Analytica Chimica Acta 809 (2014) 162–173

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Investigation and correction of the interference of ethanol, sugar and phenols on dissolved oxygen measurement in wine

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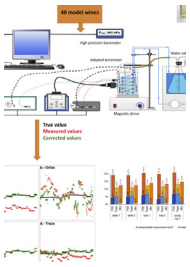
HIGHLIGHTS

- Dissolved oxygen measurements were performed with four high-performance systems.
- Ethanol, sugar and phenol influence were analysed in model wines.
- These commercial systems yield errors that underestimate DO content by up to 28%.
- A compensation value (CV) is proposed for the error made by each device.
- These errors were reduced by CV in 50–82% in model wines and 77% in real wines.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 September 2013
Received in revised form
25 November 2013
Accepted 28 November 2013
Available online 6 December 2013

Keywords:
Dissolved oxygen
Interferences
Luminescence
Electrochemistry
Wine
Correction value.

ABSTRACT

The dissolved oxygen in wine is routinely measured to control and monitor various oenological processes. The availability of devices based on different technologies and features allows a user to select a device that best meets their needs. However, grape must and wine samples each exhibit a complex composition that varies with time, which, along with atmospheric conditions, makes it necessary to evaluate the effects of these factors on dissolved oxygen measurements. This work evaluates the effects that ethanol, sugar, and phenols have on dissolved oxygen measurements in a model and real wine. The results suggest that significant errors are made in all studied systems and that the response of each device is different. Therefore, a compensation value was developed to take into account the sample composition. A compensation value was proposed to minimise the error made by each device based on the ethanol and sugar contents of the measured liquid. The best results are those obtained after using the compensation value to correct the data from the Pyro-Mini device. In all cases, errors made in DO measurements by optical systems were reduced by 50–82% by applying the compensation value for synthetic wines and 45–100% for real wines.

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http://dx.doi.org/10.1016/j.aca.2013.11.053

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1. Introduction

Oxygen is a key factor in the preparation of wine, playing an active role from grape harvest to bottling. Controlling the concentration of dissolved oxygen (DO) in wine is critical to the management of many oenological processes. DO is an especially important parameter for the management of oxygenation processes that lead to the final desired wine [1–3]. Many studies have focused on the effect of micro-oxygenation in wine but have not measured the oxygen present in wine, having considered the amount of oxygen dosed by their equipment sufficient. Lemaire [4] indicated that there are no objective measures for determining the O_2 dose for each type of wine. Recent reviews on micro-oxygenation of wine [5,6] clearly state that most studies focus on evaluating the effect of micro-oxygenation on the phenolic, colour, or aroma composition of wine. Few studies measure DO during micro-oxygenation (MOX) [1,7–10]. Knowledge of DO during the bottling process and in the bottle determines the shelf life of wine because oxygen present in the bottle preferentially consumes sulphur dioxide (SO_2). The existence of unknown quantities of oxygen in the headspace of the bottle during bottling can lead to an increase in DO upon equilibration with the liquid, which is consumed by the SO_2 added to the wine. This process decreases the amount of protective agent (SO_2) and thus reduces the shelf life of wine as protection against oxidation is lost [11,12].

The amount of DO in wine determines the type of device that should be used to measure it because appropriate features (measurement range, precision, and accuracy) are needed to perform correct concentration measurements. Pénicaud's work on different DO sensors explains in detail the existing technologies [13] and makes it clear that only electrochemical and luminescent sensors allow the construction of robust probes that are necessary for continuous monitoring of DO for integration into a process line. Most devices used to measure DO are based on these two technologies, which work by determining the partial pressure of oxygen in the liquid sample, which, in turn, is in equilibrium with the partial pressure of oxygen in the atmosphere. This implies that to establish absolute or relative values, oxygen solubility in the studied liquid must be known. For water, this is already resolved, as most equipment on the market is calibrated to perform measurements on water.

Luminescent technology is based on the property that some materials (luminophores) emit light when excited by a stimulus other than heat, which in this case is light. Luminophores can undergo reversible changes in optical properties, i.e., in their luminescence or absorbance, as a function of oxygen concentration. These changes can be quantified by dynamic quenching of the luminophore's light intensity I and response time τ in the presence of molecular oxygen [14]. The relationship between response time in the absence (τ_0) and in the presence of oxygen (τ) is proportional to the quencher concentration (i.e., partial pressure of oxygen), [O_2], which is the simplest form of the Stern–Volmer equation [15]:

$$\tau_0/\tau = 1 + K_{sv}[O_2] \quad (1)$$

where K_{sv} is the characteristic quenching coefficient or bimolecular quenching coefficient of the indicator, also known as Stern–Volmer constant.

Polarographic oxygen sensors, or polarographic membrane sensors, are electrochemical devices in which a steady current in the measuring electrode is ideally linearly proportional to the concentration, or more strictly the activity, of oxygen in contact with the outer-surface membrane. This proportionality is easily expressed in the equation derived by Mancy et al. [16]:

$$I_1 = nFAP_mC_s/Z_m \quad (2)$$

where I_1 is the detector current, C_s is the oxygen concentration, F is Faraday's constant, Z_m is the membrane thickness, P_m is the permeability coefficient, and n is the number of electrons related to reduction of oxygen at the cathode surface:

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^- \quad (3)$$

If a stricter measure of activity is used, such as the fugacity f_{O_2} or, more practically, the partial pressure of oxygen P_{O_2}, Eq. (2) becomes

$$I_1 = nFAS_mD_mP_{O_2}/Z_m \quad (4)$$

where S_m and D_m are the coefficients of solubility and diffusion of oxygen into the sensor membrane, respectively.

Some authors have reported significant variations in comparative measures of DO taken by electrochemical and luminescent devices in beer [17] and wine samples [1]. These variations are explained by contamination due to sampling and the measurement protocol used by each device, although the DO measurement can be influenced by the main compounds of these beverages when using either type of system. To better understand these interference effects, this study analysed the interference caused by the main components of wine in measuring DO and compared the major interfering factors between the different types of sensors. Although the technical specifications of most sensors provide no cross-sensitivity to ethanol or other major components of wine, the continued use of these devices in oenology has raised suspicion that certain interference effects in DO measurements are due to the