HOW TO CHECK YOUR SYSTEM'S SO_2 REAGENTS

Although we now give Vinmetrica's SO_2 Titrant (and the other reagents) a "use-by" date of two years, we occasionally get requests for a way to check the accuracy of results. Here we provide two methods you can use. Both of these are fairly technical and require some special equipment. In the past, we recommended Method II because of the technical issues mentioned in Method I. But Method I uses sulfite as KMBS or sulfite salts, which are usually at hand and presumably of known purity. So we have recently validated Method I. Method II uses ascorbic acid, which acts like sulfite in the SO_2 test, but which may not be easily obtained as a pure standard.

Method I. Check with a sulfite standard.

Here is the method for using potassium metabisulfite (KMBS) or sodium sulfite (Na_2SO_3, anhydrous) to check your SO_2 reagents. You'd think this would be the easiest way, right? Make up a known concentration of your KMBS that you already use for sulfiting your wine, take the right amount and titrate it like a wine sample. Well, you can do it, but there are some caveats.

The first caveat: how pure is your sulfite standard? When we assay solid KMBS that is used for wine and food, we typically get purities of 90% to 96%, and in at least one case we've seen stuff come in at below 85%. When the purity is 90% or less, it makes it look like your assay is off by 10% or more. That is why we recommend considering use of reagent-grade anhydrous sodium sulfite as a standard. However as you will see below, KMBS is probably OK to use, as long as you keep the purity issue in mind.

A second caveat is the effect of dissolved oxygen. Some of the sulfite that you dissolve up to make standards can be oxidized by dissolved oxygen in the water you use. This effect is difficult to predict because it appears to depend on very minor impurities that can be present in various amounts even in distilled or deionized water. So we recommend de-gassing your distilled water, though that is optional.

Dissolved oxygen is typically about 8 mg/L. Each mg/L O_2 can theoretically react with SO_2 to lower its concentration by 8 mg/L (8 ppm). This reaction is generally very slow, but its speed can vary. In our hands, SO_2 values can drop by 5 to 10 percent within an hour if the water is not de-gassed.

So be forewarned! We recommend making a relatively high concentration of the sulfite standard and taking a small volume (4.0 mL) of this, rather than trying to prepare lower concentrations of sulfite and taking the standard 25 mL. We indicate the amounts of KMBS or of reagent-grade anhydrous sodium sulfite (highly recommended) to use if you have it.

1. If possible, prepare a liter of degassed, distilled (or deionized) water (DDI water) to remove dissolved oxygen. This can be done by a) boiling DI water for 15 minutes in a stainless or glass vessel, then cooling with a tight cover and minimal headspace, or b) vigorously bubbling pure nitrogen or CO_2 gas through DI water for 15 minutes, or c) putting the DI water in a vacuum flask and drawing a good vacuum (10 mm Hg) on the flask with stirring or occasional shaking for 15 minutes. If you can't de-gas your water, your results may show slightly lower levels of SO_2 than actual.

2. Prepare a 1000 mg/L standard solution of your sulfite by dissolving 1.00 g of KMBS or anhydrous sodium sulfite in 1000 mL of degassed water (or, e.g., 0.10 g in 100. mL water). If you use KMBS, this

is equivalent to 576 mg/L (ppm) SO_2. If you use anhydrous sodium sulfite, this makes 507 mg/L SO_2.

3. Pipette as accurately as possible 4.0 mL of this sulfite solution into a titration beaker. Add about 20 mL of DDI water, 2.0 mL Reactant and 2.0 mL Acid Solution. Proceed immediately to the next step.

The volume of water added is not critical. 20-25 mL is fine.

4. Titrate free SO_2 in the usual way for a 25 mL sample using the SC-100 or SC-300. Your titration volume V should be between 4 and 5 mL.

5. Calculate in the usual way for a 25 mL sample, i.e. ppm (mg/L) $SO_2 = 20 \times V$

Each mL of SO_2 Titrant equals 20 ppm of SO_2. If you used 4.0 mL of 1000 mg/L KMBS (576 ppm SO2) in step 3, you expect a titration result of **92 mg/L (ppm)**. If you used 4 mL of pure sodium sulfite in step 3 (507 ppm SO2), you expect a result of **81 mg/L**.

