Ozone in Wineries

PART 1
Getting Beyond Myths and Mistakes

THE WINE industry seems to have a schizophrenic attitude about ozone. Many wineries use ozone and are thoroughly delighted with its efficacy as a sanitizer and its safety. Other wineries have had negative experiences with ozone in the cellar. Still others have had no experience, but have heard of workers refusing to use ozone or of ominous consequences from run-away generators. Too often, ozone's virtues seem to have been oversold and its drawbacks overblown. Myths, misinformation, conflicting claims, and even irrational fear abound.

This two part series on ozone in wineries will take a balanced look at this very useful but problematic, misunderstood and misused sanitizer. It will clarify the facts about ozone, and will provide a thorough explanation of ozone's many uses in the winery. In this first article, we'll review some ozone basics, examine a few common winery problems, and explore ozone key safety and usage considerations in the winery. The second article in the March-April issue will focus on winery applications for ozone, including an in-depth look at barrel treatment.
Part 2 also will examine surface sanitation, and the sanitation of bottling lines and other clean-in-place (CIP) applications. It will discuss building-wide ozone systems where ozonated water is available on-tap throughout the winery facility, and will explore the use of gaseous ozone to sanitize storage rooms and caves and to treat well-water and wastewater. You'll hear about some recent university research on ozone treatments in wineries, and you'll learn about some fascinating but not yet fully developed uses for ozone, including long-term winery barrel storage and vineyard insect and mildew control. All in all, we'll (ahem) fully clear the air on ozone. So let's begin.

All About Ozone

Ozone (O_3) is a naturally occurring gas, an unstable molecule made of three oxygen atoms. In nature, ozone is made when lightning or ultraviolet rays split apart oxygen gas (O_2) molecules high in the atmosphere. At the surface of the earth, ozone is usually unnoticeable at its normal concentration of 0.01-0.05 parts per million (ppm). You only become aware of ozone in the air at higher concentrations, such as after a thunderstorm—that fresh, clean, somewhat zingy smell. You'll also smell ozone near copy machines, electric motors and arc welders, all of which produce ozone as a by-product. And sadly, ozone makes its presence known in smog-filled city air, where car exhaust and other gases produce irritating concentrations of it at ground level. (Yes, smog produces ozone, not the other way around.) "Spare the Air" days are called for when the ozone level is expected to exceed 0.08ppm.

Ozone is the most reactive substance known, save only free fluoride ions. This high reactivity means that ozone doesn't last long; it immediately transfers that pesky third oxygen atom to any organic compound it touches and returns to stable oxygen. In the process, that organic compound is oxidized—chemically changed, as in burned. This means that ozone instantly annihilates enzymes, microbial

membranes and unpleasant taste- and odor-causing compounds. Ozone destroys on contact all known bacteria, virus, molds, spores, yeast, mildew, microscopic fungi and biofilms (toughened colonies of microorganisms on surfaces).

Ozone kills microbes much faster than weaker oxidizers like chlorine. Up to 5,000 times faster. But unlike chlorine, ozone oxidation leaves no harmful or foul byproducts and residue only oxygen. Further, microorganisms can't build up a tolerance to ozone as they can to less reactive chemicals like chlorine.

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Because it's highly reactive and unstable, ozone doesn't persist—any ozone not instantly consumed by contact oxidation of organics quickly reverts to oxygen. This makes ozone perfect as a final, no-rinse sanitizer. With no persistence, ozone requires no special disposal system. Ozonated water going down your cellar's drains won't kill the bugs in your biomass, pollute your pond or destroy beneficial bacteria in your septic system or wastewater treatment plant.

Ozone has other useful qualities. Ozone is just as reactive when dissolved in water, where it is pH neutral and non-corrosive. Ozone reacts with dissolved iron and manganese, precipitating those ions for easy removal. And compared to hot water or steam, its chief rival sanitizers in wineries, ozone is dramatically less expensive to produce and safer to use. Switching to ozone sanitation can cut a winery's hot water usage in half.

There's more. Ozone won't harm stainless steel, most plastics or fitting and sealant materials like viton, silicone, Teflon, kinar, and epdm. Handled correctly, ozone can be safer than SO2 or steam. There are no storage, handling or reporting requirements for ozone. And as we'll see in Part 2, ozone can maintain and improve the microbial health of oak barrels. All in all, ozone offers a number of benefits to wineries as a fast, effective, environmentally friendly sanitizer, with no residue and no residual.

Misconceptions and Concerns

But ozone isn't without its drawbacks. And despite what some overzealous advocates have said, ozone absolutely is not the panacea, cure-all, or single solution to every problem in the winery. As we examine some potentially negative aspects of using ozone in wineries, we'll explode some myths and highlight some basic but crucial facts about ozone use.

Many wineries have used ozone inappropriately, and have been disappointed in the results. For example, ozonated water is not a cleaner. It's a sanitizer. Ozone doesn't attack tartrates, minerals, scale, or corrosion. It's no more effective than cold water rinses for cleaning the lees, dirt, solids and crud from the surfaces of tanks, floors, barrels or anything else. Hot water is much more effective at cleaning, with added scrubbing and possibly caustics included for tough cleaning jobs. Ozonated water may be great for killing any bugs remaining on the surface after cleaning, but until the crud is gone using ozone is a waste of time and money. Sums up Joe Mendez of Piper Environmental Group, "Regardless of what anybody tries to sell, ozone is not a silver bullet. Ozone is not always the right answer, especially for cleaning. Ozone is a lousy cleaner. If you want to clean, go to Costco, buy yourself a power washer, and clean. Use the ozone after you've cleaned."

Similarly, ozone is not a sterilizer, just a sanitizer. Sanitizing means controlling microbial populations by dramatically reducing their numbers. Ozone will do that. But sterility is a much more difficult state to attain. Like complete destruction of absolutely all microbes. In the lab, microbial kill rates are expressed in log numbers, where each log is a reduction in about 10%. A 1-log reduction kills 10% of the bugs, leaving 90% alive. A 4-log reduction kills 99.99% of the microbes, leaving 0.01% alive. (One test of ozonated water treatments indeed shows that Brettanomyces organisms are killed at the 4-log level. See chart above.)

