The Australian wine industry produced something like 130 million cases of wine, from the 1.65 million tonnes of grapes crushed in 2002. In doing that, it used around 15 million cubic metres of nitrogen and carbon dioxide gases, from bulk supply and cylinders, plus on-site nitrogen generation. The cost of these gases was between $0.09 and $0.45 per case of wine. In addition, there was most likely a similar cost applicable to the gas related labour operations.

Many wineries continue to or still use techniques and equipment that have not changed in years. They continue to overlook the properties of the gas in use, and the inefficiencies associated with many of these operations.

If a winery is targeting quality and efficiency (key measures in today's international market) is it still acceptable to use techniques that have not changed in more than twenty years? From a cost parameter alone, there are many areas where application of the science of winery gases and technology, can result in considerable reductions. That approximate $0.08 to $0.30 labour cost per case of wine can easily be reduced, and at the same time the quality enhanced.

In addressing the question of efficiency and quality, a good starting point is to re-examine the science of gases and gas mixtures, and establish a case for revisions to current practices.

The science of gases and gas mixtures

The main inert gases in use in the Australian wine industry are nitrogen and carbon dioxide, supplied in bulk liquid form, and cylinders. In the case of nitrogen, on-site generation is increasingly being used for economic reasons. In addition, argon is now being used in Australia and New Zealand, building on experience in the USA and France. Mixtures of any two or three of these gases are possible, once again, using overseas experience and research as a guide.

Considerable research has been devoted to the science of gases, and of gas mixtures. Of particular note are the published works of Lonvard-Funel (1976), Spencer (1996), Lake (1996) and Vidal and Boulet (1996).

These four publications, ranging over a twenty-six year period, provide the basis for a re-examination of the science of gas mixtures for use in the modern winery.

In general, inert gases are used to control either gaseous oxygen, and therefore dissolved oxygen, or dissolved carbon dioxide. Each has a marked effect on wine quality and on the 'mouthfeel'. From terms of target specifications, there is probably not a definitive answer, but a guide can be provided from the opinions of a cross section of winemakers.

The dissolved oxygen level can vary from an advised target of <0.3 mg/L for a delicate white wine, to 0.5 mg/L, or even 0.6 mg/L for a red wine. Development of oxidative haze can begin at around 0.5% gaseous oxygen, depending on temperature, time and surface area.

The level of dissolved carbon dioxide, on the other hand, has a marked effect on the mouthfeel of the finished wine. Typical levels are 1.0 g/L for a white wine, and 0.4 g/L for a red wine. Levels above 1.0 g/L will result in a 'spritzig' effect, while levels below 0.4 g/L may give the appearance of a 'flat' wine.

It is possible to use an inert gas to achieve these levels in the finished wine, and the four references cited provide the scientific basis for such a decision.

The first consideration for the modern winemaker, therefore, is the properties of the various gases (see Table 1). From these, some basic decisions can be made, and procedures set in place.

<table>
<thead>
<tr>
<th></th>
<th>Nitrogen</th>
<th>Carbon dioxide</th>
<th>Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>28.0134</td>
<td>44.01</td>
<td>39.948</td>
</tr>
<tr>
<td>Normal boiling point (1)</td>
<td>-195.8</td>
<td>-78.47</td>
<td>-185.85</td>
</tr>
<tr>
<td>Specific volume (2)</td>
<td>0.8441</td>
<td>0.5336</td>
<td>0.5916</td>
</tr>
<tr>
<td>Specific gravity (3)</td>
<td>0.9669</td>
<td>1.53</td>
<td>1.38</td>
</tr>
<tr>
<td>Solubility, v/v</td>
<td>0.017</td>
<td>1.01</td>
<td>0.038</td>
</tr>
</tbody>
</table>

(1) = 1 atmosphere, temperature °C
(2) = M³ per kg at 15°C
(3) = Relative to air, (air = 1)

From these properties, it can be seen that in terms of specific gravity (i.e. is the gas going to layer?) then it appears that carbon dioxide, and to a lesser extent, argon, should offer the best choices. Nitrogen on the other hand, offers a higher specific volume, and is also relatively insoluble in wine, while carbon dioxide is highly soluble. It can also be seen that from the physical properties, argon would appear to offer benefits as it is still relatively insoluble, while at the same time offering a high specific gravity.

