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Selecting an O_2 Analyzer for Respirometry

TECHNICAL OVERVIEW

O_2 Analyzers for Respirometry: A Primer on Technologies and Accuracy

Oxygen analyzers serve a multitude of purposes and are used for many applications within the industrial, environmental, and scientific disciplines. Just as all applications are different, the proper oxygen analysis technologies differ from application to application.

O_2 Analyzer Technology	Paramagnetic Analyzers	Zirconia Cell Analyzers	Fuel Cell Analyzers
Benefits	• Unlimited life span • Very fast measurement	• Very fast measurement	• Mechanically rugged • Relatively insensitive to temperature changes • Low signal noise and low drift • Allow compensation for water vapor dilution
Drawbacks	• Demanding calibration technique • Noisy • Very sensitive to temperature changes • Sensitive to flow rates • Sensitive to water vapor • Sensitive to vibration	• VOCs introduce error • Sensitive to water vapor • Shorter life span than Paramagnetic; longer than fuel cell • Can be destroyed by condensation	• Fuel cell requires replacement • Slower than other technologies

Those studying animal metabolism have a set of needs that are unique and differentiated from other O_2 analysis applications. The experimental setups are different. The environments are different. Perhaps most importantly, metabolic researchers also have their animals to consider. The resulting needs and requirements of flow-through respirometry go beyond that captured by product specifications alone. An understanding of the technologies themselves and how those specifications are determined is critical to understanding what analyzer will best meet your needs.

Hopefully this article can provide some of that understanding for you.

Oxygen Analysis Technologies and Their Benefits and Drawbacks

Paramagnetic Analyzers are widely used in industrial applications. They utilize a focused magnetic field which attracts oxygen to the strongest part of the magnetic field. (Oxygen is paramagnetic, whereas most other gases are not.) Within this magnetic field, two nitrogen-filled glass spheres are mounted on a rotating suspension rod and a mirror is mounted centrally on the rod between the spheres. A light shines onto the mirror and reflected light is directed onto a pair of photocells. When the magnetic field pulls oxygen into it, the oxygen displaces the spheres and causes the mirror to rotate, changing the incidence of the light on the photocells.

The photocells detect this change and generate a signal, which is fed back to an electrical system which passes a current to a motor which serves to keep the glass spheres and mirror in its original position. The current being passed to the motor is what is measured. In theory, this current is directly proportional to the oxygen concentration.

Paramagnetic analyzers are specified by standards organizations for a number of critical measurements, such as medical gas testing. Additionally, the sensors do not have an intrinsically limited life span, unlike fuel cell-based or zirconia cell-based analyzers.

As paramagnetic analyzers react nearly instantly to changes in O_2 concentration surrounding the nitrogen-filled spheres, they can have very high rates of measurement if the chamber containing the motor assembly is carefully constructed with minimal volume. It should be noted, however, that a high-speed analyzer is rarely required to achieve a fast response time within a respirometry system. Given the volume of animal cages and tubing in relation to the gas flow rate, the wash-out kinetics of the system are limiting to temporal resolution and not the time required for the analyzer to respond to changes in concentration.

Paramagnetic analyzers require calibration at two different oxygen concentrations. This calibration can be extremely difficult and introduce inaccuracy to the system. Regulation at a shifting set point is very difficult to achieve mathematically and is rarely achieved by paramagnetic analyzers; this can lead to over-shooting or under-shooting in the feedback loop and the potential for introduction of significant levels of error. Additionally, the intrinsic noise level is quite high (typically > 0.002% O_2) and the mirror itself is prone to errors caused by mechanical or vibrational noise.

At any given O_2 concentration, in order for the displacement of the nitrogen-filled spheres to remain constant the flow rate of the gas also has to remain constant. Because the sample gas stream imparts a convective force to the motor assembly, any minute change in flow rate will be measured as a change in oxygen concentration.

