



Enology Briefs

Volume 1, Number 1

INAUGURAL ISSUE

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It is my pleasure to introduce this first issue of Enology Briefs to our many friends and colleagues in the California wine industry. Through this bimonthly letter we hope to keep the industry better informed about research and teaching activities of the faculty in the Department of Viticulture and Enology here at U.C. Davis. This will be a cooperative effort between myself and the enology faculty. Contributions from graduate students and others will be included as appropriate.

Initially, one copy is being mailed to each wine company listed in the Wines & Vines Directory. Since this letter is primarily intended for winery technologists, I would extend a plea to the person receiving this first issue at each winery to assist me in refining our mailing list. Please forward to the individual in your firm you feel would most likely want to receive this letter regularly and also advise me if we should make any change(s) in our mailing. Persons employed by wineries, with multi-plant locations, who wish to be added to our mailing list, please forward your name and address to me at: Department of Viticulture/Enology, University of California, Davis, CA 95616.

In addition to teaching and research activities, I will be including items on: campus and departmental events, e.g. short courses, seminars, etc.; technical notes, both current and reviews of basic and applied information; and other items deemed of potential interest to our readers. In this regard, I earnestly invite reader suggestions, comments (positive & negative), and subjects you would like to have covered in future issues. Naturally, we would be very interested to learn about wine making problems and your ideas about topics for future short courses so that we can be more responsive to industry needs.

Your editor recognizes that there are a large number of newsletters, magazines, fliers and other periodical publications on grapes and wine that at times seem to inundate all of us. Of course, we want to read all of them to keep up-to-date and not miss important news or items on technical developments. Obviously, the problem is limited time. It is sincerely hoped that this letter of communication contains information of sufficient interest that it will not just become part of those growing stacks of paper variously labeled as "pending" or "need to read", etc. Should this occur early on I trust that recipients will let me know.

TECHNICAL NOTES

"Review of Basics on Sulfur Dioxide"

We are all well aware of sulfur dioxide and its critical role in wine quality. But, are we all using it effectively at all times, considering that wine composition and processing conditions are so variable? To assist us in evaluating this question is a brief review of the properties of SO₂ and the factors that circumscribe its action. This is the first in a series on this topic and is contributed by Mr. Clark Smith, Enology Graduate Student, U.C. Davis.

"The use of sulfur dioxide depends upon fruit composition and condition; general sanitation; and the kind of wine that it is desired to produce. Additions at the crusher favor wine yeasts over spoilage organisms and also inhibit oxidative or browning enzymes in the must. This dose is nearly completely bound during fermentation, chiefly by acetaldehyde. Thus, more needs to be added after fermentation to maintain sufficient free SO₂ to prevent spoilage.

Importance of pH. Wine pH is a key indicator of a wine's resistance to oxidation and microbial spoilage, and of course must be determined with a pH meter. Tartness, or titratable acidity (TA), does not correlate well with pH. Wines with a high TA can also have high pH. This occurs when the organic acid anions outnumber the total protons sufficiently that the dissociated proton fraction is small, as in wines of high potassium.

Attempting to regulate SO₂ levels through measurement of total SO₂ alone, or free SO₂ without reference to pH, is of little value. Free SO₂ in solution is distributed into three species as follows:



The relative abundance of these species is a function of pH, and the pKa's are the pH's at which adjacent species are present in equal amounts.

By far the most important form of SO₂ for antimicrobial effect is the undissociated or molecular portion of the free fraction. This is the only form in which SO₂ is volatile and can be smelled.

The approximate concentration of this species is given by:

$$\text{SO}_2(\text{m}) = \frac{\text{free SO}_2}{1 + 10^{(\text{pH} - 1.8)}}$$

Over the pH range of wines, this varies ten-fold for a given free SO₂ value as shown in the following table. Thus, 25 mg/L of free SO₂ may be quite excessive for some wines, ruining the aroma, while in others the same concentration may be totally inadequate and undetectable in the odor.

Distribution of free SO₂ at various pH's

ph	% SO ₂ (m)	% HSO ₃ ⁻	% SO ₃ ²⁻	free SO ₂ to obtain 0.8 ppm molecular SO ₂
2.9	7.5	92.5	.009	11 ppm
3.0	6.1	93.9	.012	13
3.1	4.9	95.1	.015	16
3.2	3.9	96.1	.019	21
3.3	3.1	96.8	.024	26
3.4	2.5	97.5	.030	32
3.5	2.0	98.0	.038	40
3.6	1.6	98.4	.048	50
3.7	1.3	98.7	.061	63
3.8	1.0	98.9	.077	79
3.9	0.8	99.1	.097	99
4.0	0.6	99.2	.122	125

The proper level of molecular SO₂ will vary with temperature, ethanol content, micro-nutrient levels, and sanitary conditions of the stored wine. For normal circumstances, 1.8 mg/L is recommended for white wine. In practice, SO₂ levels are kept lower in red wines. While it is doubtful that phenolic substances have much direct microbial toxicity, their affinity for oxygen and other nutrients may render red wines more microbially stable.