In general, two (or three) part mixtures of any of the above, will provide a mix with physical properties in proportion to the percentage of either gas in the mix. This does, however, assume that the mix is done in an efficient manner. It is by closer examination of the cited publications, that sufficient data can be provided in order to fully assess the options.

The research of Lonvard-Funel (1976)
The thesis of Lonvard-Funel (1976) contained the most...
forward thinking research: it almost single handedly changed the direction of the wine industry in France, in relation to the use of mixed gases. Comprised of several parts, the initial focus centred on developing a method to accurately measure dissolved carbon dioxide in wine at low levels. It used Van Slyke equipment, and the end result was accuracy greater than 1%, in samples as small as 1 or 2 ml.

A secondary focus of the thesis was the origins of carbon dioxide in wine, i.e., from fermentation, both primary alcoholic fermentation and secondary to malolactic fermentation. The data showed that while the content of carbon dioxide from alcoholic fermentation is determined by the solubility ratio (temperature dependent) between 1.5 and 2.0 g/L, malolactic fermentation could produce levels of 1 g/L as well, and therefore restart the saturation of wine that may have been made gas free. The conclusion was that wines after malolactic fermentation require the same handling as new wines.

The influence of storage was also studied, with barrel storage identified as an area where losses of dissolved carbon dioxide may be in the vicinity of 8% per month. Losses from stainless steel storage were much lower. Racking and ventilation may (temperature dependent) allow elimination of up to 40% dissolved carbon dioxide in one operation.

The (then) new techniques of storage under inert gas were studied, and both field and laboratory trials established a formula that showed the characteristics of the equilibrium between the gaseous phase and the wine.

The net result was the development of a nomograph setting out the percentage of carbon dioxide, in a CO₂/N₂ gas mix, required to maintain a desired dissolved carbon dioxide level at a temperature. For ease of use, that initial nomograph has been reproduced in a standard Excel graph format. That graph can, and has been used by modern winemakers to calculate the gas mix needed in their particular case to achieve control over dissolved carbon dioxide, quite naturally, without the need for a sparging operation.

The research of Spencer (1996)
The research of Spencer (1996) into the group of noble gases (argon, krypton, xenon, and neon) showed that if a wine tank ullage space was purged with a gas or mixture from the above group, then it was possible to improve the colour, flavour, aroma, and shelf life of the wine, during the time that the wine was stored in the wine tank.

The research was conducted over a two-year period, using Cabernet Sauvignon, Sauvignon Blanc, and Chardonnay from the USA, Riesling from Germany, and Chardonnay (M eursault) from France. The wines varied from one to forty years old. GC and MS were conducted at weekly intervals for two years, and U.V. visible scanning spectrophotometry conducted to monitor changes in colour and turbidity.

The conclusion drawn by Spencer was that sparging, or use of an atmosphere of a noble gas, inhibited the oxidation better than nitrogen or any other gas, depending on the percentage of that noble gas. The blind taste panel concluded that these wines had shelf life, colour, flavour, aroma, and fragrance considered superior to those stored under nitrogen.

This research led to the widespread use of argon in USA, particularly in the Napa Valley, and in France, where it was used as an 80% mix, the balance being carbon dioxide.

The research of Lake (1996)
As was the case with the Spencer (1996) patent research, the thesis of Lake (1996) studied the use of nitrogen carbon dioxide, and argon, plus mixtures of each, in preventing the ingress of oxygen into wine.

The conclusion was that the blanketing ability of the gas or mix depended not only on molecular weight, but also on the equilibrium with the dissolved carbon dioxide. Where there was movement of dissolved carbon dioxide into, or out of, wine, there was a corresponding effect on the ingress of oxygen. Movement of dissolved carbon dioxide into wine, resulted in a decrease in the blanketing ability, believed to be a combination of the molar flux effect of carbon dioxide moving into and out of solution, and headspace pressure changes.

Blanketing gases or gas mixtures with high atomic/molecular/mean molecular weights offered the best blanketing abilities. However when applied over wine, the blanketing ability depends not only on the gas properties, but also on the concentration of carbon dioxide in the headspace and in the wine. This point supported the data in the thesis of Lonvard-Funel (1976) which was obtained some 20 years earlier.

