

PREPARATION OF WINE ANALYSIS SOLUTIONS

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SCOPE OF DISCUSSION

Wine (including juice and must) analysis for amateur winemakers typically consists of determining pH; TA (titratable acidity); sugar (brix); and sulfur dioxide (free, total, or both). To perform these tests, the winemaker requires appropriate equipment and specific chemical solutions of known strength. It is the purpose of this paper to describe the preparation of solutions required for these tests.

METRIC SYSTEM: BASIS FOR ALL TESTS AND SOLUTIONS USED

All tests involving chemical analysis mentioned above are routinely conducted through utilization of equipment and procedures which employ the metric system. The English system of measurement (pounds, ounces, etc.) *does not* lend itself to reasonable or intuitive procedures for these tests, for reasons which will become evident as we describe the various analyses utilizing the metric system.

PREPARATION OF WEIGHT/VOLUME SOLUTIONS (w/v)

A number of solutions available for our use (as well as solutions we may wish to prepare), are solutions expressed by *weight percent*. For all water solutions, this is further taken as a *weight percent per unit volume (w/v)*. This is where the metric system comes into play. In the metric system, by definition, a *liter* of water (or *1,000 milliliters*, typically expressed as *1,000 ml*), weighs *1,000 grams*, or *1 kilogram*. A single *milliliter (ml)* weighs *1 gram*. Now: anytime we have a weight % solution, *for our purposes* whatever volume of solution we measure (*in ml*) will weigh that amount in grams, and the total amount of active ingredient will be that weight in grams (from the volume) multiplied by the weight % of the active ingredient specified on the label. Example: We have purchased a 37% solution of reagent grade hydrochloric acid which we need to dilute to 5%. How much 5% acid can we prepare from 100 ml of concentrated acid?

100 ml of 37% HCl (hydrochloric acid) weighs 100 grams
100 grams x 37/100 = 37 grams active HCl

We then use the formula

$$\begin{aligned}\text{Adjusted total volume of solution} &= \frac{\text{weight of active ingredient}}{\% \text{ solution desired (as decimal)}} \\ &= \frac{37}{0.05} = 740 \text{ ml total volume at 5\%}\end{aligned}$$

Thus we must add our 100 ml of 37% hydrochloric acid to 640 ml of additional water (740 ml total).

PREPARATION OF VOLUME/VOLUME SOLUTIONS (v/v)

When the active ingredient to be diluted with water is a liquid, we have a simple *volume/volume (v/v)* solution. For example, to prepare the commonly used "1 + 3" sulfuric acid solution from concentrated sulfuric acid, simply add (*see safety notes regarding sulfuric acid on page 4!*) 1 part (by volume, such as 250 ml) concentrated sulfuric acid to 3 parts (by volume, in this case 3 x 250 ml = 750 ml) distilled or deionized ("d/d" water, used throughout this paper) water. (NOTE: This example is for v/v solution illustration purposes only. I don't recommend keeping concentrated sulfuric acid in most households, especially those with children).

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MOLARITY AND NORMALITY {MOLAR (M) AND NORMAL (N) SOLUTIONS}

These terms can be confusing to non-chemists. Their use relates to describing a solution concentration that specifies, in simplest terms for explanation purposes, the *relative number* of molecules or ions of the active molecules or ions in question, *instead of* a weight percentage.

Rather than taking one or more detailed pages to explain the derivation and relevance of molarity and normality at this point, I've decided to just specify the proper quantities of the commonly used chemicals in typical solution strengths. For those who plan to prepare any of these solutions and would like additional background, please see the pages 5-7 of this paper.

| CHEMICAL | GRAMS/L | M | N | REMARKS |
|---|---------|--------|--------|--|
| sodium hydroxide (NaOH) | 41 | 1.0 | 1.0 | |
| sodium hydroxide (NaOH) | 2.73 | 0.0667 | 0.0667 | See below ¹ |
| potassium hydroxide (KOH) | 56 | 1.0 | 1.0 | |
| sodium thiosulfate (Na ₂ S ₂ O ₃) | 15.81 | 0.1 | 0.1 | I ₂ primary standard |
| sulfuric acid (H ₂ SO ₄) | 10.0 | 0.1 | 0.2 | See below ² |
| iodine (I ₂) | 12.9 | 0.1 | 0.1 | For Ripper SO ₂ test ³ |
| potassium acid phthalate | 20.423 | 0.1 | 0.1 | Primary standard |
| potassium bitartrate | 9.4 | 0.05 | 0.05 | pH standard ⁴ |

¹ 0.0667N sodium hydroxide directly yields the (tartaric acid) TA. For example, if 6.35 ml of 0.0667N NaOH were required to neutralize 5.0 ml of wine to pH 8.2, the TA of the wine would be 6.35 grams/liter as tartaric acid.

