SPECIALTY GAS ZONE

Maximising margins

Trends in gas analysis instrumentation for improved argon recovery

By **Stephen B. Harrison**

The air that we breathe into our air separation unit (ASU) costs money in the form of electrical power. Our return comes from selling the oxygen, nitrogen and argon that we compress. Whilst the oxygen and nitrogen have contracted customers with pipeline supplies, the profitability of modern ASU operations is often driven by what we do with the argon molecules that we have access to.

In the early days of industrial gases, people thought of argon as a by-product but today, it is often at the heart of industrial gas economics.

The idea of selling by-products is common in the chemicals industry and the two main challenges are to extract them effectively from the process and extract their full commercial value in the market. In fact, the term 'by-product' is often substituted with 'co-product' to give them equal status and recognise their true value. At times of peak argon demand, industrial gas operators may be running their ASU extra hard

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to maximise argon production and spilling excess oxygen or nitrogen. On days like this, the argon is not the by-product, it's the lead product. So how can ASU operators maximise the amount of argon they produce?

Yes, turning up the power, blowing more air through the ASU and producing more of everything is one option. But it is expensive. One of the alternatives is to ensure that as many as possible of the argon molecules which are sucked into the ASU leave the ASU with the argon product stream and are not blown away with other gases. The characteristics of the distillation process mean that most of the argon leaving the ASU will either do so as pure argon, or with the gaseous oxygen product. Given that the market value of argon can range from two to five times the market value of oxygen, letting argon molecules slip out with the oxygen is like letting profits slip through your fingers.

To ensure that argon recovery from the ASU is maximised, operators can invest in process optimisation, automation and accurate instrumentation. In this respect, high accuracy gas analysers have a key role to play. To keep the argon slippage under control better than ever before, ABB has recently improved its Magnos28 gas analyser. The Magnos28 has been used for decades by ASU operators to measure the amount of oxygen in the feed to the argon column and to analyse the final oxygen purity. It is the final oxygen purity in particular, where repeatable and accurate oxygen gas analysis is essential to minimise argon losses. The monetary value of an inaccurate oxygen reading at 99.7%, when the reality is an oxygen purity at 99.6%, means that 0.1% of the oxygen flow is argon which is being sold at the price of oxygen…now that's a discount that few of us can afford to offer when we are supplying hundreds or thousands of tonnes per day of oxygen.

Steve Gibbons, Head of Product Management for the continuous gas analyser product range within ABB's Measurement & Analytics business line, says, "The key innovation behind our new Magnos28 is its microwing. This is a solid-state version of the gas-filled dumbbell that has been used in paramagnetic gas analysers for decades: we have digitalised the dumbbell! Less drift on the measurement and better accuracy means that ASU operators can know exactly where their argon is going."

"Upgrading to the new Magnos28 enables ASU operators to stretch their revenues and maximise their margins."

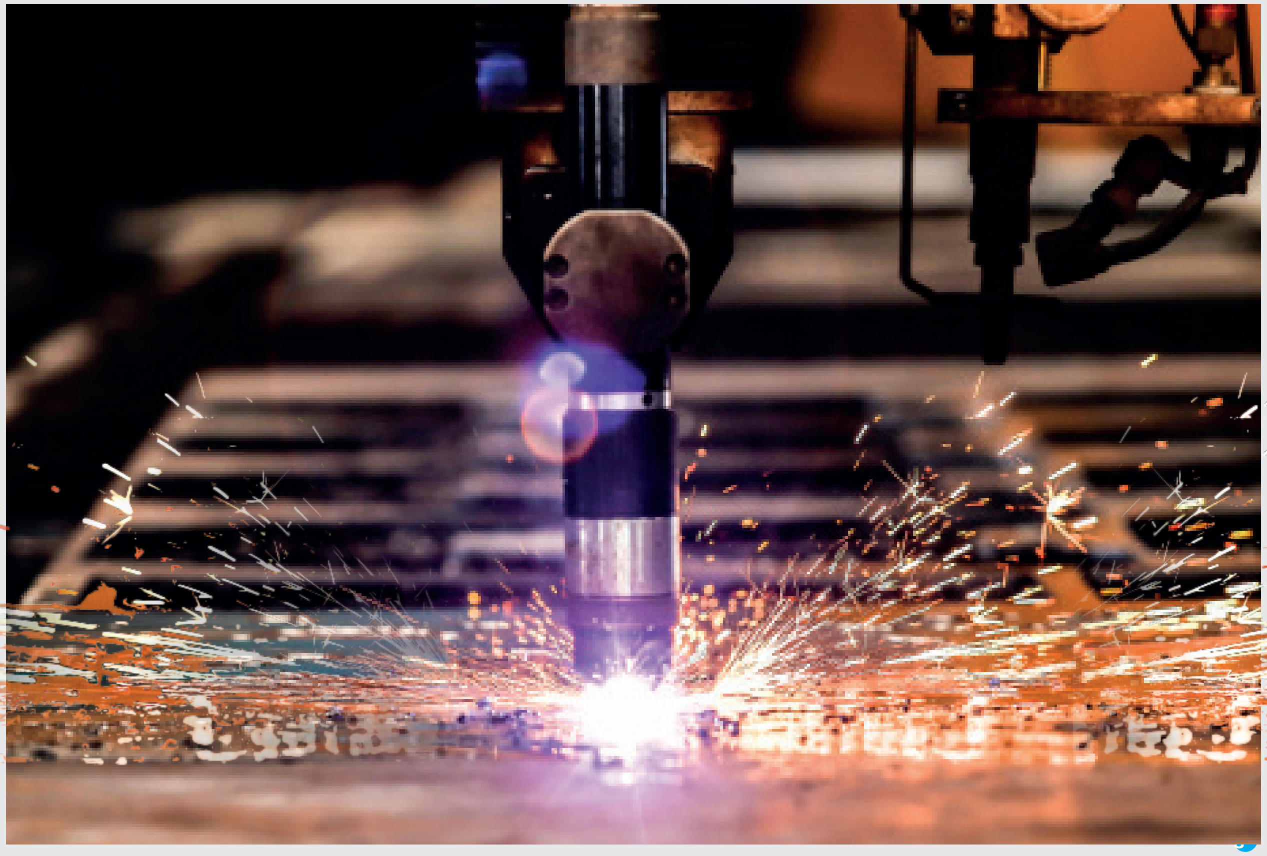
The difficulties associated with accurate measurement at and above the 98% level have, until relatively recently, meant the continued use of time consuming, offline wet chemistry techniques. With a measured value of pure oxygen from an ASU typically at 99.8% the Magnos28 shines in this application. "When we developed the Magnos28," Gibbons adds, "one of our priorities was to make the instrument compatible with advanced ASU process control strategies. With that in mind, we can customise the instrument to zoom in on the 98-100% range using its 'suppressed zero' capability. In doing that, we compress all the data that would normally be gathered in the 0-100% range into that tiny 2% band between 98-100%. That's how sensitive the Magnos28 is."

