
SULFITES & WINE
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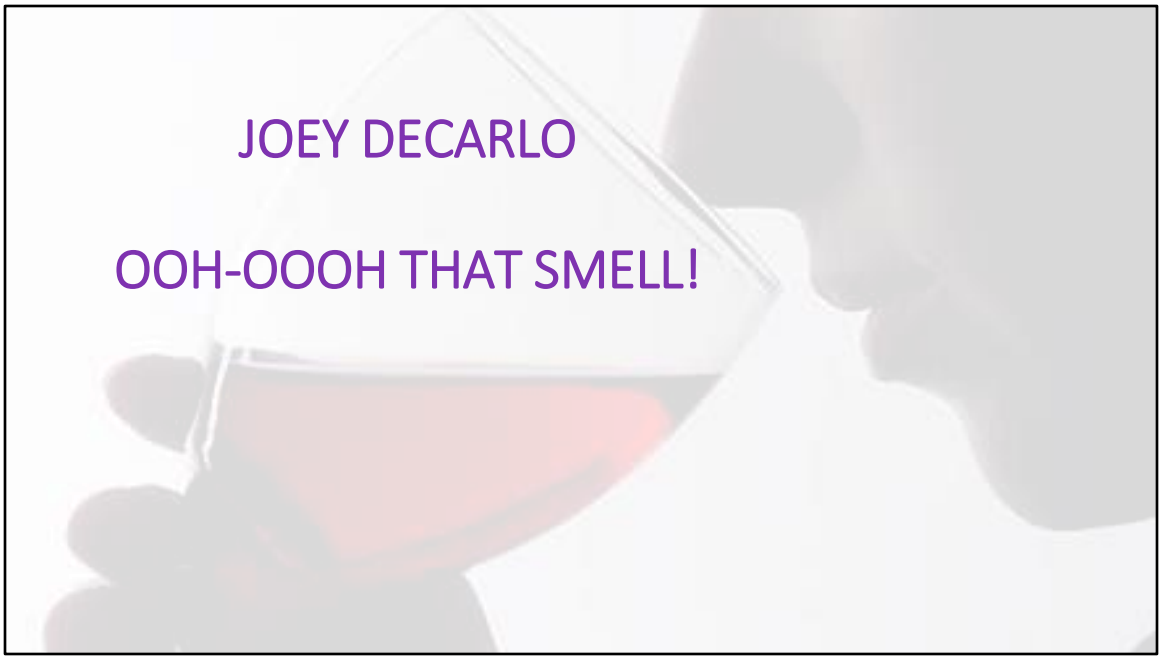
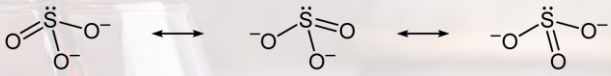
The PurpleFoot WineClub
Making Fine Wines Since 1971


JOEY DECARLO
OOH-OOOH THAT SMELL!

WHAT ARE SULFITES?

- SULFITES ARE CHEMICAL COMPOUNDS BASED ON SULFUR AND OXYGEN THAT CONTAIN A SULFITE ION SO32– (1 SULFUR, 3 OXYGENS, AND A -2 CHARGE.)



- Sulfites are good at binding with other compounds, which is why they are useful in winemaking. More on that soon.
- Typically added to wine as potassium metabisulfite, or K2S2O5 (or more casually, k-meta) in which it forms sulfur dioxide, or SO2.
- Ultimately, the SO2 is what matters to winemakers. It is a "sulfiting agent" that produces sulfites in wine.

WHY DO SULFITES MATTER IN WINE?

- CAN INHIBIT WILD YEASTS IN MUSTS
  - KEEP IN MIND THAT YEAST STRAINS DEVELOPED FOR WINE ARE TYPICALLY MUCH "STRONGER" AND MORE RESISTANT TO SULFITES THAN WILD YEASTS
- PROTECT MUSTS AND WINES FROM OXIDATION AND MICROBIAL SPOILAGE
- PRESERVES FRESHNESS AND COLOR
- ESSENTIAL FOR AGING WINES
- HIGH ENOUGH DOSE CAN GET RID OF AN INFECTION OR CUT A FERMENTATION SHORT. RECOMMENDED MORE AS A LAST RESORT.