² While sulfuric acid is a liquid, it cannot be measured in ml for this use in a graduated cylinder or other measuring vessel! It must be weighed, in grams, preferably in a borosilicate (Pyrex) beaker. When transferring the acid to water in a volumetric flask, add *SLOWLY* using the procedure below. As some sulfuric acid will remain on the inside beaker wall, rinse the beaker wall 4 or 5 times with additional bits of distilled/deionized water and add these rinsings to the volumetric flask.

³ The amount of iodine specified is correct for solutions of this strength. However, the Ripper iodine solution requires an additional ingredient (potassium iodide) for completion prior to use.

⁴ The pH of this solution at 25°C (77°F) is 3.55. This is well with the range of wine pH values, especially reds, and is useful as a meter check.

PROCEDURE: In all cases above, chemical weights *in grams* should be accurately weighed and dissolved in 600-800 ml distilled/deionized (d/d) water in a 1 liter volumetric flask (*see remarks about distilled water in final section*). When fully dissolved, add additional d/d water to bring volume to exactly 1 liter (*use a fine tipped wash bottle for the final amount*). Mix in the final water by inverting and shaking gently several times. That's it!

NOTE: You may wonder why a number of chemicals used in some standard procedures are not included here (such as starch; hydrogen peroxide; potassium iodide; phenolphthalein; and potassium metabisulfite). The reason is that these particular materials are normally used in *weight % (w/v)* solutions, OR are added (such as the Ripper potassium iodide) in excess or a specified weight amount.

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IMPORTANT NOTES (I hate to do this, but. . . .)

1. For any standard test solutions you plan to prepare, use the most accurate measuring containers and appropriate equipment possible. Any inaccuracies will only be compounded by successive compromises. For measuring liquids, following is the order of preference: volumetric flasks; measuring cylinders; measuring beakers. For TA and SO₂ determinations, a 10 ml buret is more accurate than a 25 ml buret. For weighing, use the most accurate balance or scale available, and use the full inherent accuracy of the unit employed. For pH meters, units measuring to thousandths of a pH unit are preferable to units measuring to hundredths (though the latter are certainly adequate for our purposes); the latter are far preferable to units measuring to tenths of a unit.
2. CHEMICALS: Within reason, but especially for titrations, obtain the purest form of the chemical available. In order of purity, these are: (1). Analytical Reagent Primary Standard: An ultra-pure grade that's too expensive to justify for our needs. (2). Analytical Reagent, ACS: The purest grade normally available, certified to meet standards set by the ACS (American Chemical Society). (3) C.P. or Chemically Pure: The best grade that falls short of meeting ACS standards. Less common now than 10-20 years ago. (4). USP: Typically a grade more or less equivalent to C.P., that meets standards for food use and specs published by the U.S. Pharmacopeia. (5). Lab Grade: A suitable grade adequate for wine analysis needs. (6) Commercial or Technical Grade: For some products, adequate for our use. Not all grades of all chemicals are normally available.
3. DISTILLED/DEIONIZED WATER: Here's a real can of worms. If you buy your "distilled" water, as I do, you may assume anything that says "Distilled Water" on the label will do. Unfortunately - not so! READ the label. It should say "steam distilled," "deionized," or "reverse osmosis". Over the last year I've been checking labels of so-called "Distilled Water" gallon bottles in supermarkets, drug stores and discount stores. What I frequently find is a "Distilled Water" label followed by: Source: deep well; artesian well; high quality municipal supply; or some such source which, while possibly fine for many uses, can *not* be used as distilled water. The two brands I've found that are truly steam distilled (distilled is best - better than deionized or reverse osmosis) are Crystal Lake and Arrowhead, both found at Rite Aid; the latter is also found at Safeway and possibly other stores. An acceptable deionized or RO water is Safeway's "Purified".
4. SAFETY AND SUITABILITY: When handling strong alkalis (caustics) such as sodium hydroxide beads or pellets, always wear at a minimum both rubber gloves (preferably with gauntlets) and either safety glasses or better a face shield. For storage of hydroxide solutions, plastic is more suitable than glass as the latter is slowly etched (attacked) by caustic solutions. Use plastic caps, preferably with plastic liners (seals). Concentrated sulfuric acid is even more hazardous! It is extremely corrosive to the skin and (especially *after* dilution) most metals, and generates intense heat when added to water. NEVER add dilution water to straight sulfuric acid! Wearing protective clothing as with the alkalis above, ALWAYS add the acid *VERY slowly* to the coldest possible water - and stop and wait if the solution starts to boil, which is not unusual (if the solution boils at a reasonable rate, only water is boiling off. The sulfuric acid component will still be full strength). Allow the diluted acid to cool before storing in plastic or glass. Use plastic caps with plastic liners; paper liners (seals) will soon be useless and contaminate the acid. Iodine solutions, if prepared,