But leaving alive only one ten-thousandth of the organisms on the surface of a barrel does not mean that the barrel is completely sterile. Microbes are small and exist in large numbers. If there were a million Brett cells before the ozone treatment, a 4-log reduction means that about 100 are still alive and kicking. That isn't sterility, but it may be good enough microbial control for a working winery. We'll come back to this sterility-versus-control issue in Part 2 when we talk about treatment times for problem barrels and bottling lines.

Problems in the Cellar

Beyond inappropriate usage, ozone can create some significant problems for wineries. Significant damage can occur to cellar equipment which isn't ozone-ready. For example, ozone will attack and destroy any natural rubber compounds. Gaskets, fittings, pump seals and hoses made of rubber-based elastomers will be quickly destroyed on contact with ozone. Ditto for unlined fiberglass tanks. (Ozone attacks fiberglass resins.) Before you use ozone, you need to make doubly-sure that all of your cellar equipment-every internal piece and part of it which might come in contact with ozone- will stand up to it.

Most wineries use ozone dissolved in water. And while ozone gas itself can be used in wineries (we'll discuss this in Part 2), a real problem is created in the cellar when ozone gas unintentionally gets into air as a gas by escaping-"off-gassing"-from the water in which it is dissolved. Off gassing is unavoidable; it's caused by the laws of physics which affect every kind of gas. The laws are simple: If you put any gas in contact with a liquid, the gas will dissolve into the liquid until a natural equilibrium concentration is reached. If you increase the pressure of the gas in contact with the liquid, more gas will dissolve into it. If you decrease the pressure of the gas, some of the dissolved gas will come out of solution. The more surface area of the liquid is in contact with the gas, the faster the dissolved gas will go in or come out of solution.

You know these laws from drinking soda pop. Soda bottles or cans are pressurized with CO2. While closed, there is CO2 dissolved invisibly in the liquid pop. When the containers are opened, the much lower concentration of CO2 in normal air pressure makes the dissolved CO2 bubble out. If you pour the soda into a wide-topped drinking glass, the bubbles come out faster than in the narrow-necked bottle, and faster still if you spill the pop onto the floor where it's in near complete contact with the air.

The same thing happens with ozonated water. In the ozone-generating machine, lots of ozone gas is put in contact with water, so some of it dissolves. (Some of it doesn't. We'll come back to this below.) Meanwhile, the ambient cellar air has very little ozone in it. As soon as the ozonated water touches the air, some of the ozone comes out of solution and enters the air as a gas. The larger the surface of ozonated water in contact with air, the more ozone is off-gassed. A small amount of ozone will be off gassed from a thick stream of ozonated water from an open

hose, more if the ozonated water is sprayed with a nozzle, and more still when the ozonated water spreads out over the floor.

Just like ozone in water, ozone gas in air reacts immediately with organics -it instantly toasts any airborne organics and becomes oxygen. But there are far fewer organics in cellar air than on cellar surfaces, and ozone gas in the air serves no useful purpose. Gaseous ozone spreads out quickly and tends to pool in low areas since it is heavier than air.

What airborne ozone does do is make people damned uncomfortable. As the ambient concentration goes up, ozone first becomes unpleasant, then a serious irritant, then quickly insufferable. The natural reaction of anyone to ambient ozone is to quickly get the hell away from it. While high ozone concentrations cause vomiting and extended exposure can cause pulmonary edema, such severe effects are rare; ozone gas is very noticeable and remaining in its presence requires a ruthless exercise of will. (Happily, victims of ozone overexposure have recovered completely, and no long-term health effects have been observed.)

The severe discomfort ozone gas creates is a significant issue for wineries- cellar workers really hate being around it. Employees can be made to wear ozone-absorbing masks or breathing apparatus when ozone is being used. But personal protection gear is a third rate approach to worker comfort and safety, for when ozone is used properly, the concentration of ozone gas in cellar air should never approach the discomfort level. Three factors will ensure this: thorough training of winery staff in standard operating procedures for ozone usage and safety; using only properly designed, correctly sized and carefully maintained ozone generating equipment; and appropriate testing and monitoring of ozone concentrations. We'll look at each of these now.

Training & Regulations

Training in ozone safety and standard operating procedures (SOPs) is essential. It should be thorough, repeated, and given in English and Spanish. Every worker in your winery should be completely trained when your ozone equipment is first installed. Every new worker hired thereafter should get the same training. All workers should periodically have refresher training so proper ozone usage and safety is completely understood. Your ozone equipment supplier should provide the ozone monitoring and generator operation training. Your supplier also should offer assistance to your safety staff in researching industry safety standards and developing winery- specific SOPs. If your supplier can't or won't provide this training and SOP assistance, find another who can and will.

Besides fostering the prudent and effective use of ozone, safety and SOP training will help ensure that government regulations for ozone use will be observed. But there are surprisingly few of these. OSHA sets maximum human exposure to ambient (gaseous) ozone at 0.1ppm for an 8-hour period, and 0.3ppm (a very irritable level) for any 15-minute period. In Southern California, wineries may be required by the Air Quality Management District to obtain a $100 permit when installing ozone-generating equipment. The Federal EPA lists ozone as a pesticide, but totally exempts it as "Generally Recognized As Safe" (GRAS) for use on and around food. The Federal FDA accepts ozone as an anti-microbial agent for use in contact with food and food processing equipment, requiring only that good manufacturing processes be followed. The Uniform Fire Code specifies some basic labeling and installation requirements for ozone generators producing more

than two pounds per day. There are no State agriculture or pesticide department regulations for ozone, probably because with ozone's short life you can't ship it, store it or spill it.

At some future time, it is possible that the OSHA or some other agency will require wineries to keep records and submit reports of ozone use-concentration produced, hours used, etc. Such regulations are now being considered for the bottled water industry. But even without a legal requirement, there are two reasons why monitoring and maintaining records of ambient ozone levels and cellar usage may be a smart strategy. First, this will continually keep ozone safety and SOPs in the minds of cellar workers. Second, such records could be useful as a liability defense if an employee were to say, 'I was exposed to ozone, I'm sick and I'm going to sue.'