BOTTOM LINE: IF YOU WANT TO CONSISTENTLY MAKE STABLE, HIGH QUALITY, AGE WORTHY WINES, THEN MANAGING SULFITES IS VERY IMPORTANT.

HISTORY OF SULFITES IN WINE

- IT'S DOCUMENTED THAT SULFITE USE IN WINEMAKING GOES ALL THE WAY BACK TO ANCIENT ROME, WHERE SUPPOSEDLY SULFUROUS CANDLES WERE BURNED IN AMPHORA, WHICH DEPOSITED SULFITES ONTO THE VESSEL WALLS, WHICH THEN WOULD HELP TO CLEAN THE TANK AND PRESERVE THE WINE.
  - ANCIENT GREEKS ALSO DID THE SAME, HAVING GREAT ACCESS TO VOLCANIC SULFUR.
- LATE MIDDLE AGES, STARTING DIRECT ADDITION OF SULFUR TO PRESERVE WINES.
- EARLY 1900S, WIDESPREAD DIRECT ADDITION TO WINE.

SULFITES IN WINE (PARTS PER MILLION) PPM = MG/L

- SULFITES IN WINE ARE REGULATED IN THE US TO A MAX OF 350 PPM.
  - EU MAX IS 210 PPM FOR WHITES AND 160 PPM FOR REDS
- MOST WINES HAVE LESS THAN THE EU MAX LEVELS.
- AVERAGE DRY REDS HAVE 50 - 80 PPM; WHITES TYPICALLY HAVE MORE (~100 PPM)
- IN THE US, OVER 10 PPM MEANS THE BOTTLE MUST SAY "CONTAINS SULFITES."
- "NO SULFITES" MEANS <1 PPM
- SULFITES ARE A MINOR BIPRODUCT OF FERMENTATION, SO IN TRUTH NO WINE WILL EVER HAVE EXACTLY ZERO SULFITES.
- "ORGANIC" MEANS NO ADDED SULFITES
- "MADE FROM ORGANIC GRAPES" MEANS UP TO 100 PPM ADDED
- FDA "GENERALLY REGARDED AS SAFE" (EXCEPT FOR RED MEATS, PRODUCE)

SULFITES IN FOOD

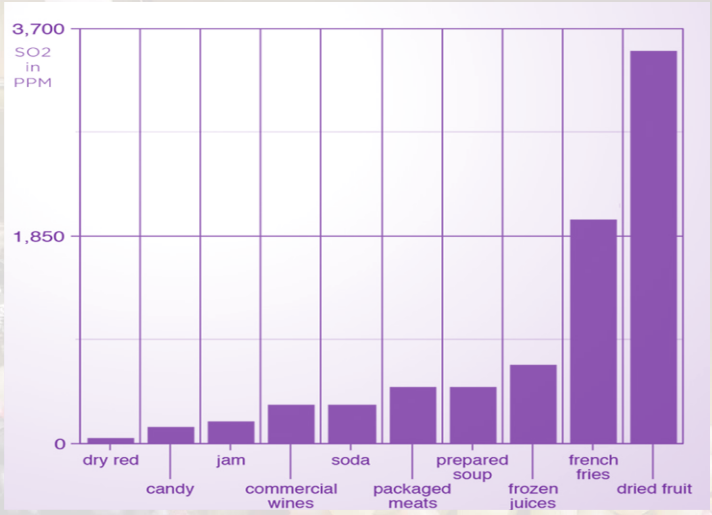
- USED IN MANY DIFFERENT FOODS AS A FOOD AND COLOR PRESERVATIVE.
- PROCESSED AND PREPACKAGED FOODS
- SEAFOOD
- POTATO PRODUCTS
- DRIED FRUIT
- BEVERAGES LIKE SODA AND JUICE

WINE VS. FOOD SULFITE LEVELS

AS IT TURNS OUT, THE RELATIVE SULFITE CONTENT IN WINE IS FAR LOWER THAN MOST FOODS THAT CONTAIN SULFITES.

WHEN SOMEONE SAYS THEY DON'T LIKE SULFITES IN WINE, ASK THEM IF THEY'VE EVER HAD FRENCH FRIES!