Argon purification unit process control instrumentation

Many ASUs produce 'crude argon' containing approximately 2% oxygen. To purify the argon further using cryogenic distillation on the ASU is not always cost-effective. It can be more economic to build a separate argon purification unit (APU). In this process the oxygen in the crude argon is reacted with hydrogen to produce water vapour, which is then separated using adsorption bed dryers. The resulting mixture of argon, excess hydrogen and nitrogen is distilled at cryogenic temperatures to release the lighter hydrogen and nitrogen gases – yielding pure liquid argon.

Process control on the APU relies on accurate dosing of the hydrogen to yield a precise stoichiometric reaction with the oxygen. Higher crude argon flow rates or higher oxygen concentrations in the crude argon require additional hydrogen to fully consume the oxygen. One of the most effective process control strategies is to use a slight excess of hydrogen to ensure that all the oxygen is converted to water. Measurement of the hydrogen leaving the so called 'deoxo' unit can be achieved with a thermal conductivity detector, or TCD.

Sudhakar R. Saladi, a specialist industrial gases plant Commissioning Engineer with international experience at Air Liquide, Air Products & BOC explains what additional measures are required. "To ensure that the deoxo unit has functioned properly and to guarantee the final argon product purity, an additional gas analyser measuring the oxygen concentration at the outlet of the deoxo unit is used. It should be reading only a few parts-per-million →



(ppm) of oxygen – as close to zero as possible."

"The kind of analyser used to measure these trace oxygen concentrations is very different to the paramagnetic instrument that is ideal for percentage level oxygen measurement on the ASU."

Saladi concludes that "for many years, electrochemical cells have been used for trace oxygen measurement. They are inexpensive to purchase but have high maintenance requirements and relatively slow response times."

"So, whilst the capital costs are low, the cost of ownership can be high. For trace oxygen measurement, it is becoming increasingly common to use a zirconium oxide detector in the gas analyser."

This type of gas analyser has proven its usefulness in combustion control applications, where they are the industry standard for measuring the excess oxygen in burner flue gas. They are now beginning to penetrate industrial gases operations to the same extent.

Argon applications – where purity matters most

High purity argon is used to create high temperature plasma for cutting metals or ionising molecules for chemical analysis.

The plasma discharge temperature from an inductively coupled argon plasma laboratory gas analyser used to validate drinking water quality is around 6,000°C. And in the argon plasma of a metal cutting nozzle the temperature will be more than 20,000°C. The surface of the sun is around 5,500°C – moderately cool in comparison.

At these temperatures, argon purity is critical. A few parts-per-million is the upper limit of oxygen that these processes will tolerate. And how do we go about finding those few ppm? Gibbons explains, "In essence, we are trying to find the needle in a haystack. But, at ABB, we've got that covered. Our ZO23 trace oxygen analyser does just what it says: it finds tiny traces of oxygen that are hiding in other gases. In this example, we are looking for trace oxygen in a background of argon. In other cases, such as ASU product purity control, it could be looking for a few parts-per-million of oxygen in high purity nitrogen."

In another advanced metals processing application – additive manufacturing (AM) – lasers are used to melt metal powders of tungsten, aluminium or iron to create complex structures. The presence of moisture or oxygen in proximity to the molten metal would form oxides and could mean that days or weeks of time that has been invested in forming the part are wasted. So, an inert gas is used to ensure that oxygen and moisture are not present. Nitrogen is generally considered to be inert.

"In other cases, such as ASU product purity control, it could be looking for a few parts-per-million of oxygen in high purity nitrogen"

But in this application, it would form undesirable metal nitrides. So, high purity argon is the preferred inert gas. As with the plasma application, ensuring that the argon has only a few parts-per-million of oxygen is key to this end use.

With purity being so important, the detection of trace oxygen impurities during the cylinder filling process is advisable. Industrial gas companies around the world rely on highly sensitive gas analysers to ensure that their high purity argon conforms to its specification. Gibbons explains, "The ZO23 uses an yttria-stabilised zirconium oxide layer to find tiny amounts of oxygen with a detection limit of only 1 ppm. It sounds like high-tech, but we've bundled that up into our EasyLine range of gas analysers so that industrial gas producers can benefit from 'plug and play' simplicity."

"Whether it's argon purification unit process control, argon product purity confirmation and cylinder filling quality assurance applications, we'll help them find that needle in the haystack." gw