Machine Design

Ozone must be made on-site at the winery, and used immediately. The equipment, which produces ozone, can be referred to by several different names. For simplicity, we'll use the term "ozone generators" for the machines that make ozone in wineries.

How do ozone generators work? First they compress ambient air, then separate out and concentrate the oxygen. A few generators make ozone by exposing the oxygen to ultraviolet light, but most run the oxygen through a high-voltage device called a corona, essentially 'lightning-in-a-bottle.' (Copy machines produce ozone because they use a corona to fix toner onto paper.) The generator then "injects" the gaseous ozone into water using negative pressure or a vacuum.

With just those parts, you'd have a generator, which would produce ozonated water. But without thoughtful design and some other key components, such minimal generators would be inefficient and unsafe, as some wineries discovered to their dismay. Recalls Tom Beard, whose company produces automated barrel washers and other barrel handling equipment, "The early machines weren't designed to stand up to winery use or to simple but likely mistakes. Some had plastic internal fittings. The simplest rookie mistake by a cellar hand-hooking it up to hot water at 160-170°-pretty much melted the inside of the machine. Other generators injected the ozone in horizontal pipes, where it quickly floated to the top. When the water came out of the spray wand or barrel washer, the ozone came out as a gas rather than being dissolved in the water."

Fortunately, continual development and competition have now improved the design of winery ozone generators. Paddles stir the water so the ozone dissolves more efficiently. Compressors and concentrators are sized to a certain production amount; so on-board pumps boost the f low rate of water through the generator to optimize its output. Larger mixing tanks are used to make more ozonated water available. Special features can create higher concentrations of ozone, drying and cooling the concentrated oxygen, chilling the incoming water, and using recirculating pipes to run the ozonated water repeatedly through the blending tank. (We'll talk more about concentration capacity below.)

Safety and Efficiency

There are better safety features too. Off-gas destruct units vent off and destroy (turn back to oxygen) any ozone, which is not fully dissolved in the water stream inside the generator. Waterproofing around high-voltage components and encasing

sensitive parts in rugged materials help generators stand up to cellar environments. Airtight connections within the generator and inside barrel washing equipment reduce ozone off gassing in the cellar. Dissolved ozone sensors and loggers measure and record the generators' output. Other sensors sound alarms or shut down the generator if there is too little incoming water, if the water is hot, or if vacuum leaks or ambient ozone are detected. Note however that these safety components may be sold as extra-cost add-ons to ozone generators rather than being standard features.

Lee Ditzler, Founder, Inventor, and VP of Sales at Novazone, Inc. offer several important notes on ozone generator usage and safety. "First of all, be sure your generator is properly sized for the amount of water you will be treating. Also, all ozone generators are very temperature sensitive-they need to be cooled to sustain their highest output. Where generators are air-cooled, warm air will significantly lower their output, so it's not a good idea to put generators outside in the sun, or even inside against a south-facing exterior wall. If you do decide to site your generator outside, be sure that the cabinet will stand up to weather. Remember, all ozone generators have high voltage internally, but they all are required by fire codes to have air vents. That's why it's important that your generator isn't hosed down or hit directly by high-pressure washers. Finally, good routine maintenance is really important. Don't skimp on this."

How Much Dissolved Ozone Can I Get?

As mentioned above, ozone generators should be appropriately sized for your expected usage. But whether you need 1 gallon per minute of ozonated water or 1,000 gallons per minute, what concentration of dissolved ozone should you be getting out of your generator? Before we answer that, we have to look at what you're putting into it- your cold water.

Any organic material in the water going into your generator will be the first thing attacked by the ozone. The consequence will be that the organics in water-bacteria, mold spores, yeasts, algae, protozoa, sugar, alcohol, vinegar, enzymes, etc.-will be removed, and the just-added ozone will be reduced commensurately. Dissolved iron and manganese in the water also will be removed, with equivalent reductions in ozone concentration. So if your water contains organics, iron or manganese, you might consider sending it through a separate ozone-based water treatment circuit before piping it into your ozone generator.

And if you feed it only organic-free, iron-free and manganese-free water, what is the best ozone concentration your generator should achieve? Again, that depends on physics. The amount of ozone, which can be dissolved in water, varies with temperature and pressure. Colder water will allow more ozone to be dissolved into it, and as we discussed earlier, high-pressure systems closed to atmospheric air can force lots of gas into solution. But as soon as the cold or pressurized water hits normal cellar temperatures and atmospheric pressure, the extra gas bubbles out of solution.

Thus, there are theoretical ozone saturation concentrations achievable by exotic generators in airtight laboratories, manufacturer test-benches or clean-room environments with special ventilation systems and required worker breathing apparatus. But what should be important to you is the practical, real-world ozone concentration as it comes out of the generator in your cellar. Some suppliers quote dazzling ozone production ratings for certain generator sub-components. Fine. Just be sure to know how much ozone actually will come out of the 'tail pipe' for you.

How much can you expect? A typical amount of ozone that cold water in most winery environments can hold is somewhere around 2.5-3.0 ppm. Higher concentrations, perhaps up to 8-10ppm, can be created inside generators using special concentrators, super-chilled water or recirculating systems.

And how much do you need? Ozone is called a 'C·T' material-everything it does varies with Concentration times Time. As the ozone concentration gets higher, the time necessary to produce a given microbial kill rate goes down. But ozone off gassing into ambient air also happens faster at higher concentrations. This means that high ozone concentrations are most efficient in closed sanitation systems like CIP, where the ozonated water doesn't come in contact with cellar air. High concentrations are least efficient in surface sanitation, where the ozonated water is sprayed through the air and splashes off of the surfaces being treated.