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IMPORTANT NOTES, CONTINUED

should be stored in amber glass bottles with plastic caps and kept refrigerated and out of direct light when not in use.

5. SHELF LIVES of prepared solutions: All except sulfuric acid solutions can be maximized by storage in dark (amber) glass at cool temperatures (*not* refrigeration, *except* for starch, iodine and sodium thiosulfate solutions):

| | |
|--------------------------------|---|
| sodium hydroxide, 0.0667 N | 6-12 months |
| sodium hydroxide, 1N | Indefinite |
| potassium hydroxide, various | Same as NaOH |
| sodium thiosulfate, 0.1N | 6 months <i>when refrigerated</i> , less if not |
| sulfuric acid, various | Indefinite |
| iodine, 0.1N | 1-3 months <i>when refrigerated, kept dark</i> |
| potassium acid phthalate, 0.1N | 3 years <i>when refrigerated, kept dark</i> |
| potassium bitartrate, 0.05N | 1 year |

(Figures are from Vinquiry Catalog of Services & Supplies, 2002-2004).

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While I will try to minimize chemical theory and chemical reactions in this discussion, a basic example of an acid-base (acid-alkali) reaction, such as we carry out when we determine TA (titratable acidity) is relevant and helps to illustrate the concepts of molarity or normality.

For the purposes of our discussion (which is simplified but perfectly valid), acids in solution yield hydrogen ions (H^+) and bases (alkalis) yield hydroxide (OH^-) ions. When equal *numbers* of hydrogen and hydroxide ions (*NOT equal WEIGHTS*, as hydroxide ions weigh more than hydrogen ions) are placed in solution, they react with and neutralize each other to produce water: $H^+ + OH^- = H_2O$. If there were truly equal numbers of hydrogen and hydroxide ions in the above case, our solution would be *neutral* (neither acidic nor basic: pH 7). On the other hand, while there can be an excess of either hydrogen or hydroxide ions in a solution, there cannot be an excess of *both* at the same time. If there are more hydrogen ions present, the solution is acidic, and the more hydrogen ions there are, the *lower* the pH of the solution will be. Conversely, if there are more hydroxide ions present, the solution will be alkaline, and the higher the hydroxide ion concentration, the *higher* the pH will be.

Because chemists know that one hydrogen ion will neutralize one hydroxide ion, they figured it would be useful to prepare solutions which would have known *relative NUMBERS* (per unit volume) of either hydrogen ions (in acids) or hydroxide ions (in bases). Similarly, when *using* a solution defined by the relative *number* of active ingredient units, chemists would immediately know how this solution concentration compared with other solutions which might be utilized in a test procedure. So: how to do this? Recall (yes, more chemistry) that, by definition, an atom is the smallest unit of matter with specific chemical *and* physical properties; a molecule is the smallest unit of combined matter (examples: SO_2 , H_2O : routinely referred to as *compounds*) with the same properties; and ions are electrically charged atoms *or* combined atoms with these same properties that at times conveniently exist for our purposes in aqueous (water) solutions. Now, refer to a periodic table of the elements. Each element has its own atomic number (related to its structure), and its own *atomic weight*. All atomic weights are relative, and equally important, are consistent regardless of the form of matter in which each atom is found. Thus, once we know the chemical formula of any compound we wish to consider, we can easily obtain the *molecular weight* of that compound by adding up the atomic weights of all of the atoms found in that compound. Examples:

| | | | |
|-------------------------------------|-----|-----------------------------|------|
| sodium hydroxide (NaOH) | 40 | hydrochloric acid (HCl) | 36.5 |
| potassium hydroxide (KOH) | 56 | sulfuric acid (H_2SO_4) | 98 |
| sodium thiosulfate ($Na_2S_2O_3$) | 158 | iodine (I_2) | 254 |

{For example, sodium hydroxide above: atomic weights for sodium (Na) = 23; for oxygen (O), 16; and for hydrogen (H), 1. Thus, $23 + 16 + 1 = 40$. For compounds with multiples of the same atoms, multiply the atomic weight of the atom by the number of atoms present in each molecule, based on the formula. Thus, sulfuric acid is: hydrogen (1×2) + sulfur (32) + oxygen (16×4) = 98}.