Although bound SO₂ has little or no effect on most yeasts and many bacteria, high concentrations of acetaldehyde-bisulfite complex seem to suppress malolactic fermentation even in the absence of significant free SO₂. The addition at the crusher should be restricted to 50 mg/L in wines designated to undergo malolactic, even though early on all free SO₂ would be bound by yeast fermentation. A level of 100 mg/L of bound SO₂ is often sufficient to suppress metabolism of malic acid by these bacteria. The influence of pH on this type of inhibition is unclear at present.

The wine's pH will also affect the SO₃²⁻ concentration. Although the proportion of sulfite is always quite small, it varies over the pH range of wine (note table above), and the loss of sulfite to sulfate through oxidation has a first-order dependence on the sulfite concentration. High pH wines not only require very high free SO₂, but also lose it quite rapidly. In such wines, SO₂ at any level is no substitute for methods which lower pH such as calcium sulfate addition or cation-anion exchange, depending on the scale of operation. If buffer capacity and TA are low, acid addition may lower pH sufficiently. Of the legally approved acids, tartaric gives the largest pH shift for a given TA rise, and cold stabilization will lower pH still further if the starting pH is below 3.6.

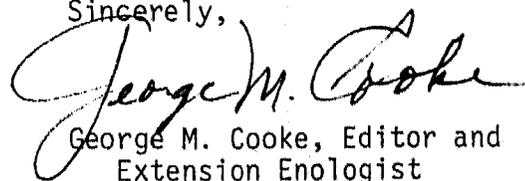
Conversely, procedures that are successful under quite low pH conditions, such as the trend toward eliminating SO₂ at the crusher in Germany, may not be appropriate with musts and wines of higher pH, which are more prone to oxidation and spoilage". More in the next issue (Ed.).

SHORT COURSES

February 20, 1982:	An Introduction to Fruit Wine Making	Davis
February 27-28, 1982:	Sensory Evaluation of Wine	Davis
March 8-12, 1982:	Statistical Quality Control for the Food Processing Industry: Methods/Techniques and Application/Decision Making	Davis
April ²³⁻²⁴ 16-17 , 1982:	Continuing Education in Enology: North Coast Counties	Santa Rosa

For further information on these courses contact James Lapsley, University Extension, University of California, Davis, CA 95616; 916/752-6021.

Sincerely,


George M. Cooke, Editor and
Extension Enologist

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Enology Briefs

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CAMPUS AND DEPARTMENTAL TEACHING SER. REC. - LIBRARY



At a time when enrollments in the California College and University systems have been approaching a "steady state", the Davis Campus of the University of California noted a 1.6% increase in total enrollments for the past Fall quarter. Fall, 1981 campuswide enrollment totaled 19,189 compared with 18,887 recorded for Fall, 1980. This set an all time record for UC Davis.

Likewise, student "majors" in viticulture and enology (undergraduate and graduate) continue at high levels, with about 180 recorded before the end of last year. This is the heaviest teaching load in the College of Agricultural and Environmental Sciences and is the equivalent of 42 students per faculty member. The average student/faculty ratio in the College is 22:1. No wonder some of the faculty are not as frequently visible in the industry as they were 10 and 15 years ago. Alas, many of us recall the era of the 1950's and early 1960's when viticulture and enology "majors" averaged between 15 and 30. More about faculty and students in issues to come.

WORDS OF ENCOURAGEMENT!

Your editor is most grateful for the many complimentary cards and letters readers have sent about the first issue of Enology Briefs. I would also appreciate receiving ideas and topics readers would like to have discussed in future issues. Also, a reminder for those wine industry members who are employed at a winery location other than the address as given in the Wines & Vines Directory, and who would like to receive Enology Briefs, please let me know so that you may be added to our mailing list. Write: George M. Cooke, Department of Viticulture/Enology, University of California, Davis, CA 95616, or Phone: 916/752-1906.

TECHNICAL NOTES

"Review of Basics on Sulfur Dioxide -- Part II"

Editor's Note: Part I of this series on sulfur dioxide in the first issue of Enology Briefs stimulated quite a few inquiries. Notably: In the table showing "Distribution of free SO₂ at various pH's", were the free SO₂ values listed in the right hand column determined by the usual Ripper method or by the vacuum aspiration procedure? The answer is neither; the values were derived by calculation using the equation given on the bottom of page 2, Issue #1. A second frequent question: What is the origin of the recommended

level of 0.8 mg/L molecular SO_2 ? Again, the article's author, Clark Smith, provides the answer: "This is based upon evidence [Beech, F. W., et al. 1979. Bull. O.I.V., Paris. 52(586):1001-1022] that this level of molecular SO_2 achieved a 10,000 fold reduction in 24 hours in the number of viable cells of *Brettanomyces* sp., certain lactic acid bacteria and other wine spoilage microorganisms". Briefly, the intended message in the first article, is that for SO_2 to be an effective antimicrobial agent, application rates must be determined in relation to pH!