Observes David Mahaffey, winemaker and ozone expert at Carlsen & Associates, "There is a minimum amount of ozone needed for use in wineries. The generators work better if they produce more ozone. But they don't have to produce copious amounts, and there may be some down side to having a machine that is scaled too large, that is putting out more ozone than is really necessary for the task. Extra ozone is useful only if it can be applied to killing microbes. But if it is likely to be released as a gas into the air, then the extra amount serves no useful purpose and it is just an irritant for the people who have to work around it. But not to worry: 1.8-2.5ppm is more than enough."

Organism	Reduction
Trichophyton mentagrophytes (ATCC 9533)	6 log (99.9999%)
Salmonella choleraesuis (ATCC 10708)	6 log (99.9999%)
Staphylococcus aureus (ATCC 6538)	6 log (99.9999%)
Pseudomonas aeruginosa (ATCC 15442)	6 log (99.9999%)
Campylobacter jejuni (ATCC 33250)	4 log (99.99%)
Listeria monocytogenes (ATCC 7644)	4 log (99.99%)
Aspergillus flavus (ATCC 9296)	4 log (99.99%)
Brettanomyces bruxellensis (ATCC 10560)	4 log (99.99%)
*Escherichia coli** (ATCC 11229)	5 log (99.999%)

Test results on the antimicrobial power of ozonated water produced by two winery sized generators from DEL Agricultural. The National Sanitation Foundation (NSF) conducted the study. Chart courtesy of DEL Ozone.

Measuring Ozone

Ozone is a lot like chlorine in a swimming pool- you should never use it without measuring. Too little chlorine doesn't kill the bacteria and algae in the water. Too much irritates the swimmers. Since chlorine is invisible in the water, you must test the water to measure how much chlorine it contains. After testing, you use the chlorine measurement to calculate your additions. Ditto that for ozone.

What do you use to measure ozone concentration? There are electronic ozone meters, which provide instant, digital accurate readings. But these devices are both delicate and expensive. Your ozone equipment supplier for the initial calibration of your generator and for periodic re-validation best uses these. More practical are the automatic monitoring and data logging systems some suppliers build right into their ozone generators.

But the most useful ozone concentration testing is that done manually by cellar personnel. It's just like testing pool chlorine-a small water sample is taken, a reagent or test strip is added, and the concentration of the dissolved ozone is determined by colors. Ozone test kits are inexpensive, fairly accurate and ideal for use in cellar environments. All ozone equipment suppliers offer them.

Now you know what to test with. But knowing where to measure ozone concentration is essential to its effective use in the winery. Test results will be irrelevant if you measure ozone in the wrong place. But measuring it in the right place is simple. There are two key principles: First, measure the ozone concentrations where you use it. If you're sanitizing a closed CIP system, as we'll discuss in Part 2, you measure the ozone concentration inside or at the outlet of the generator. These locations give accurate readings because the atmosphere never enters the CIP circuit. But inside-the-generator measurements aren't accurate for open-atmosphere ozonated water uses like surface sanitation with a hose or wand or washing barrels with a spray ball. For these, you need to measure the ozone concentration of the water in ambient cellar air.

Here's how: Connect the output of your ozone generator as usual to the wand or spray ball, then use them to fill a 5-gallon bucket to overflowing. Take some water from the bucket for your ozone concentration testing. Using this procedure accounts for the natural loss of dissolved ozone from the water when it hits the atmosphere of your cellar, and more accurately shows the concentration of ozone, which actually touches the surfaces you're trying to sanitize.

John McClain of McClain Ozone teaches his clients that ozone concentration measurement is essential for effective usage. "When you do barrel rinsing, one of the things you need to know is 'What concentration am I running today?'. You need that to calculate your rinse time. You have to measure ozone in the water that's going to the barrel, not how many grams per hour of ozone your machine is theoretically capable of creating."

The Hach Company makes two ozone test kits. The kit above will measure dissolved ozone concentrations of 0.2-4.0ppm and is good for about 100 tests.

The kit below measures 0-15ppm ozone concentrations and is good for about 25 tests.

The second ozone measurement principle is fully applicable only to CIP systems, but it still has relevance for ozone use in open-air: measure the ozone concentration both before and after it hits the surfaces you're sanitizing. Remember that ozone instantly oxidizes any organics it touches, and the ozone itself is destroyed (turned back to oxygen) in that process. Let's say you want to eliminate all of the organic stuff on the inside surface of a tank-wine, juice, yeast, bacteria, whatever. After you clean the inside surface of the tank, you treat it with ozonated water. While organic material remains in the tank, all of the ozone in the water is consumed as the organics are oxidized, and the ozone concentration of the effluent water coming out of the tank will be zero. But eventually, all of the organic material in the tank will be destroyed. From then on, there is nothing left for the ozone to oxidize, so the effluent water will still contain dissolved ozone. In fact, the concentration of ozone in the effluent will be just a tad less than the concentration of the water going in. (Temperature and distance traveled will cause some dissolved ozone to be destroyed even without organics present. More will be consumed if the water is jostled through pumps, pipe and fitting junctions, just like shaking soda pop causes CO2 to bubble out.)

In fact, measuring residual ozone in effluent water is one way that complete sanitation is determined with closed, air-free CIP ozone systems; the presence of dissolved ozone in effluent means that no more organics remain and the surfaces touched by the ozonated water have been fully sanitized. (Microbial testing verifies this.) But with open-air use, off gassing of ozone into the ambient air can reduce the effluent concentration to near zero, even from very clean surfaces. When your open-air effluent water does contain a significant ozone concentration, it means that you're spraying wastefully too long, with excess ozone serving only to irritate your cellar staff.

What to Watch Out For

What should you think about when considering or using ozone in your winery? Be sure your system is well designed and serviced, get your people trained, have sensible expectations and use ozone knowledgeably. Winemaker Jeff Virnig at Robert Sinskey Vineyards sums it up realistically: "There are several things winemakers should understand going in. Ozone won't replace all of the cleaning agents in the cellar. Ozone output is dependent on the water going in, so check your water quality for high biologics or minerals like iron or manganese. Be very sure you know how much ozone you are getting, what your concentration is- using the 'sniff test' to see whether the ozone machine is working is not a good solution. Ozone machines can be temperamental, so get one that's cellar- tested tough. Watch the seals in your cellar, and make sure to replace anything that you think might be damaged with ozone-safe materials. Most of all, nail down your service arrangements. I have had a very hard time getting qualified service personnel to take care of my needs. Be sure that you get a good service contract and warranty in writing, and make very sure that the service person actually will be available to help you."