{We can even more easily obtain the molecular weights of desired compounds from some labels, most any MSDS (if available - always ask), or chemical reference books}.

Anyway: once we have these molecular weights, we can directly use these to prepare MOLAR solutions of these compounds. For example, to prepare a 1M (spoken "one molar") solution of sodium hydroxide, weigh

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out and add 41 grams of reagent grade (ideally) NaOH (this quantity from page 2) in 600-800 ml of distilled or deionized water in a 1L volumetric flask. (Is this a typo? Use 41 grams NaOH when the molecular weight is 40? Yes, but only because even the purest NaOH happens to be only about 97-98% pure). Stir until dissolved, and dilute this to exactly 1 liter with additional d/d water. That's it! (Similarly, sulfuric acid has a molecular weight of 98, but we specify using 100 grams per liter. It just happens, again, that even the purest sulfuric acid is only 97-98% pure). - It should be mentioned that the term *molar* is derived from a *gram molecular weight*, or *mole*, of a compound, which by definition is its molecular weight in grams; when a mole of any compound is dissolved in water and the solution diluted to 1 liter, we have a 1M solution of it.

So, if that's all there is to MOLARITY, how about NORMALITY? Look at sodium hydroxide. From its formula, we know that for each molecule of NaOH dissolved in water and converted to ions we get *one* sodium cation (a positively charged ion is by definition a cation, pronounced "cat'ion") and one hydroxide anion (a negatively charged ion is by definition an anion, pronounced "Ann'ion"). Any molecule that yields only one active hydrogen cation or hydroxide anion is referred to, by definition, as a *monobasic* acid or base, respectively.

Now, look at sulfuric acid. When a single molecule of sulfuric acid is dissolved in water, it contributes *two* hydrogen ions and one sulfate (SO_4^-) ion. Thus, a 1M (or 0.1M - or *any molar* concentration) sulfuric acid solution contributes *twice* as many hydrogen or acid ions, as an equivalent *molar* solution of sodium hydroxide contributes hydroxide or basic ions. To describe this characteristic of sulfuric acid, chemists refer to it as a *dibasic* acid, that is, *twice* as acidic per molecule as *monobasic* acids (like hydrochloric, or acetic, or many others). Now, this can be confusing to people who aren't chemists or those unfamiliar with sodium hydroxide and sulfuric acid, who might assume that these 1M or 0.1M solutions have equal acidic and alkaline strengths. So, to clarify things, chemists went another step and decided to characterize solutions according to their *monobasic* acid or alkaline *contributions*, and to call this concentration NORMALITY.

As you now can see, for chemicals such as sodium hydroxide, the molarity and normality of sodium hydroxide solutions are by definition exactly the same. 1M and 1N sodium hydroxide (called "one molar" and "one normal", respectively) are equal, and the terms are interchangeable. Always.

But, if we now compare 1M and 1N sulfuric acid, are these the same? 1M sulfuric acid contributes *two* hydrogen ions to solution, so this cannot by definition be called 1N. As its acid contribution is *double* that of a monobasic acid, it has to, by definition, be 2N (called "two normal"). Does that meet the definition test? Well, we've seen that 1M NaOH and H_2SO_4 *aren't* equal in alkalinity and acidity, respectively, the latter being twice as strong. But, we can also see that either (1) taking *half* the volume of equal molar sulfuric acid compared to NaOH now make these equal in total acid-base strength (thus confirming their dibasic-monobasic characteristics, and normality concentrations), or (2) first diluting 1M H_2SO_4 to half its concentration (0.5M, 1N) with water and then using equal volumes of sulfuric acid and 1M/N NaOH, also creates equivalent total acid-base systems and similarly validates our concept and definition of normality.

If you're curious - yes, there are even *tribasic* acids and bases, though they are less relevant to tests which we as winemakers routinely employ. Examples are citric acid and phosphoric acid.

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However, there are no *tetrabasic* acids or bases of consequence, for reasons not readily understood by non-chemists.

When all is said and done, both molarity and normality are specific, valid definitions of chemical concentration. However, because normality is so totally consistent for all materials and systems (not just acid-base, but oxidation-reduction, etc.), and more intuitive for both trained and untrained users, this has become the standard and preferred choice for current descriptions.

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Questions and comments may be directed to the author. Consult your WVAWS membership list for contact information.