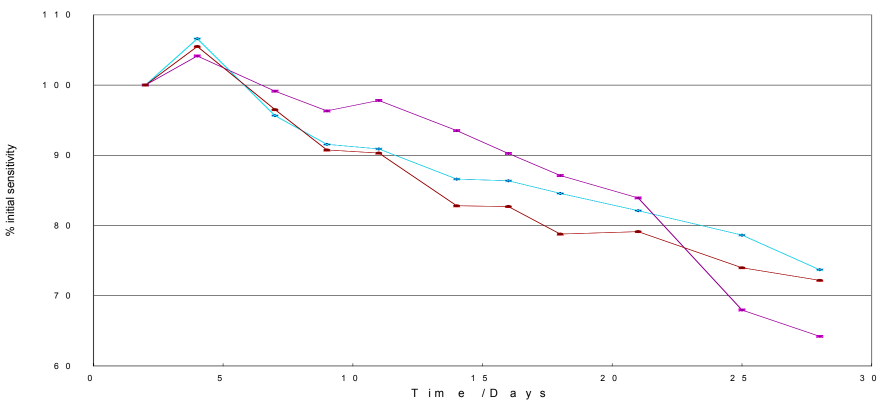

Figure 6. Sensitivity for CO sensors remains constant during dehydration at 0%rh.

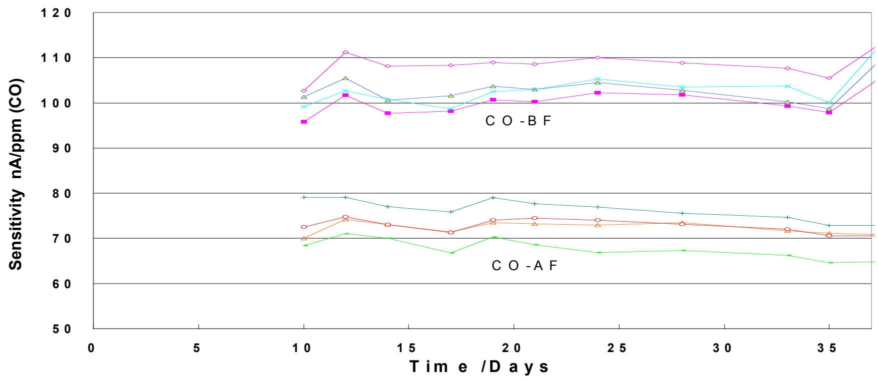

Figure 7. Sensitivity decreases for H_2S sensors during phase 1 when dehydrated at 0%rh.

The critical points to note about these graphs are:

- CO sensor sensitivity is stable during both phases 1 and 2 of dehydration.
- H_2S sensitivity decreases during phase one of dehydration but stabilises during phase two.
- CO sensor response time increases from typically 20-25 seconds to 30-40 seconds during stage one but will eventually stabilise if the humidity is greater than 15% rh. H2S sensors appear not to change their response time even during drying out.

Other properties such as noise and zero current are not affected by dehydration or water absorption.

Recovery

If a sensor has been exposed for a long period to an ambient humidity significantly different than the equilibrium relative humidity of about 60% rh then its properties may change. However, this is reversible and if exposed to a high humidity after dehydration or a low humidity after water adsorption, then the sensor will return to its original state. Operation for extended periods outside the 15-90% rh range will invalidate the warranty.

Figure 8 shows a group of CO-AF sensors increasing their weight after being dehydrated for a long period at low humidity. The rate of water absorption after dehydration is at about the same rate as the rate of water loss during dehydration.

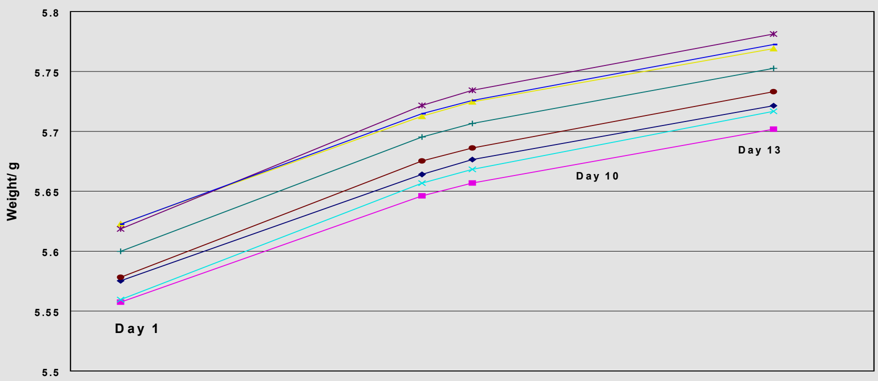

Figure 8. Weight gain of CO-AF sensors during rehydration after dehydration at 0%rh.

Failure Analysis

A simple way to check for excessive dehydration or water absorption is to weigh the sensor. Although each sensor is not weighed by Alphasense, we weigh a sample of every sensor batch and can tell you the mean batch weight when manufactured. If the sensor weight is more than ±250 mg from the original weight then the sensor will either show performance change if dried out or potential leakage if used in high humidities. Contact Alphasense Technical Sales for batch weights.

Case Cracking in Extreme Conditions

The polymer used in Alphasense toxic sensors is polycarbonate. This engineering plastic shows excellent strength and impact resistance, but if the sensors are exposed to temperatures below -30C, then cracking may occur. This is outside the specified environmental conditions; contact Alphasense if you suspect that your sensor has been exposed to temperature and humidity extremes, outside of the specified ranges.

Conclusions

- Toxic gas sensors will lose weight (dehydrate) or gain weight when exposed to humidities significantly away from the equilibrium relative humidity of 60% rh.
- Sensors absorbing water at high humidities (>90% rh) for long periods may leak.
- Sensors exposed to humidities greater than 15% rh but less than 60% rh will lose water but then stabilise within 5 to 25 days, depending on the sensor type and ambient temperature.
- When CO sensors dehydrate, the sensitivity remains constant but the response time slows.
- When H2S sensors dehydrate, the sensitivity initially decreases before stabilising but the response time remains constant.
- Sensors that have dehydrated will gain water and return to their original performance if stored in a high humidity (<90% rh) environment for 5 to 25 days.
- Sensors that have gained water but have not leaked (between 60% and 90% rh) will lose water when exposed to a low humidity (between 15% and 60% rh) environment.
- Short-term excursions into very low or very high humidities are permissible. Figure 3 shows the rate that sensors lose water when exposed to zero relative humidity.
- If a sensor is exposed to a long-term ambient relative humidity far away from 60%rh, then allow the sensor to stabilise for about 25 to 30 days, then check calibration.