Health Effects of Ozone			
	Concentration (ppm)	Duration of Exposure	Health Effects
ACCEPTABLE ZONE	0.01-0.04	—	Odor threshold.
	>0.1	few minutes	Continuous headache, shortness of breath.
	0.1	—	Minor eye, nose and throat irritation.
	0.1	*8 hour average exposure limit*	
HAZARDOUS ZONE	0.25-0.5	2-5 hours	Reduction in lung function and the ability to do physical work (for persons with a history of heart or lung disease).
	0.3	*15 minute exposure limit*	
	0.4	2 hours	Reduction in lung function during moderate work for all persons.
	>0.6	1-2 hours	Chest pain, dry cough.
	1	1-2 hours	Lung irritation (coughing), severe fatigue.
	>1.5	2 hours	Reduced ability to think clearly. Continuing cough and extreme tiredness maybe lasting for 2 weeks. Severe lung irritation with fluid build-up.
	9	intermittent	Severe pneumonia (arc welders).
CRITICAL ZONE	*10*	*Immediately dangerous to life & health*	
	11	15 minutes	Rapid unconsciousness.
	50	30 minutes	Expected to be fatal.

This OSHA chart shows the health effects of various concentrations of ambient ozone gas.

This OSHA chart shows the health effects of various concentrations of ambient ozone gas.

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PART 2
Barrels and Beyond

THIS IS the second of a two-part series on ozone sanitation in wineries. In the Jan-Feb 2003 issue, the first article explained the properties of ozone, described how it is generated, and outlined winery safety and training issues. With that theory and background covered, we now can begin our exploration of winery uses for ozone, starting with a detailed look at barrel sanitation. From there, we'll examine other common applications like surface sanitation, clean-in-place (CIP) treatments for pipes, tanks and fill lines, and water treatment. We'll also look at newer uses including mold control in caves and cork storage rooms, building-wide ozone systems, and vineyard mildew and insect control.

Organic wines that do not contain sulfites have established a niche market of their own-one, which especially appeals to consumers who have asthmatic or allergic reactions to sulfites.

Barrel Sanitation

David Mahaffey of Carlsen & Associates describes barrel sanitation as the killer application for ozone. Says Mahaffey, "It's because there aren't any good alternatives- nothing but ozone can sanitize barrels without tainting the wood, as chlorine chemicals will, or without extracting something out of the wood. Proxycarb will kill microbes in wood, but it is a soda ash-based product, and it strips out oak essence. That's what we winemakers spend all of the money on oak barrels to get. "The best system for cleaning and sanitizing barrels is a two part process. The first part uses hot water at high pressure to dissolve tartrates and blast the barrel clean. The hot water also opens up the wood pores. Then the second stage is a cool rinse with ozonated water, which sanitizes and shrinks the pores in the oak. While larger wineries automate this process with barrel washing machines, smaller wineries do everything manually: Barrels are cleaned with hot water using a pressure washer, then a flashlight is used to illuminate the barrel to confirm that it is clean. After this, the cleaned barrel is rinsed with ozonated water from a hose connected to the ozone generator.

"We use ozone for barrel maintenance and keeping them neutral," says Felipe Martinez, Barrel Room Foreman at Kendall-Jackson's Oakville facility. "When a barrel is emptied, it gets rinsed on the floor, then it comes to our barrel washing machine. We do a minute and a half of hot water and three minutes with ozone. The ozone comes in with cold water, so besides sanitizing it cools down the barrels. It's working really well.

"Three factors-the type and age of the barrel, its microbial health, and the concentration of ozone in the treatment water-affect how long your ozone treatments should last. Higher concentrations of ozone in the treatment water will destroy a given level of microbes faster. And the larger quantities of microbes in problem barrels require longer treatments than the smaller quantities in healthy barrels. Says John McClain of McClain Ozone; "You just don't throw SO 2 at your

barrels. You just don't throw ozone at them either. Determining barrel rinse times is based primarily on the concentration of ozone in the water, and the age and the degree of contamination of the barrel. The more ozone you can get into saturation in the water, the faster your rinse time. For example, at10ppm, the rinse time for healthy barrel son a 4-head barrel washer is 30seconds. At 5ppm it would be one minute. "

Mahaffey goes further. "In general, if a barrel is deemed healthy and the wines that come out of it are untainted, a treatment time of one and a half minutes is sufficient to sanitize the barrel. This is with the typical 2.0-2.5ppm concentrations produced by ozone machines in most cellars. Treatment times are longer if there is a perceived problem with a barrel. For example, if a barrel has a small elevation in the level of 4-ethyl phenol (4EP), the indicator for Brettanomyces, then the wash time can be extended to 4-5 minutes. The same 4-5 minute treatment would be appropriate for a barrel with any other problem-Acetobacter, Lactoba-cillus, Pedicoccus, anything where the wine has shown some problems."

Continues Mahaffey, "If you have a significantly damaged barrel with very high 4EP levels, a barrel which you'd consider retiring but would like to save because it's still young, give it a 4-5 minute treatment on three successive days. I've also used these extended ozone treatments to bring tainted oak uprights and ovals back to health. Of course, not every barrel on death's door can be fixed-ozone is not a panacea or a silver bullet. But it's probably worth trying the three-successive-day treatment regime on any problematic barrel-you can always retire it afterwards if it is still unhealthy."

Thomas Chrisco, Production Manager at Kendall-Jackson's Oakville winery, echoes this. "With our problem barrels, we wash them good, leave them alone, wash them again, leave them alone. And we do this for three or four days. Our experience has been that this seems to work. Now, does it get rid of all of the Brett? No-you'll never do that. What we're doing is controlling the population-that's the goal."