Lake concluded by commenting that a mixture of argon and carbon dioxide, of a percentage corresponding to the optimal level of dissolved carbon dioxide, worked best.

The research of Vidal and Boulet (1996)
The research study of Vidal and Boulet (1996) undertaken at the I.N.R.A. Pech Rouge station took the results of the Spencer (1996) research, and extended it to assess the real effectiveness of nitrogen, carbon dioxide, argon, and a 20% carbon dioxide in argon mix on wine held in commercial stainless steel tanks. Oxygen analysers were set up at the tank range valve, plus 200mm above the wine surface, and monitored at 1-minute intervals. By doing this, it was possible to see the effect of each treatment, and the method of operation. Flow rates and temperatures of each of the gases used were identical.

The nitrogen result, when graphed at both points (purge valve outlet and 200 mm above wine surface) showed a similar curve for both areas, meaning the gas was working by diffusion. This meant the oxygen reading on the wine surface was about the same as at the purge valve outlet. To be effective (which is taken as an oxygen reading below 1%) the operation with nitrogen would require greater than 3 volumes of gas (12,000 L in 4,000 L ullage). This figure coincided with data from England (Distillers) that showed a nitrogen usage of three volumes to get surface oxygen to 1%, and Air Liquide Italy trials that gave a usage of 5 volumes.

Carbon dioxide, and the argon plus argon mix, on the other hand, operated by displacement. This showed clearly that an effective result, on the wine surface, could be achieved with a usage of about 0.6 volumes (2,400 L in 4,000 L ullage). In other words, these gases layered. Further, when the tank lid was opened fully, these gas covers lasted more than 12 hours before the oxygen concentration rose at the surface.

I.N.R.A.’s conclusion was that the drawback with nitrogen was its density, while carbon dioxide had high density, but its solubility was a problem. Argon combined...
the advantages of both, and its extra cost could be balanced by mixing it with another gas. In the research, the mixture performed as well as straight argon and carbon dioxide.

Vidal and Boulet further concluded that whatever gas is used, care needs to be taken to maintain the initial dissolved carbon dioxide level. Further, a diffuser is recommended to reduce gas velocity, and consequently, turbulence. When a tank lid is opened, there is a loss of argon or carbon dioxide due to convection. If this can be minimised, theoretically there is nothing to prevent the argon layer from remaining indefinitely.

The publication of this I.N.R.A. data led to the widespread use of a mix comprising 20% carbon dioxide in argon in France, where, at last count, in excess of 200 wineries were using the gas in the Bordeaux and nearby regions.

So what results can be taken from these four research papers that will be of benefit to the modern winemaker? Clearly the use of an appropriate mixture of carbon dioxide and nitrogen, carbon dioxide and argon, or even argon and nitrogen should be considered in preference to a straight gas. This is clearly the case where the current operation is to use dry ice snow, where conversion losses also have to be taken into consideration. The carbon dioxide and nitrogen mix has quality benefits identified 26 years ago, and proven over that period. It is efficient, and with changes in the supply of nitrogen, i.e. the introduction of on-site production, it is also economical.

Argon has decided advantages, but if using this gas it is essential, that the equipment and procedures be very carefully set up and monitored, as the initial purchase cost is higher than for other gases. Whichever gases are used, quality and efficiency are critical, as are constant audits of winery practices, and achieved results. Wine tank construction has improved, but attention is still required on the integrity of the lids. No gas system is effective if a screw down lid is left ajar, or a water seal lid has no water.

Gas mixtures are relatively easy to set up, provided care is given to the engineering aspects of the operation. It is also likely that a compromise may be necessary between the theoretical gas mixture required for each of the wines, and the practicalities of distributing the gas mix to each wine tank. A large winery may well have to balance the theoretical mixtures required, and compromise on a middle of the road mix.

The future direction of the Australian wine industry is clearly towards the extensive use of gas mixtures. This is evidenced by the increasing use of large gas mixing systems. The industry is also examining the possibility of the introduction of new gases and techniques, particularly following on from the Chicago (Spencer 1996) research. There is enough scientific data and practical winery experience available to support the use of gas mixtures, but in some cases old habits may still need to be overcome.

References: