

Technical Note - TN02 Using Zirconia Oxygen Analysers to Measure the Dewpoint of Furnace Atmospheres

A Zirconia Oxygen Analyser will measure dewpoint only under certain conditions. They are, that the gas to be measured: 1) Contains a known amount of hydrogen: 2) The balance of the gas is either nitrogen or inert. So it works in pure hydrogen, cracked ammonia, and hydrogen/argon or hydrogen/ helium mixtures; not in carburising gases which also contain CO/CO2, although very useful measurements can be made in these atmospheres too - see Technical Note TN03.



To appreciate the advantages of applying Hitech zirconia oxygen analysers to furnace atmospheres it is useful to understand why the dewpoint of such atmospheres is measured. The measurement of the dewpoint of a gas is really just a way of measuring its water content. This is important because too much water in the furnace atmosphere will spoil the work going through it; not because of the water itself, but because at the high temperatures within a furnace it dissociates into hydrogen and oxygen. This is illustrated by the following chemical equation:

$$2H_2O = 2H_2 + O_2$$

It is the oxygen that then reacts with the work in the furnace causing staining or scaling. At any given temperature the ratio

$$\frac{p^{2}[H_{2}] \times p[O_{2}]}{p^{2}[H_{2}O]}$$

is a constant. (p is the concentration or activity of the reactant in the bracket). Similar equations can be written to describe a metal in equilibrium with oxygen. The values of the constants are well defined by standard data. In fact what is happening inside the furnace is a kind of competition between the contents, say iron and hydrogen, for the oxygen. At any particular temperature a metal will have a precise oxygen concentration, or activity, at which it will oxidise. If the oxygen activity is kept below that point no oxidation will take place, and

vice versa. What the above formula illustrates, for example, is that by adding more hydrogen to an atmosphere, the oxygen activity will be reduced. This is because the only way the ratio of activities can be maintained at the constant determined by the laws of chemistry is by the oxygen decreasing and/or the water increasing. Adding more hydrogen is a standard cure for overcoming problems when the water content (dewpoint) goes too high.

So the reason that the furnace operator asks for dewpoint measurement is that, in less enlightened times, it was the only way to determine how much oxygen was in the furnace. To avoid the complication of translating this figure into 'oxygen', the habit has been to express atmosphere quality in terms of dewpoint and hydrogen concentration. The key component however is oxygen and its activity, and Hitech zirconia oxygen analysers measure this directly. The zirconia sensor is uniquely capable of measuring the extremely low concentrations of oxygen to be found in these atmospheres. For convenience, some analysers can be fitted with a meter scaled in dewpoint. However there is no real reason to have the analyser scaled in dewpoint; we offer it only because some users are used to it. It could be scaled in parts per million water vapour, sensor millivolts or, more pedantically, in oxygen potential; the figure that the user really needs to know. Oxygen potential is no more than the oxygen activity expressed in chemical units. As such it relates easily to the oxygen values that a chemist would use when determining the point at which a metal would oxidise



at a particular temperature. All of Hitech's microprocessor based analysers of this type display in oxygen potential (kilocalories or kilo-joules). See Technical Notes TN01 & TN03 for a fuller explanation of zirconia oxygen cell theory, etc.

The following table shows the relationship between dewpoint and the water concentration. It also gives the output in millivolts of the Hitech zirconia oxygen sensor at those concentrations in various concentrations of hydrogen.

Dewpoint		ppm H₂O	Cell output in mV (634°C)		
°C	°F		100% H ₂	75% H₂	5% H₂
0	32	6025	1192	1180	1076
-10	14	2566	1227	1215	1110
-20	-4	1021	1256	1244	1140
-30	-22	376	1302	1291	1186
-40	-40	127	1346	1334	1228
-50	-58	39	1392	1380	1274
-60	-76	10.6	1442	1432	1326
-70	-94	2.55	1498	1487	1382
-80	-112	0.53	1560	1549	1443

The graph below illustrates the relationship of dewpoint to cell output and oxygen potential at various concentrations of hydrogen.



Note: Hitech analyser models Z210 and Z1110 are used in this type of application.