Jon Johnson of Carlsen & Associates adds, "I don't tell people what to do-wineries need to establish their own SOPs. But I do tell them what other folks are doing, and I help and encourage them to do their own testing. You see, barrel treatment times can vary quite widely. The density of the wood, age of the barrel, and the amount of microbial presence is what determines how long is long enough. So experiment! The chemistry is out there to check for microbial levels, Brett, VA, etc. by swabbing and plating. See what you consider to be effective results for your own types of barrels with their unique microbial situation."

Mahaffey agrees. "Could higher ozone concentrations reduce the treatment time while still fully sanitizing the barrel? Possibly. But the only way to know for sure is to test."

How Effective Is Ozone in Barrels?

It's important to note that barrel sanitation with ozone is not barrel sterilization. Barrels have no discrete surface, more like a 4-5mm sponge, often with blisters. That amount of porosity provides far too many hidden nooks and crannies for ozone in any concentration or duration of treatment to completely eradicate all microbes. So ozone treatment of barrels is de-signed not to eliminate microbes, but to control them. This concept of microbial control is especially important when ozone is used to treat problem barrels, those with high populations of microbes

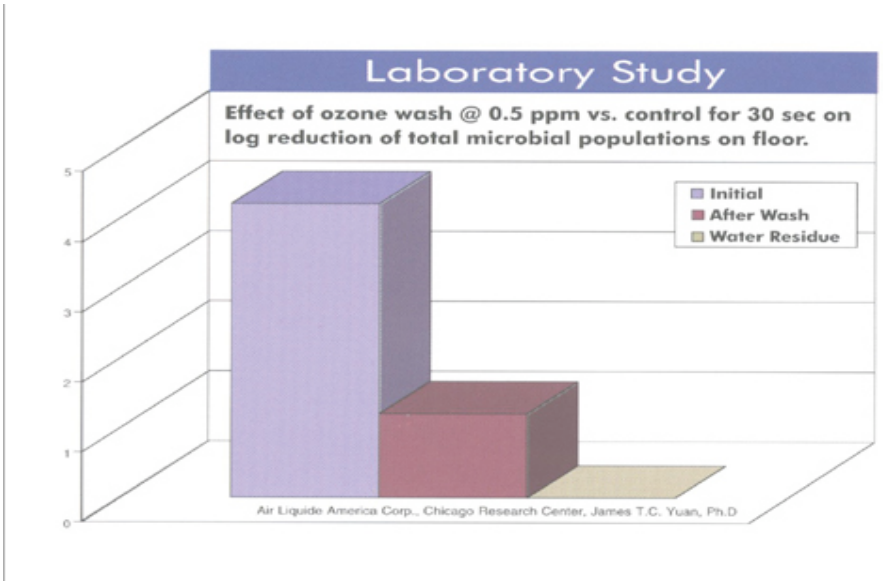
which produce off-flavors or cause wine spoilage. Three Factors - the type and age of the barrel, its microbial health, and the concentration of ozone in the treatment water - affect how long your ozone treatments should last. Higher concentrations of ozone in the treatment water will destroy a given level of microbes faster. The larger quantities of microbes in problem barrels require longer treatments than the smaller quantities in Healthy barrels.

Says Matt Lowe of DEL Ozone, "Wineries haven't required a huge amount of data to adopt ozone. Their acceptance has been based on colleagues' opinions that Brett is being controlled when it wasn't before. Winemaking is an art that requires real living organ-isms, so winemakers don't really want truly sterile barrels. They're looking for some level of control. And they're get-ting it."

Until very recently, there has been no scientific research on the effects of ozonated water on barrel micro flora or on oak flavors. But there is plenty of in-formal sensory evidence that winery ozone treatment does maintain and correct barrels health without degradation or loss of flavors from the oak. Recalls McClain, "When I first went to wineries advocating ozone, I was practically thrown out the door. That led to a whole lot of proving that ozone worked in barrels, and doing blind tasting of barrels to see that there was no impact. Now winemakers are believers."

Damian Parker, VP of Production at Joseph Phelps Vineyards, agrees. "Whenever we empty a barrel, we clean it on our Tom Beard machines, first with a hot-water wash of varying length, and then with a 1-minute ozone rinse. We do this every time, and we have close to 8,000 barrels. So I just laugh when I hear people say that ozone degrades the oak. I sure haven't seen it. But we only keep our barrels for five years. Maybe that's part of it."

Mahaffey concurs. "One of the first questions we had to answer was is ozone going to adversely affect barrels? We did those duo- and trio-tastings, and with experienced tasters we could not ascertain any difference in ozone treated barrels, even with extended treatment."



The graph above shows the effectiveness of ozone in the surface sanitation at a concentration of 0.5ppm. Taken from laboratory analysis of the DEL Ozone AGW-0500 by Air Liquide America Corporation. (Graphic courtesy of DEL Ozone.)

And now, laboratory science has begun to verify that ozone sanitation does indeed destroy spoilage microbes in oak while not affecting the desirable flavors imparted to wine. Last fall, two graduate researchers working under Dr. Erin Dormedy at California State University Fresno released their preliminary findings in studies of ozone treatments of oak. (Caveat: These two laboratory studies had not been formally peer-reviewed at press time, and both have yet to test ozone treatments in actual barrels.) Using French oak blocks supplied by Inner stave and an ozone generator from Piper Environmental Group, researcher Steve Marko simulated two-minute barrel treatments with 1, 5 and 10ppm ozone in water. He found that the ozone had no statistically significant effect on the oak's volatile aroma compounds, including vanilla, smoky, and toasty oak notes. (Marko's sensitive equipment did find tiny changes, including some increases, in the concentration of oak aroma compounds in the ozonated blocks, but these were likely due to the variability of the oak itself.) Meanwhile, researcher Nicolas Cantacuzene used a generator donated by DEL Ozone to treat 1cm oak blocks infected with Brettanomyces. With ozone gas treatments, the Brett organisms were destroyed on the surface and inside the blocks. Tests on ozonated water treatments had not been completed at press time.