In this issue, Clark Smith, U.C.D. Enology graduate student, continues with: "Sulfur Dioxide As An Antioxidant: The bisulfite ion species (HSO_3^-), whose concentration is relatively independent of pH in the wine range, protects wines from oxidation in various ways. It inhibits polyphenoloxidase browning reactions, scavenges H_2O_2 (formed enzymatically), stabilizes red color, and retards a whole series of non-enzymatic browning reactions by combining with intermediate compounds.

However, there are important limitations on the capabilities of SO_2 as an antioxidant. In particular, its reaction with molecular oxygen itself is very slow, on the order of months to deplete a saturated solution under wine conditions. It is therefore impractical for scavenging oxygen from wines exposed to air.

Ascorbic acid (or its isomer, erythorbic acid) reacts quickly with O_2 , but is also an important source of binding of bisulfite. Therefore its use should normally be restricted to bottling time. This is an effective strategem when the wine is sterile filtered and bottled aseptically so that a high molecular SO_2 in the bottle is not required.

Sulfur dioxide is also essentially ineffective in inhibiting the botrytis browning enzyme 'laccase'. Wines containing it will continue to brown by this reaction even after bottling. Pasteurization of the must can be used to prevent this type of browning.

Analytical Methods for SO_2 : Since it is quick, inexpensive, and sufficiently accurate and reproducible for most uses, the iodometric titration (Ripper) procedure is generally the analytical method of choice for determination of free and total SO_2 in white wines. If the shelf life of reagents is a problem, an iodate standard may be titrated instead of iodine, and an excess of KI added to the flask to convert it to I_3^- as it enters the flask. Alternatively, sodium thiosulfate (dried, weighed as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, dissolved, and titrated) may be used periodically to standardize the iodine titrant.

The Ripper method is poorly suited to red wines, where it is neither precise nor accurate. Iodine reacts with anthocyanins to give false and unpredictably high values. The endpoint is not sharp and is very difficult to see.

The vacuum aspiration procedure overcomes these difficulties. Both free and total SO_2 can be determined reproducibly if a condenser is employed to reflux the sample for the latter. However, these values do not represent the true free SO_2 because they include the portion loosely bound to anthocyanins; the antimicrobial effect of anthocyanin-bound species is presently unclear. A spectrophotometric method may be employed to estimate the actual free SO_2 value (A.J.E. & V. 1975. 26:25-29).

Whatever method is used, the free SO_2 is best determined at cellar temperature. The equilibria which exist with many binding species are quite temperature dependent.

Forms of Sulfur Dioxide: Compressed SO₂ in cylinders is the easiest and least expensive way for many winemakers to introduce SO₂ and does not increase K or Na ion content. It may be metered directly, or dissolved in water to make a saturated solution (≈5%).

Potassium metabisulfite (K₂S₂O₅) and potassium bisulfite (KHSO₃) are commonly employed, but should not be added after cold stabilization.

Sodium metabisulfite (Na₂S₂O₅) is too unstable for normal use, and often contains disagreeable impurities. The addition of sodium salts to wine should be avoided whenever possible; however, the use of sodium bisulfite to make small adjustments after cold stabilization may be countenanced for small-scale operations where liquid SO₂ may be less practical.

None of these salts is effective in a sterilizing or barrel-storage solution unless the pH is adjusted below 3. This may be accomplished by the addition of a roughly equivalent quantity of citric acid.

All forms by which SO₂ may be added to wine are subject to loss of potency over time. Elevated storage temperatures, moist conditions, and unsealed containers contribute to loss of strength. Some may even yield initial concentrations above theoretical purity. It is therefore advisable to monitor periodically the potency of these reagents.

Calculation of the Addition of Various Salts

$$\text{Grams of reagent to add} = \frac{\text{Increase in SO}_2 \text{ (mg/L)} \times \text{Gallons wine} \times K^*}{\text{Fraction of full potency} \times 1000}$$

*K values for various reagents: K₂S₂O₅ = 6.57; KHSO₃ = 7.10 and NaHSO₃ = 6.15." This is the final article on sulfur dioxide (Ed.).

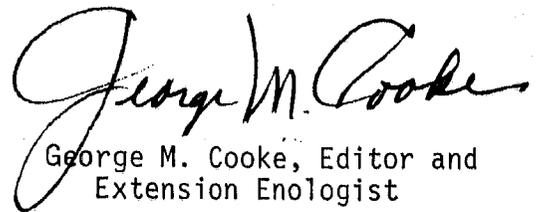
SHORT COURSES

1982

April 23-24	Continuing Education in Enology: North Coast Counties	Santa Rosa
April 24	Topics in Sensory Evaluation of Wine: Sparkling Wine and Cabernet Sauvignon	Davis
May 15	Topics in Sensory Evaluation of Wine: Chardonnay and Pinot Noir	Davis

May 18-19	Economics of Small Wineries	Davis
June 12-13	Introduction of Sensory Evaluation of Wine	Davis
July 13-29 (Tuesday & Thursday evenings)	Fundamentals of Wine Chemistry	Davis
August 14-15	Wine Microbiology	Davis

For further information on these courses contact James Lapsley, University Extension, University of California, Davis, CA 95616; 916/752-1906.


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