ESTIMATED 5% OF ASTHMATICS MAY HAVE SULFITE SENSITIVITY. HEADACHES ARE MOSTLY LIKELY DUE TO DRINKING TOO MUCH ALCOHOL AND TOO LITTLE WATER.



COMMON FORMS OF SULFUR IN WINE

- SULFUR, S
  - PRESENT IN PROTEINS
  - USED ON GRAPES TO PREVENT ROT
  - SOURCE OF SULFIDES
- SULFIDES
  - REDUCED SULFUR (OPPOSITE OF OXIDIZED)
  - H_2S (ROTTEN EGG)
    - YEAST AND BACTERIA REDUCE SULFUR IN THE ABSENCE OF OXYGEN
    - PRIMARILY DUE TO LACK OF YEAST NUTRIENT
    - DISSOLVED GAS - SPLASH RACK IMMEDIATELY TO DRIVE OFF THE H_2S GAS
    - COPPER TREATMENTS ARE A LAST RESORT
  - MERCAPTANS (CABBAGE, GARLIC, AND SKUNK)
    - FORMED WHEN H_2S REACTS WITH ORGANIC COMPOUNDS
    - NO GETTING RID OF THIS!
    - REASON FOR URGENT RESPONSE TO H_2S

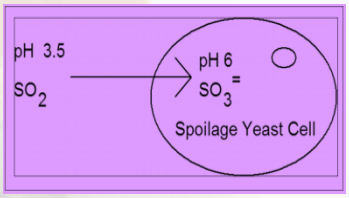
- SULFITES
  - OXIDIZED SULFUR
  - CHEMICAL SPECIES RESPONSIBLE FOR PROTECTION OF WINE
  - THREE SULFITE SPECIES IN WINE
    - SO_2 (GAS) – MOLECULAR SULFUR DIOXIDE (MOST IMPORTANT)
    - HSO_3^- (ION) – BISULFITE
    - $SO_3^=$ (ION) – SULFITE (INSIGNIFICANT AMOUNT AT WINE PH)

STATES OF SULFITES IN WINE

What you measure	Defined as	Why you care	Typical target or constraint
Molecular SO_2		Antimicrobial	Microbial stability: 0.5-0.8 mg/L (dry) or 1 mg/L (sweet) Sensory threshold: > 2 mg/L is irritating
Free SO_2	Molecular SO_2 + Bisulfite (HSO_3^-)	Antioxidant	Oxidative stability: 20-40 mg/L
Bound SO_2	Includes both strongly and weakly bound forms	Contributes to total SO_2; Can have minor antimicrobial activity. Weakly bound may eventually contribute to free SO_2 pool.	
Total SO_2	Free SO_2 + Bound SO_2	Regulatory, health issues	< 350 mg/L, TTB regulation (varies depending on country)

IMPORTANCE OF SULFITES IN WINE MAKING

- ANTI-OXIDANT
  - IN WINE, SULFITES DON'T REACT DIRECTLY WITH OXYGEN, O_2
  - REDUCES ACTIVITY OF OXIDATIVE ENZYMES
  - BINDS WITH PRECURSORS TO PREVENT OXIDATION
  - CAN REVERSE SOME EFFECTS OF OXIDATION
- ANTI-MICROBIAL
  - SO_2 – DOMINANT ANTI-MICROBIAL SPECIES
  - SO_2 CAN ENTER CELL WALL, IONIC SPECIES (HSO_3^-, $SO_3^=$) CANNOT
  - DISRUPTS ACTIVITY OF PROTEINS AND ENZYMES TO KILL CELL
  - YEAST AND BACTERIA SUSCEPTIBILITY VARIES BY SPECIES



IMPORTANCE OF SULFITES IN WINE MAKING (CONT.)