But Tom Beard, whose automated barrel cleaning and sanitizing machines allow wineries to use ozonated water in the cold rinse step, is cautious. Says Beard, "We have rigged all of our elastomers and what not to stand up to the use of ozone. If our customers choose to use ozone, that's great; everybody I have spoken to who is using ozone with our barrel cleaning equipment is comfortable with it. But when wineries pay $300-700 for oak barrels, they're buying oak essence. If ozone reduces the lifespan of the barrel by negating, reducing or altering the oak essence, then you're not doing anybody any favors. The barrel may be clean, but if you diminish what the barrel contributes to the wine, that's a problem. Studies of ozone on oak are ongoing, but long-term results aren't in yet. Until they are, we'll be ozone compatible and won't denigrate its use. But we won't advocate it either."

Surface Sanitation

Many wineries sanitize surfaces with ozonated water. It can be sprayed directly on floors, drains, walls, destemmer-crushers, tanks (inside and outside), fruit bins and any other wet-table, non-rubber, non-fiberglass equipment or surface in a winery. Typically, the equipment is first cleaned, then ozonated water is used as a final sanitizing rinse. This very effectively reduces microbial loads on the surfaces. (See chart above.)

With repeated use, surface applications of ozonated water will remove biofilms. These are tough, resilient layers of microbes which adhere tenaciously to surfaces. Biofilms can be invisible or they can create a foggy haze on tank walls and cellar floors. First-time users of ozone sometimes measure post-treatment surface bacteria counts higher than pre-treatment counts. This is due to the destruction of the upper part of the biofilms by the initial ozone treatment, exposing the microbes below. Subsequent treatments quickly destroy those microbes, leaving the surface microbiologically sanitized as well as clean to sight and touch.

Phelps' Damian Parker is a fan of ozonated water for surface sanitation. "Ozone is not a panacea. It's not a cure-all. But if you use it, and you continually use it, your place will get cleaner and cleaner and cleaner. I don't just spray ozone once and the cellar is spotless. It doesn't work that way. Its effect is incremental but cumulative."

Continues Parker, "During harvest, using caustic cleaners is just a pain in the ass. So when the shoveling is done and the grunge has all been removed, we get inside the tank and do a simple hand-scrub with a telescopic pole and a white scrubby, but no cleaning solution at all. Then we rinse the tank out and put the ozone rinser in it for 5-10 minutes. You can tell by the off gassing when the tank is clean. Ten minutes is more than enough. Also, our older barrel room had a mold problem in 1996-black specs on all of the walls. We took a power sprayer and cleaned the ceiling and walls, then went back and ozoned everything. That room has stayed clean ever since; we just knocked the population down to nothing."

But off-gassing issues and the susceptibility of common cellar components to degradation by ozone often make ozone surface sanitation problematic. Lowe observes, "For some surface sanitation needs in wineries, ozone can replace current sanitizers. For others, ozone provides an additional point of intervention. However, if you spray ozonated water for 30-60 minutes in an enclosed space-a small room, a cave, a tank-it's unavoidable that some ozone gas will become noticeably present in the air." Johnson adds, "Before you wash anything with ozone, make very sure that everything that might be sprayed, intentionally or accidentally, is compatible with it. For example, mild steel hit with ozone will be forever changed. You don't want to chemically damage equipment or cellar paraphernalia."

Joe Mendez of Piper Environment Group agrees, adding, "Ozone is not a great cellar surface sanitizer because of the off-gassing issues. If you're trying to sanitize an inside wall, for example, the best thing you can do is just coat it with quaternary ammonia and go away. If you want to sanitize a pneumatic press, the ozone would degrade a rubber-based bladder. But if you do choose to use ozone, apply just the amount that you need. Anything extra, any ozone that you smell, doesn't do you any good."

CIP-Clean In Place

Wineries have all kinds of equipment which cannot be taken apart to be cleaned. To sterilize these tanks, runs of pipe, hoses, bottling lines, fillers, etc., they must be cleaned in place (CIP). First, the CIP equipment is cleaned with soap and/or surfactants and thoroughly rinsed. For the sanitizing step, ozonated water is recirculated through the equipment using a closed loop of pipe or hose. The circulated ozone reacts with organic material in the CIP equipment. When there are no organics left to destroy, dissolved ozone will be detectable in water leaving the equipment. To ensure that sterility has been achieved, ozonated water is left to recirculate a few additional minutes after the effluent concentration of ozone matches the output of the generator.

Without ozone, CIP sanitation must be done either by chemicals (usually chlorine or iodaphore solutions), requiring multiple rinses afterwards to remove noxious residues, or by heat (usually high-temperature water or steam), which is very expensive to produce and creates a danger for cellar workers. In contrast, ozone achieves CIP sanitation at low cost, at ambient cellar temperatures, and without chemical residues. Further, hot water or steam causes the expansion and contraction of welds, one of the biggest causes of line degradation and repair. Heat also can bake on materials inside the lines, making them more difficult to clean. Since ozone is used in cold water, it avoids these and other problems of heat-based CIP sanitation.

Oded Shakked, winemaker at J Vineyards and Winery, uses ozonated water in a CIP system. "Once a week during bottling, we sanitize our filler with chlorinated TSP. But the other four out of five days we don't use chlorinated cleaners. Instead, we sterilize the filler with ozone. We use hoses to connect the filler to our ozone generator in a closed loop, and we run the whole thing at the end of the day. Then we shut it off, and the next morning the systems ready to roll. It's pretty slick."

While bottling lines would seem to be ideal for ozone CIP sanitation, two issues usually make them problematic. First, the filters, fittings and seals in bottling lines often are made of ozone-degradable materials. Granted, these components can be replaced with ozone-resistant versions, but ozone-proof filters are generally more expensive. The other concern is nooks and crannies. Ozone dissolved in water will kill whatever it comes in physical contact with. But complex bottling lines often are rife with tiny hidden harbors, corners, cracks or voids. All of these are potential places for microbes to hide. Steam or high temperatures reliably reach these nooks-and-crannies, but ozonated water might not, even with lengthy circulation. (Gaseous ozone could potentially overcome this situation. See below.)

