A testing time for gas analysis

Tim Wilkes, Servomex Marine Market Manager, reviews marine gas analysis trends and why owners and managers must take care in specifying technologies that benefit them

The measurement of gases such as oxygen and hydrocarbons plays a vital role in ensuring the safety of a tanker and her crew. As with many things though there are a variety of ways in which a gas can be measured. A shift to "lowest cost" when building tankers in the Far East seems to have encouraged use of less robust technologies but, as with other marine equipment, many owners and operators are now realising there are benefits in specifying the type of analysers they want.
The reasoning behind this can be best understood if we look at the different technologies available for measuring gas concentrations on ships. These fall into five main types - electrochemical, thermal effect, infra-red, zirconia based and paramagnetic.

Electrochemical
Electrochemical sensors are based on the fact that cells can be constructed that react with the measured gas and generate an electric current. This can be measured and the amount of gas determined as a result. These sensors are low cost and small enough to allow several to be incorporated into the same instrument easily, making them suitable for simple detection applications such as ambient monitoring in pre-checked enclosed spaces. Typical combinations in this application are sensors for oxygen deficiency and traces of hydrogen sulphide, carbon monoxide and hydrocarbon vapours.
The disadvantages of electrochemical sensors are that, like batteries, they need replacing once all the chemicals inside them are consumed, and being chemical based they are affected by temperature and the presence of background components (which may alter the reactions taking place). The other significant problem is that, especially with oxygen, it is not easy to determine whether a low reading may be due to low levels of the measured gas or that the sensor has consumed its chemicals. For this reason they are frequently not acceptable for use on critical low oxygen monitoring applications on land based facilities.
In the marine industry portable multi-gas electrochemical analysers are commonly used for personnel protection and the small size of these makes them attractive. Electrochemical analysers were also once commonplace on inert gas systems, where alarm points of 5% and 8% oxygen are typical. However, exposure to the risk of false low readings and the need to replace cells every six months to two years (and the administration of having to obtain spares and show inspectors a check is kept of use-by dates on stored cells) means most IGS suppliers are being asked to move away from their use.

Feeling the heat
The second technology being used on marine vessels is thermal effect. Again used in portables this technology is the traditional method for measuring hydrocarbon gas concentrations. These analysers use either the change in temperature of a bead or "pellistor" when hydrocarbons burn on its surface, or change in thermal conductivity when gas mixtures change in a known way. The former technology is appropriate for measuring trace levels of hydrocarbons in air but the pellistor can be very quickly burnt out if higher levels of hydrocarbons are present.
When measuring hydrocarbons in inert gas the lack of oxygen means that the pellistor method is not possible and so a method using thermal conductivity variation

is usually employed. Both thermal effect technologies have found widespread acceptance but the consumable nature of the sensors and the need to have two separate analysers has encouraged some users to look for an alternative, hence the emergence of infra-red analysers.
Infra red technologies utilize the absorbance of specific wavelengths of IR radiation by different gases. Such sensors are generally larger than electrochemical or thermal effect types but have the advantages of long life and being able to operate both in air and inert gas. Care must however be taken by the manufacturer in selecting appropriate wavelengths that avoid cross interference from water vapour and by the user to ensure calibration with the most appropriate gas mixture, according to the most likely expected gas and the makers instructions. (The latter also applies to thermal effect units).
Infra red and thermal effect techniques are also used in fixed systems for detecting the presence of hydrocarbon gases in ballast tanks and enclosed spaces. Infra red sensors typically cost more initially but remove the need for regular replacement.

Zirconia
Following on from the earlier notes on dissatisfaction with electrochemical sensors, fixed analysers for oxygen monitoring on inert gas systems are now generally either zirconia based or paramagnetic. Zirconia analysers make use of the unusual properties of zirconium oxide, "zirconia". If placed between two different concentrations of oxygen and heated to around 650°C this material allows oxygen ions to pass through it. If an electrode is attached to each side of the zirconia the flow of ions can be detected as an electric current - this current is proportional to the difference between the two concentrations. Analysers based on this principle expose one side of the zirconia to air and the other to the sampled gas in order to determine the oxygen present.
The advantages in favour of using zirconia analysers are that they are fast response, they do not suffer the "false low" characteristics of electrochemical sensors and that they require minimal sample gas preparation. For the same reasons sophisticated variants are commonly used on land for controlling combustion processes in power plants.
Unfortunately the high temperatures involved with zirconia based measuring techniques mean that limited cell lifetimes are inevitable. The most expensive, high-grade zirconia cells for power stations typically last around 3-5 years, but those used in marine applications do not typically function this long - though they generally work for the length of the shipbuilders warranty period.
Lifetimes can be maximised by turning a unit off when not in use but a warm up period of around an hour must be allowed when it is next switched on. (Ionic conduction properties are highly temperature dependant so allowing the zirconia to stabilise before calibration is essential). Care must also be taken to ensure that the air side of the zirconia cell is always open to hydrocarbon free air, otherwise these will combust on the hot zirconia, decrease the oxygen contacting it and affect the reading.

Paramagnetic
Due to the high price of spare zirconia cells, the rather unpredictable nature of their failure and the high cost of being off charter when the inert gas system is out of use, many discerning owners and operators now opt to specify paramagnetic analysers for IGS control. These analysers make use of the magnetic properties of oxygen and as a result the sensors are non-consumable. This enables them to be left continually ready for use and if appropriately designed gives them a typical lifetime of over ten years.
Portable marine oxygen analysers based on paramagnetic cells have also been developed and are widely used for gas freeing control, where accurate, fail safe

analysis is necessary. Vapour recovery systems are another application where paramagnetic analysers come to the fore, as the high levels of hydrocarbons and critical nature of the application mean that zirconia or electrochemical based analysers are not suitable. It is important to note that not all paramagnetic analysers are suitable for use in marine applications as certain techniques are more susceptible to vibration and tilt than others.
The disadvantages of paramagnetic oxygen analysers are that the precision engineering involved in manufacturing the sensors makes them up to £5000 more expensive than zirconia or electrochemical units. This makes them unattractive to shipyards and IGS manufacturers being asked to supply "lowest cost" equipment, but shrewd owners and operators often specify them and agree to pay a little more as the extra cost is easily recouped in reduced maintenance time. Alternatively owners wait until the original equipment fails and then replace the units with paramagnetic ones as a matter of course.

Two philosophies emerging
As the discussions above show, with the exception of vapour recovery system monitoring there are effectively two routes for each of the major gas analysis applications on board a tanker. Those looking for the lowest initial cost will probably opt for electrochemical and thermal effect portable analysers, thermal effect ballast tank monitoring systems and zirconia based IGS monitors. Those looking for maximum reliability will accept electrochemical sensors only for personal monitors and opt for paramagnetic and infra red portables, infra red ballast tank monitoring systems and paramagnetic IGS analysers.
With regards to suppliers of gas analysers there are several large and many smaller players, though only a few have specific marine products. Servomex (www.servomex.com) is one of these and offers paramagnetic oxygen analysers for inert gas system control (the 1800 Marine) and portable use (the Servomex 262). They are also obtaining marine approval for the Servomex 1900, a version of the 1800 designed for use in areas at risk of flammable gases such as those around vapour recovery systems.