- EQUIPMENT SANITIZER
  - ANTI-MICROBIAL PROPERTIES OF SO_2
  - EFFECTIVE, LOW COST AND CONVENIENT
  - PREPARATION
    - POTASSIUM OR SODIUM METABISULFITE POWDER
    - 3 TSP PER LITER OR 3 TBSP PER GALLON (RULE OF THUMB)
    - EQUAL VOLUME OF CITRIC OR TARTARIC ACID (EXPLAINED SOON)
    - CONTACT ALL SURFACES AND LEAVE FOR AT LEAST 5 MINUTES
    - RINSE THOROUGHLY WITH CLEAN WATER
    - WARNING! – SO_2 GAS EVOLVED
      - RESPIRATORY IRRITANT
      - CAN TRIGGER ASTHMA ATTACKS
      - WELL VENTILATED AREA

Thanks joey. Well now that you know what they are and where they came from and what they do, I would like to go over how they work, and how to use them to help you make the best wine you can. Now, full disclosure and fair warning…

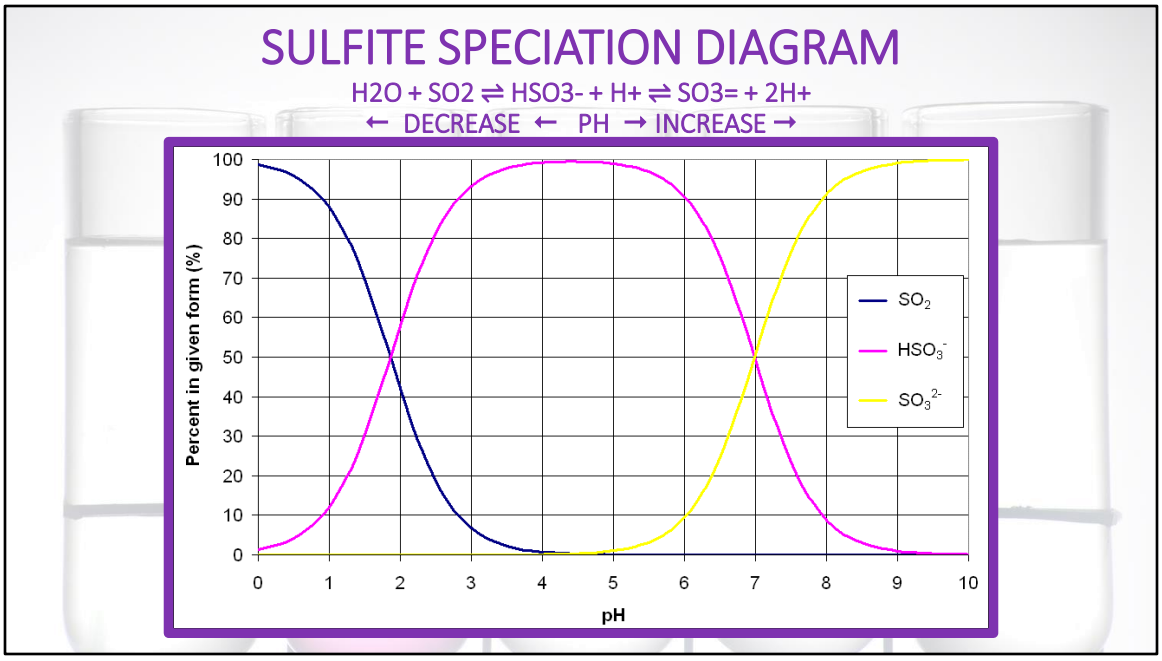
SULFITE EQUILIBRIUM

- SULFITE SPECIES EQUILIBRIUM EQUATION

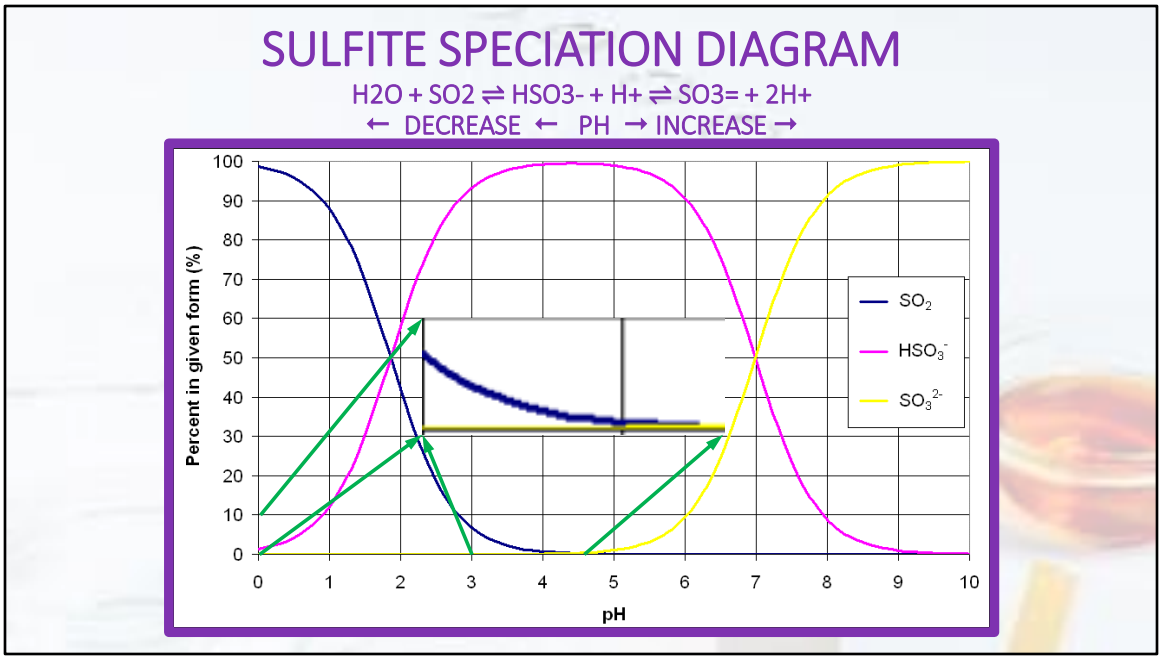
$$H_2O + SO_2 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^=$$

- "⇌" – BI-DIRECTIONAL REACTIONS AT EQUILIBRIUM OCCUR AT EQUAL RATES
- ADDITION OF ANY SPECIES SHIFTS REACTION AWAY FROM THAT SPECIES
  - ↑H^+ (ACID) = ↓PH = SHIFT TOWARD HIGHER % MOLECULAR SO_2
- LIKEWISE, REMOVAL OF A SPECIES (SO_2) SHIFTS TOWARD THAT SPECIES
  - CONSUMED SO_2 = SHIFT TO MORE SO_2 BUT DEPLETES FREE SULFITES

In chemistry, that relationship is show by an equilibrium equation. You can see here the three molecules, molecular sulfur dioxide, which is actually a dissolved gas, bisulfite ion, and sulfite ion that Joey introduced you to. When that kmeta, or whatever sulfite source you use, hits the wine, the "meta" part reacts with water and creates all these species. Notice that if we add the water, H2O, to the sulfur dioxide, SO2, we get two hydrogen atoms, one sulfur atom and three oxygen atoms. Now go across this, kinda weird equal sign, and we can see there are the same number of Hs, Os and Ss. So, about that weird equal sign. That's the chemistry way of saying this is an equilibrium reaction. At equilibrium, the reactions are happening in both, directions and at equal rates. So, at that point there isn't any relative change between the amounts on either side. But, If we add or subtract any species, they are no longer at equilibrium, and the reaction will shift to achieve a new equilibrium. The point being, there are certain conditions that can affect the relative amount of each side of the equal sign. So what is pH? pH is a measure of acidity or the basicity. To be specific, that little H+ you see up there is exactly what makes the wine acidic, and the more H+s, hydrogen ions, there are, the more acidic the wine is. That amount of acidity is what the pH number represents. So, if we add more acid, say tartaric acid it decreases the pH.