But McClain argues that "Numerous wineries are currently using ozone to sanitize their bottling lines, and have been successfully for an extended period of time Wineries have compared ozone and hot water, and reported ozone to be significantly better than hot water. What is important is that you get your lab personnel involved early to develop your SOPs for using ozone on your line and contact the bottling line manufacturer for their chemical CIP procedure. In fact, several bottling lines from the manufacturer can now be ordered with ozone CIP protocols."

Centralized Ozone Systems

When wineries rely on ozone so much that stationary ozone generators for barrel washing and ozone carts for CIP and surface sanitation aren't enough, the next step is to install building-wide ozone systems. McClain has installed centralized ozone systems at a number of wineries. He says, "Cakebread, for ex-ample, has bubble-free ozonated water on tap throughout their new winery. It's right there next to the hot and cold water at their crush pad. They can wash the crush equipment from that station. There also are taps for ozonated at cleaning stations in the winery, even up on the catwalks where they go to clean the tanks."

Ozone is an unstable molecule; warm temperatures and jostling travel through pipes cause it to de- compose to oxygen, as will sitting in pipes for extended periods of time (e.g. overnight). So centralized ozone systems must be carefully designed to control these factors so that proper ozone concentrations are available at all times and in all locations throughout the winery. Some systems may require flushing each morning to get freshly ozonated water to peripheral taps. Others can maintain a continuous circulation of ozonated water through the system. Still other central ozone systems are designed to serve multiple applications- barrel washing, surface sanitation, water treatment, etc.-with separately controlled loops.

Gaseous Ozone

Up to now, we have described winery applications using water with dissolved ozone. But ozone gas itself has interesting uses for wineries. One mentioned briefly above is CIP sanitation, since gaseous ozone will penetrate and sterilize the hard-to-reach nooks and crannies that ozonated water might miss.

Another, somewhat covert use for ozone gas is barrel sanitation. Some wineries disconnect their generator's gas-destruct unit during barrel treatments, leaving actual bubbles of ozone gas in the water stream. Inside the barrel, these gas bubbles can penetrate into crevices, around blisters, and into pores, nooks and crannies far better than ozonated water. This same effect can occur even without disconnecting the gas-destruct unit when using water with very high concentrations of ozone. When the concentrated ozone solution hits the barrel walls, ozone gas bubbles out naturally. This creates a 'cloud' of ozone gas and water vapor inside the barrel, which can penetrate deeper into the porous inner surfaces. Clearly, using ozone gas is a bad idea for manual washing of barrels in racks or on the cellar floor. However, it could work with well-sealed automatic barrel washers, especially those installed outdoors. But any winery choosing to use ozone this aggressively should take special care to establish sensible SOPs so that cellar workers' exposure to ozone gas will be carefully con-trolled and minimized.

Storage rooms and caves also can benefit from ozone gas treatment. Ozone gas can control the mold growth and sporulation fostered by the natural dampness of caves or the presence of volatile organics in barrel storage rooms. Corks stored in sealed rooms can be treated with ozone gas to re-duce cork taint from trichloroanisol (TCA). Ozone gas levels of 5ppm show excellent effectiveness. (The eight-hour worker exposure limit from OSHA is 10ppm.) But wherever ozone gas is used, serious engineering controls, air monitoring and SOPs must be maintained to prevent worker expo-sure to the gas.

McClain notes, "We've set up winery cork storage rooms which we treat with ozone gas for 30-90 minutes nightly. We turn the system on and have a f lashing light on the outside while the room is above 0.1ppm. We calibrated the system until the desired concentration is achieved and there is no remaining ozone in the room when workers arrive in the morning. If the room was empty, ozonating it for 15 minutes could leave residual ozone in the air the following morning. With 20 sacks of corks in the room, however, we can run ozone for an hour and there'll be no ozone remaining the next morning."

But water treatment is the most important winery use of gaseous ozone. Incoming water, especially water from wells or ponds, can be treated with ozone gas to remove microbes, organics, iron and manganese without residual flavor or odor effects. Wastewater also can be treated with ozone gas, allowing effluent to leave the winery devoid of any annoying odors, organic compounds (including alcohol) or microbes. However, Mendez cautions, "Be careful with very high bacterial or organic levels. This requires a lot of ozone, and high capital costs."

Ozone Frontiers

There are three wine industry applications where ozonated water isn't used now, but soon may be. One is long-term barrel storage, replacing SO 2 gas. It is theoretically possible to connect a daisy-chained circuit of empty barrels to an ozone generator in a CIP-like system. A continual, slow f low of ozonated water through the barrels would keep them hydrated and free of microbial contamination. Mendez also notes, "We're working on a similar sys-tem for safe, long-term barrel storage using ozone gas."

The second application is bottle washing. In Europe, where many wine bottles are recycled and reused, it is common for wineries to sanitize all bottles with ozonated water before they are filled. In the U.S., all bottled water containers and many soft

drink and food containers receive pre-bottling sanitary rinses with ozonated water, although this practice is rare in the wine industry. But health concerns, valid or not, may soon prompt a government near you to require that wine bottles be sanitized with ozonated water before filling.

The final 'frontier' application for ozone is out in the vineyard-control-ling mold, mildew and insects by spraying vines with ozonated water. The process involves hitting the vines with a real strong shot of ozone, in the 9ppm range. In addition to the hoped-for control of powdery mildew, the ozonated water treatments appear to be effective on leafhoppers and thrips, and especially on mites. Since ozone is non-residual and non-polluting, successful vineyard control of mildew would be a great boon to sustainable vineyard management, and the promising results from testing last summer ensure that research will continue in the coming season. However, thorough investigation will be needed on potential negatives, including effects on wine flavor and vine health, and especially on unwanted kills of desirable insects or destruction of beneficial microbes like soil microrhizae and native yeasts on berries.

In the O-Zone

Versatility with a punch! Ozone works on barrels, walls and floors, tanks and pipes, well and wastewater, caves, and even the vineyard. And that's just today's list. More uses are sure to spring up as creative cellar masters and ingenious vendors find new ways to harness ozone's strong, residue-free sanitizing power. Stay tuned!