We recommend you do this at least two times and average the results. If you get values that are within 10% of expected, you can be reasonably certain that your SO_2 reagents are good enough.

Vinmetrica results:

A solution prepared from winery KMBS per step 2 was titrated in steps 3 and 4. The titration volume to reach the SC-300 SO_2 endpoint was 4.3 mL. So 4.3 x 20 = 86 ppm, vs. the expected value of 92 ppm. However, we assayed the KMBS in a separate method and determined it to be 94.7% pure. So the "real" expected value was 92 x .947 = 87 ppm, showing that the Vinmetrica SO_2 method was quite accurate in determining an actual standard sulfite level.

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Method II using ascorbic acid.

Ascorbic acid ("AA", also known as vitamin C) reacts with the iodine (I_2) generated by Vinmetrica's SO_2 Titrant just as SO_2 does, that is

$$AA + I_2 + H_2O \rightarrow 2I^- + \text{dehydroAA} + 2H^+$$

So you can use pure AA, or a known source of AA, as a relatively accurate standard to determine the strength of your Titrant. Note that since AA is not a "primary standard", i.e., a certified reference material, this procedure does not provide a precise value for the Titrant strength. Rather, this procedure will give you a result that is good enough to determine whether the reagents and the instrument are working to deliver results within the expected range.

1. Obtain 500 mg tablets of vitamin C. We recommend vitamin C-only tablets, i.e., do not use multivitamins. A good source is Nature's Bounty Pure Vitamin C-500mg, but any similar source will do. (or you can contact us at info@vinmetrica.com for advice) If you have pure ascorbic acid, weigh out accurately about 500 mg (i.e., 0.5 g) and note the actual weight to the nearest mg.
2. Heat up about 200 mL of distilled or RO water (dH_2O) to boiling for 5 min. A convenient way to do this is to fill a clean coffee mug about 2/3 full and put it in the microwave on high for 5 minutes. [Note that this does 2 things: a) drives out dissolved oxygen which reacts with the

ascorbic acid; and b) speeds dissolution of the tablet/ascorbic acid]

3. As soon as possible (i.e., minimize the time allowed to cool) measure out 100 ml of the very hot water into a beaker or flask using a graduated cylinder or other accurate device. In a pinch you can use your 25 ml pipet 4 times. Add the vitamin C tablet or ascorbic acid sample. Stir until dissolved. [Note: some tablets have excipients that may not dissolve. Stir or swirl thoroughly for 2 minutes and then let any solids settle briefly.]

4. If you used a 500 mg tablet, your concentration of ascorbic acid (C) is now about 0.057 meq/mL (we say "about" because vitamin tablets can be formulated with 5 – 10% excess). If you used different amounts of ascorbic acid or water in step 3, calculate the concentration of ascorbic acid as

$$C = m/(88 * V_w)$$

where C is the concentration in meq/mL, m is the actual weight (in mg) of the ascorbic acid and V_w is the volume of water (in mL, e.g, 100) used to dissolve it. (Note: The factor 88 is the "equivalent weight" of ascorbic acid in mg/meq).

5. Pipet as accurately as possible 1.0 mL of this solution into the titration vessel. Add about 20 mL dH_2O. Then proceed in the usual manner, i.e., add 2 mL Acid Solution and 2 mL Reactant solution, then titrate with the SO_2 Titrant, following from step 4 of the free SO_2 procedure in the User's Manual.

6. Determine the volume of Titrant, Vt (in mL) needed to reach the endpoint. Calculate the normality of the Titrant as

Normality 'N' (meq/mL) of Titrant = C/Vt (i.e., C, divided by Vt)

Where C is the concentration of the ascorbic acid in meq/mL determined in step 4; V_t is the mL of titrant to reach the endpoint (assuming you use 1.0 mL in step 5). The expected value is 0.0156 N . If you are within the range 0.0140 to 0.0172, your error in the free SO_2 value will be less than 10%, which should be fine.

We recommend you do this at least two times and average the results. Do not try to use the ascorbic acid solution after 2 hours or so, as it will oxidize slowly in air.