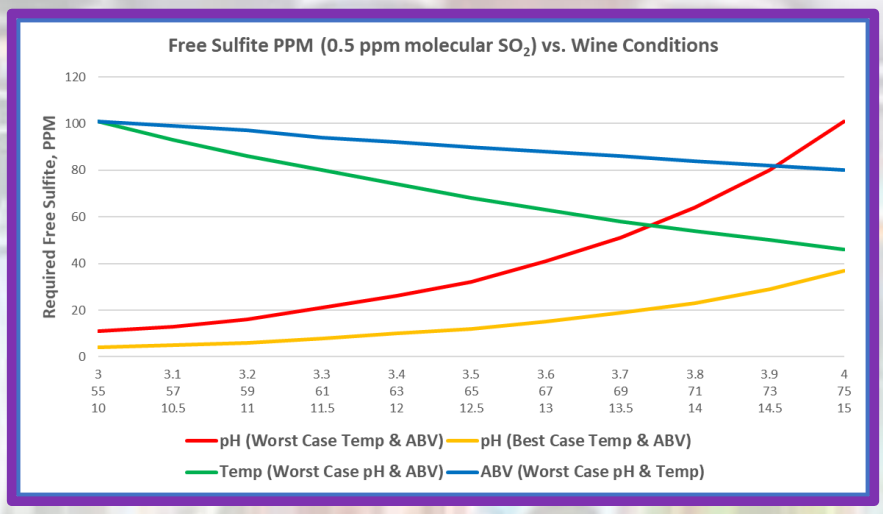
The speciation diagram here is a way to visualize that relative amount of the sulfite species at different pH values. The blue line is the percent molecular SO2. The pink line is the percent bisulfite. And the yellow line is the percent sulfite. So we know our wines are typically in the range of 3.0 to 4.5 pH. So lets just take 3.0. You can see that at 3.0 only about 7% of the three species is molecular SO2. Interestingly enough, there is a miniscule amount of that sulfite ion. The sulfite ion plays very little role in the protection of your wine. It is an antioxidant, but with so little and a very slow reaction, it's inconsequential. At a pH of 3.0, the bisulfite is the most significant species, at about 93%. So, lets focus in on the area of this chart that we winemakers care about.



So here's what your wine pH range looks like from 0 to 10 %. So for the all important molecular SO2 only ranges from essentially zero at pH 4.5, to about 7% at pH of 3.0. But it shows that the percentage of molecular SO2 does increase with decreasing pH. More importantly, the molecular SO2 decreases to nil by a pH of 4.5. Since molecular SO2 is the primary antimicrobial species and a contributor to antioxidation, this means that at pH of 4.5 there is very very little protection for your wine. Interestingly, pH isn't the only condition that has an impact on that equilibrium, therefore the amount of SO2 and the protection. On top of that, alcohol, while it doesn't effect the equilibrium, it does have an antimicrobial effect on the protection of your wine. So how big of an effect do these three conditions have on the amount of sulfite we are dealing with?

CONDITIONS AND SULFITE EFFECTIVENESS

(DO NOT USE AS A LOOKUP CHART. USE A FREE SULFITE CALCULATOR.)



This chart is for comparison purposes only. This shows the amount of sulfite you would be required to add based on the pH, temperature and %ABV, to get to the recommended amount of molecular SO2 of 0.5 ppm (more on that later). I've picked the typical range of the three we tend to deal with. pH 3 – 4, temperature 55 – 75, and %ABV 10 to 15. First, pH obviously has the largest impact. These three also impact each other. So if you take the case of temp and abv, 55 and 10, you see the required free sulfite has a very large range, more than twice the others. At the best case temp and abv, 75 and 15, you can see their additional contribution over the range of pH. We can also see that abv has an effect but it the smallest of the three. Temperature has a fairly significant effect, about half that of pH. Those two trends are based on the worst case of the other two. That's why they are so high on the chart. Now that we (hopefully) have an idea how our winemaking conditions effect the ability of sulfite in protecting our wines, in the process of managing sulfites, the first thing we need to know is how much free sulfite is actually in our wine. We will need to know that to be able to figure out how much we have to add to get us to that just enough level.

HOW MUCH FREE SULFITE DO WE HAVE?

ANALYTICAL METHODS

GENERALLY NOT RECOMMENDED

- TEST STRIPS
  - COLOR COMPARISON
  - COLOR INTERFERENCE WITH RED WINES
  - LOW ACCURACY
  - LOW DIFFICULTY
  - LOW COST
- TITRETS
  - RIPPER METHOD IN A VIAL
  - RECOMMENDED FOR DRY WHITE WINES ONLY
  - ACCURACY (MEDIUM WHITE), (LOW RED)
  - LOW DIFFICULTY
  - LOW COST
- RIPPER METHOD
  - TITRATION WITH IODINE AND STARCH INDICATOR
  - LAB EQUIPMENT/KIT REQUIRED
  - COLOR INTERFERENCE WITH RED WINES
  - MEDIUM-HIGH ACCURACY (CAN OVER-ESTIMATE)
  - MEDIUM DIFFICULTY (ONCE LEARNED)
  - MEDIUM COST

