Research in Plain English (RIPE)

Determination of Molecular and "Truly" Free Sulfur Dioxide in Wine: A Comparison of Headspace and Conventional Methods

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The Takeaway

- Free sulfur dioxide SO_2 forms (molecular SO_2 and bisulfite) are related to the microbial and oxidative stability of a wine. However, most methods used for measuring in the wine industry overestimate the amount of SO_2.
- "Truly" Free SO_2 can be determined measuring the headspace concentration of SO_2 but current methods for headspace SO_2measurement are challenging to automate.
- Researchers developed a new, automatable method to measure "Truly" Free SO_2 using headspace gas chromatography (HS-GC).

Background

Winemakers have historically utilized sulfur dioxide (SO_2) as a wine preservative. Researchers have discovered that when SO_2 is added to wine, it exhibits five effects:

1. Inhibits microbial growth, especially of spoilage organisms.
2. Protects wine from oxygen exposure by consuming hydrogen peroxide and other oxidation byproducts.
3. Limits browning of juices prior to fermentation by inhibiting polyphenol oxidase enzymes.
4. Bleaches wine pigments.
5. Binds to aldehydes and ketones associated with off odors in wine.

Sulfur dioxide (SO_2) exists in free (molecular and bisulfite) and bound forms in solution. Free SO_2 has protective antimicrobial qualities, antioxidants and enzyme-inhibition. Bound SO_2 molecules do not exhibit these characteristics). Together, free and bound sulfites are added together to determine total sulfite concentration.

To be useful for winemakers, SO_2 analyses must differentiate between free and bound SO_2. Current methods for measuring SO_2 include A-O (aeration-oxidation) and Ripper (iodometric titration). Both methods overestimate free SO_2, especially in red wines, and thus measure “Apparently” Free SO_2. This overestimation can be avoided, and the “Truly” Free SO_2 determined, by measuring the headspace SO_2 concentration in a wine sample. The Sacks lab has previously reported a method using colorimetric gas detection tubes (GDT) to measure “Truly” Free SO_2, but this earlier method was challenging to automate.

Results and Discussion

Researchers built on previous approaches to measure volatile sulfur compounds by collecting a headspace (HS) sample followed by separation on a gas chromatography column and detection by a sulfur chemiluminescence detector (HS-GC-SCD or HS-GC for short).The optimized method required ~10 min per sample, and was easily automated.

The researchers evaluated a diverse group of 27 wines with two traditional “Apparently” Free SO2 methods (A-O and Ripper) and two methods for “Truly” Free SO_2 (HS-GDT, and the new HS-GC method). As expected, A-O and Ripper consistently overestimated SO_2 values than the headspace, especially in red wines. On average, “Apparently” Free SO_2 values were over 2-fold higher than “Truly” Free SO_2 in red wines, with certain wines having as much as 20 mg/L higher Apparent Free SO_2. Wines with big discrepancies were more likely to have high anthocyanin concentrations.

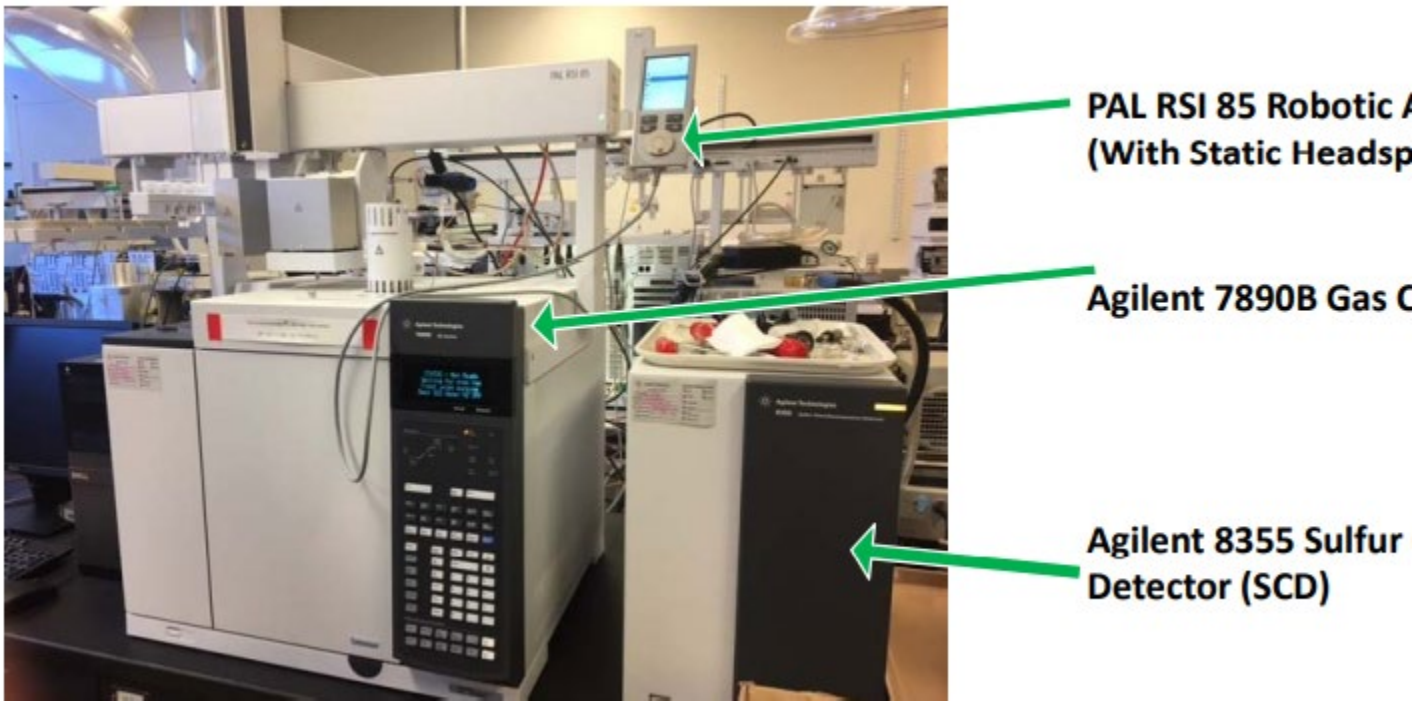

Figure 1 Researchers utilized the PAL RSI 85 Robotic Autosampler with Static Headspace Syringe to measure headspace in wine bottles for free sulfur dioxide levels.

Conclusions and Practical Considerations

Researchers developed a new analytical procedure for measuring "Truly" Free SO_2 based on headspace gas chromatography (HS-GC). The method requires little sample preparation or reagents, requires ~10 min per sample, and is easily automatable. The work confirmed that the current methods for measuring "Apparently" Free SO_2 in wines (A-O and Ripper method) consistently overestimate molecular and free SO_2 in red wines. . Previous work has shown that "Truly" Free SO_2 is a better predictor of microbial stability than "Apparently" Free SO_2, and researchers hope that the new HS-GC method can be used by the wine industry to better predict wines at risk of spoilage.

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