Technical Report: Optimization of Sulfur Analysis in Wine – Official Methods Compared with the CDR WineLab® System

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1. The Strategic Role of Sulfur Dioxide in Modern Oenology

Sulfur dioxide (SO2) is the cornerstone of oenological stability. It should not be considered a mere additive, but rather a multifunctional agent essential for antioxidant protection and microbiological preservation. In an increasingly stringent regulatory and health context—considering that approximately 75% of total sulfites exposure in adults comes from wine consumption—analytical precision is not only a legal requirement, but a guarantee of organoleptic quality.

From a chemical perspective, sulfur dioxide (SO_2) in aqueous solution exists in a complex equilibrium between different forms. In wine, at a typical pH (usually between 3.0 and 3.8), the free SO_2 fraction is composed of 92–99% bisulfite ion (HSO_3^-), while molecular SO_2 (the form truly active against microorganisms and oxidation) represents only a small minority. Wines labeled as "without added sulfites" typically have concentrations between 10 and 50 mg/L, produced naturally by yeast activity during fermentation. The need to monitor such concentrations necessitates a detailed comparison of the various analytical methodologies available.

2. Overview of Official Methods: Complexity and Operational Constraints

The methods defined by the International Organisation of Vine and Wine (OIV) represent the gold standard for legal compliance. However, their application in routine winery operations requires advanced technical expertise and complex laboratory setups.

The main official protocols include:

- **Aeration/Oxidation (Rankin/Pocock Method - OIV-MA-AS323-04A):** This method displaces SO2 from the acidified sample using a constant air flow, strictly set at **1 L/min** , into a hydrogen peroxide solution where it is oxidized to sulfuric acid and subsequently titrated with NaOH. Although robust and free from matrix interference, it requires round-bottom flasks, condensers, and constant supervision to avoid volatility losses.
- **Iodometric Titration (Ripper Method - OIV-MA-AS323-04B):** Based on the reaction between bisulfite and iodine in the presence of starch solution. Despite its rapidity, it presents insurmountable challenges for precision management: the color of red wines masks the color change point, and the presence of ascorbic acid reacts **quantitatively** with iodine, causing a systematic overestimation of the result that requires separate analyses to compensate.
- **Molecular Method (OIV-MA-AS323-04C):** Used for specific determinations of the gaseous fraction.

Critical points of traditional methods:

- **Setup and Space:** Bulky glassware (extractors, burettes) and utilities (natural gas for burners or heating systems) required.
- **Reagent Instability:** Solutions such as iodine or NaOH require frequent standardization because they degrade rapidly.
- **Operating Times:** The AO method requires approximately 20 minutes for a single sample, making the sequential testing of numerous tanks a logistical bottleneck.

3. Simplify the analytical process with CDR WineLab®

CDR WineLab® system is designed to overcome the constraints of the traditional laboratory, integrating photometric precision with in-house operational flexibility. The analytical principle for the determination of **free** and **total sulfur dioxide** is based on the reaction of sulfur dioxide with an **organic disulfide** ; the resulting color development, measured at **420 nm**, is directly proportional to the SO_2 concentration .

Operation is optimized for the cellar technician through specific procedures for each matrix:

- **Wine as is:** Direct analysis without pre-treatment.
- **Musts:** Centrifugation or filtration to eliminate turbidity.
- **Sparkling or fermenting wines:** Mandatory degassing using the appropriate ultrasonic bath to eliminate CO_2 interference.

The system uses pre-filled reagent kits in ready-to-use tubes, eliminating systematic error resulting from the use of degraded titrants, ensuring superior reproducibility compared to manual methods where reagent preparation is a critical variable.

4. Comparative Analysis: Time Efficiency and Ease of Use

Analytical efficiency is an economic variable: SO_2 performs its function in a **"sacrificial" manner**, decreasing over time depending on the type of closure, the oxygen in the headspace, and storage conditions. Rapid monitoring helps prevent degradation below microbiological safety thresholds.

Parameter	Aeration/Oxidation (AO) Method	CDR WineLab ®
Time for Test	~20 min / sample	1 min (Total) / 2 min (Free)
Concurrent Sessions	Single (Sequential)	Up to **16 samples**
Technical Skills	Experienced laboratory technician	Cellar Operator (Guided Method)
Interferences	Minimal, but critical flow (1 L/min)	Absent (color, ascorbic acid)
Sample Treatment	Complex (Acidification/Heating)	Centrifuge/Ultrasound (if necessary)

CDR WineLab® 's ability to analyze up to 16 samples simultaneously allows for the optimization of an internal quality control protocol, making it affordable for any organization. While official methods make detailed post-bottling monitoring a burdensome burden, CDR WineLab® allows for real-time action. This prevents the wine from entering the "danger zone" of oxidative alteration, allowing for immediate corrections before the sensory damage becomes irreversible.

5. Validation and Reliability of the Analytical Data

CDR WineLab® system thus allows for a fully optimised workflow in which speed and simplicity do not compromise precision: **correlation studies conducted by the University of Florence** have confirmed the excellent linearity of the system compared to OIV reference methods.

Analyses	Measurement Range	Resolution	Repeatability
SO_2 Free	1 - 60 mg/L	1 mg/L	2 mg/L
SO_2 Total (Whites)	15 - 250 mg/L	1 mg/L	4 mg/L
SO_2 Total (Rossi)	20 - 250 mg/L	1 mg/L	6 mg/L

The system demonstrates particular robustness on red wines, where it eliminates the color reading error typical of the Ripper method, and on musts, thanks to the standardization of pre-treatment protocols (centrifugation/filtration). The method's versatility and analytical robustness allow monitoring the entire winemaking process, from must to bottling.

6. Conclusions: The Impact on Cellar Management

Integrating a system like **CDR WineLab® allows** the laboratory to transform from a reactive cost center to a true strategic decision-making hub. Modernizing wine analysis translates into three operational pillars:

1. **Speed and Autonomy:** Immediate results without dependence on external laboratories, essential during pre-bottling.
2. **Procedural simplicity:** Reduced risk of human error thanks to ready-to-use reagents and standardized sampling systems (ultrasound/centrifuge).
3. **Sustainability and Precision:** In line with OIV-OENO resolution **631-2020** , frequent monitoring allows for a reduction in overall sulphite dosages, responding to the demand for more natural and healthy wines.

In conclusion, the adoption of advanced photometric technologies in the determination of **free** and **total sulfur dioxide** allows for dynamic management of dosages, ensuring the stability of the final product and full compliance with international legal limits, raising the standards of control in modern wineries.