RECOMMENDED

- AERATION OXIDATION
  - ACID/BASE TITRATION FOLLOWING AERATION/OXIDATION
  - LAB EQUIPMENT/KIT REQUIRED
  - GOOD FOR BOTH RED AND WHITE WINES
  - HIGHEST ACCURACY
  - MEDIUM DIFFICULTY (ONCE LEARNED)
  - MEDIUM COST
- VINMETRICA SC-100A, SC-300
  - TITRATION FOLLOWING REAGENT ADDITION
  - EQUIPMENT KIT REQUIRED
  - GOOD FOR BOTH RED AND WHITE WINES
  - HIGH ACCURACY
  - LOW DIFFICULTY
  - HIGHER COST
- VIDEOS OF SOME METHODS COMING SOON TO PURPLEFOOT.ORG

HOW MUCH FREE SULFITE DO WE NEED?

- BOTTOM LINE – ADD ENOUGH SULFITE, AT YOUR STORAGE CONDITIONS (PH, TEMP, %ABV), TO BRING THE MOLECULAR SO_2 CONCENTRATION TO THE RECOMMENDED LEVEL PLUS ESTIMATED EXCESS FOR BINDING AND OXYGEN UPTAKE
- REDS – 0.5 MG/L MOLECULAR SO_2
- WHITES – 0.8 MG/L MOLECULAR SO_2
- DO NOT EXCEED 0.8 MG/L IN A SINGLE DOSE UNLESS THERE IS A CRITICAL ISSUE THAT MUST BE DEALT WITH – DETECTABLE BY SENSITIVE TASTERS
- NEVER EXCEED 2.0 MG/L – DETECTABLE/IRRITANT FOR MOST TASTERS
- SULFITE CALCULATORS – DETERMINE HOW MUCH YOU NEED TO ADD
  - ONLINE CALCULATOR (PH, TEMP, %ABV)

    WINEMAKER MAGAZINE - SULFITE CALCULATOR
  - STEVE KROLL SPREADSHEET CALCULATOR (PH) – PURPLE FOOT WEBSITE
  - PURPLE FOOT FACEBOOK

HOW DO WE ADD SULFITE TO OUR WINE?

- POTASSIUM METABISULFITE POWDER
  - ADDED TO WINE BY WEIGHT
  - 57.6% AVAILABLE SULFITE
  - COMMONLY USED FOR MOST WINE MAKING VOLUMES AND EQUIPMENT SANITIZATION
  - MUST DISSOLVE IN WARM WATER BEFORE ADDING TO WINE
    - DON'T ADD POWDER DIRECTLY TO WINE/JUICE
    - WON'T DISSOLVE COMPLETELY OR PROVIDE THE EXPECTED FREE SULFITE
- SODIUM METABISULFITE POWDER
  - ADDED TO WINE BY WEIGHT
  - 67.4% AVAILABLE SULFITE
  - EFFECTIVE, LOW-COST EQUIPMENT SANITIZER
  - NOT A GOOD WINE ADDITIVE DUE TO SALTINESS AND HEALTH CONCERNS
  - MUST DISSOLVE IN WARM WATER BEFORE ADDING TO WINE
    - DON'T ADD POWDER DIRECTLY TO WINE/JUICE
    - WON'T DISSOLVE COMPLETELY OR PROVIDE THE EXPECTED FREE SULFITE
- CAMPDEN TABLETS
  - ADDED TO WINE BY FRACTION OF TABLET
  - 44% AVAILABLE SULFITE PER TABLET
  - SIMPLE MEASUREMENT AND DELIVERY FOR SMALL WINE VOLUMES
  - SMALLEST EFFECTIVE MEASUREMENT = ¼ TABLET
  - BINDERS/FILLERS USED TO FORM TABLET
  - MUST CRUSH TABLET AND DISSOLVE IN WARM WATER BEFORE ADDING TO WINE
- 10% SULFITE SOLUTION
  - QUICKER AND EASIER TO ADD TO WINE BY VOLUME
  - DON'T HAVE A PRECISE SCALE
  - LARGE NUMBER OF ADDITIONS

HOW DO WE MANAGE SULFITE CONSUMPTION?