Magnets themselves have a large temperature coefficient, so the powerful magnets in paramagnetic analyzers can have serious drift problems in the event of slight temperature changes. The Curie Effect introduces further temperature sensitivity to the paramagnetic effect itself.

Paramagnetic analyzers interact with water vapor because water vapor is diamagnetic (it creates an induced magnetic field in a direction opposite to an externally applied magnetic field, and is repelled by the applied magnetic field). Therefore, water vapor will oppose the paramagnetic effect of O_2.

Zirconia Cell Analyzers determine oxygen concentration using the conductivity of a zirconia ceramic cell. The cell is comprised of two electronically conducting electrodes attached to either side of a solid electrolyte tube. The measured gas flows through the inside of the tube and a reference gas is on the outside. Zirconia is an electrolyte that conducts only oxygen ions at temperatures in above 600°C; therefore the voltage generated between the electrodes is a function of the ratio of the oxygen partial pressure across the inner and outer electrodes and its temperature. Zirconia electrodes are typically operated at temperatures between 700°C and 800°C. They respond rapidly to changes in O_2 concentration because O_2 migrates rapidly through the red-hot zirconia electrolyte.

Zirconia cells are capable of very rapid measurements due to the rapid diffusion of O_2 through the literally red-hot electrolyte.

Zirconia cells have a number of drawbacks which makes them unsuitable for respirometry applications. Volatile organic compounds (VOCs), such as methane, immediately combust when coming into contact with such extreme temperatures. This combustion reaction consumes oxygen and results in measurement error. As all animals produce VOCs, use of a zirconia cell to detect oxygen concentration will lead to overestimates of oxygen consumption rates. Additionally, any trace of liquid water will cause heat shock to a zirconia cell and damage or destroy it, and zirconia cells may also be damaged by the presence of water vapor.

Zirconia cell analyzers are power-hungry (because of the high operating temperature of the zirconia cell) and bulky. Due to Johnson-Nyquist noise caused by high temperatures, they are also quite noisy, with noise levels similar to those of paramagnetic analyzers.

Fuel Cell Analyzers measure the partial pressure of oxygen as it diffuses through a semi-permeable membrane. The cell consists of an enclosure containing two electrodes separated from the gas sample by the semi-permeable membrane, which controls the rate at which oxygen can enter the cell. Oxygen combines with the metallic anode, creating a current between the cathode and anode. The current produced is proportional to the concentration of oxygen present.

Fuel cells are mechanically rugged and insensitive to vibration. They are also relatively insensitive to temperature and completely insensitive to VOCs, which are isolated from the cell's electrochemistry by the membrane, which is permeable only to O_2. Oxygen analyzers incorporating fuel cell technology have long-term stability, very low signal noise (down to 0.0001%) and low drift. Unlike zirconia and paramagnetic analyzers, they do not interact with water vapor, other than via the dilution effect of water vapor. The dilution effect of water vapor on oxygen is easily accounted for mathematically by measuring water vapor pressure and barometric pressure and using Dalton's law of partial pressures, thus allowing automatic compensation for water vapor dilution in a complete system (equations in Lighton, 2008).

While fuel cells are slower than the other technologies (due to the time required for O_2 to diffuse through the electrolyte) this is not rate-limiting in animal respirometry setups because speed can be increased mathematically. The response characteristics of fuel cells are precisely known and their response speed can be enhanced to values equivalent to the other technologies while maintaining their low noise. This is done by use of the instantaneous transform (originally discussed in Bartholomew et al, 1981).

The life of a fuel cell is approximately two years(+), after which the fuel cell will need to be replaced. Replacement of the fuel cell is a minor expense.

The appropriate O_2 analyzer for will ultimately depend on the nature of the application as well as the accuracy and resolution that are desired. In respirometry applications, an O_2 analyzer is usually part of a larger system. In addition to the design of the O_2 analyzer, the design of the system as a whole needs to be considered, as other elements of the system may place constraints on your ability to accurately determine oxygen consumption. Selecting the best analyzer for your application is important, but it must be used as part of a properly designed system in order to reap its full benefits.