- BINDING
  - YOUNG, TURBID, SWEET, RED WINES = MOST BINDING
  - CLEAR, DRY, WHITE WINES = LEAST BINDING
  - BINDING DECREASES AS WINE BECOMES MORE CLEAR, MORE DRY, MORE BOUND
  - ADD EXCESS SULFITE BASED ON ESTIMATED BINDING AT EACH ADDITION
  - RESEARCH RULES OF THUMB % EXCESS BASED ON YOUR STYLE AND STAGE OF WINE
- OXYGEN UPTAKE
  - PROCESSING OPERATIONS: RACKING, TRANSFERRING, AGING, FILTERING, BOTTLING
  - REQUIRES MORE SULFITE TO PROTECT AGAINST OXIDATION
  - DIFFICULT TO PREDICT AMOUNT OF UPTAKE
  - MINIMIZE EXPOSURE TO AIR DURING PROCESSING
  - MINIMIZE HEADSPACE AFTER AF BY TOPPING UP AS MUCH AS POSSIBLE
  - ENSURE AIRLOCKS AND CLOSED OPENINGS HAVE A GOOD SEAL - POSITIVE PRESSURE

HOW DO WE MANAGE SULFITE CONSUMPTION? (CONT.)

- Purging headspace and vessels with "inert" gas
- For headspace, topping up is most important!

♦ ARGON
- HEAVIER THAN AIR – WON'T DISAPPEAR ABOVE THE WINE
- NOT SOLUBLE IN WINE – WON'T DISAPPEAR INTO WINE
- LESS READILY AVAILABLE
- HIGHER COST

♦ NITROGEN
- SLIGHTLY LIGHTER THAN AIR
- WILL MIX READILY WITH AIR – DISTURBING BLANKET
- NOT SOLUBLE IN WINE– WON'T DISAPPEAR INTO WINE
- READILY AVAILABLE
- LOWER COST

♦ CARBON DIOXIDE
- HEAVIER THAN AIR AT SAME TEMPERATURE AND PRESSURE
- SOLUBLE IN WINE – WILL DISAPPEAR INTO WINE
- READILY AVAILABLE
- LOWER COST

♦ WINE PRESERVE
- BLEND OF GASES
- IN AN AEROSOL CAN
- VERY LOW VOLUME
- GOOD FOR OPEN BOTTLE AND HEADSPACE
- HIGH COST

♦ BEER GAS
- BLEND OF NITROGEN AND CARBON DIOXIDE
- TYPICALLY USED IN BEER STORAGE/DISPENSING
- CAN BE USED WITH WINE
- HIGHER COST

SULFITE MANAGEMENT SUMMARY

1) HOW MUCH FREE SULFITE DO WE HAVE?
   - ACCURATE FREE SULFITE ANALYSIS
2) HOW MUCH FREE SULFITE DO WE NEED?
   - FREE SULFITE CALCULATOR
3) HOW DO WE ADD SULFITE TO OUR WINE?
   - SULFITE SOURCES
4) HOW DO WE MANAGE SULFITE CONSUMPTION?
   - WITH DILIGENCE AND CARE!

SULFITE MANAGEMENT SUMMARY (CONT.)

- OVERALL MANAGEMENT TO ENSURE CONTINUOUS PROTECTION
  - MOLECULAR SO_2 IS KEY!
  - MOLECULAR SO_2 REQUIREMENT IS A FUNCTION OF PH, TEMPERATURE AND %ABV, AT LEAST PH SHOULD BE USED
  - TEST AND ADJUST EVERY THREE MONTHS OR MORE OFTEN
  - TEST AND ADJUST BEFORE/AFTER EVERY PROCESSING EVENT
  - TEST AND ADJUST AS LAST STEP BEFORE BOTTLING
  - PURGE VESSELS BEFORE PROCESSING STEPS
  - OVERDOSE BEFORE/AFTER PROCESSING STEPS FOR OXYGEN AND BINDING
  - OVERDOSE BY 10 – 20 PPM AS THE LAST STEP BEFORE BOTTLING
  - PURGE BOTTLE HEADSPACE WITH PRIOR TO CORKING
  - DON'T LET YOUR FREE SULFITE DROP BELOW OR ADJUST BELOW 25 PPM

SOURCES

- HTTPS://YOUTU.BE/MHPOIQUVKXY
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- SULFUR DIOXIDE.PDF