

 Open Access Full Text Article

ORIGINAL RESEARCH

Laser-based measurements of $^{18}\text{O}/^{16}\text{O}$ stable isotope ratios ($\delta^{18}\text{O}$) in wine samples

Manish Gupta¹J Brian Leen¹

Elena Simone Franklin

Berman¹Aldo Ciambotti²

¹Los Gatos Research, Mountain View, CA, USA; ²Consiglio per la Ricerca e la Sperimentazione in Agricoltura, Centro di Ricerca per l'Enologia, Asti, Italy

Abstract: Wine counterfeiting is an international, multi-billion dollar issue, with some estimates suggesting that up to 5% of wines sold at auctions or secondary markets are fraudulent. Isotope ratio mass spectrometer (IRMS) measurements of the $^{18}\text{O}/^{16}\text{O}$ stable isotope ratio ($\delta^{18}\text{O}$) of water-in-wine have been used for wine authentication; however, these analyses are time-consuming and costly. In this preliminary study, off-axis integrated cavity output spectroscopy (OA-ICOS) is used to quantify $\delta^{18}\text{O}$ in wines. This laser-based method has been extensively used to study water isotopes for hydrological and medical applications. Recently, the development of a spectral contaminant identifier (SCI) has extended the application of these OA-ICOS analyzers to contaminated water samples (eg, plant, soil, and leaf waters). Here, we utilize OA-ICOS with the SCI to characterize wine samples (9%–15% ethanol), and show that the laser-based instrument provides a $\delta^{18}\text{O}$ measurement precision of $\pm 0.07\text{‰}$ (1σ) and agrees with IRMS to within $\pm 0.63\text{‰}$ (1σ). Moreover, by training the SCI on isotopically-characterized wines, the agreement with IRMS improves to within $\pm 0.30\text{‰}$ (1σ). The utility of the instrument is demonstrated by measuring watered and mixed wines. The method presented here can be readily extended to address other food authentication applications.

Keywords: wine isotopes, wine fraud, counterfeit wines, OA-ICOS

Introduction

Wine counterfeiting is an international, multi-billion dollar issue, with some estimates suggesting that up to 5% of wines sold at auctions or secondary markets are fraudulent.¹ Fraudulent activities include misrepresented watering, mislabeling, wine blending, and including unauthorized additives. Researchers use a wide variety of analytical techniques to detect fraud and authenticate wine, including chromatographic separation techniques, mass spectrometry,² emission spectrometry, and nuclear magnetic resonance (NMR).³ Recently, measurements of the $^{18}\text{O}/^{16}\text{O}$ stable isotope ratio (expressed as $\delta^{18}\text{O}$) of water in wine have been used for wine authentication, and extensive databases of wine isotope ratios are now being developed.^{4–7} These technologies have also been extended to fruit juice extracts,⁸ concentrated spirits,⁹ and other food authentication applications.

Currently, measurements of $\delta^{18}\text{O}$ in wine are made using isotope ratio mass spectrometry (IRMS).^{10,11} The wine sample is typically equilibrated with a carbon dioxide gas standard at a constant temperature for 6–12 hours to permit exchange of oxygen atoms between the water in the wine and the gas-phase carbon dioxide. The oxygen isotope ratio of the carbon dioxide is then measured against an isotopically-characterized carbon dioxide (CO_2) gas sample using IRMS. The measurement process

Correspondence: Manish Gupta
Los Gatos Research, 67 East Evelyn Avenue, Suite 3, Mountain View, CA, USA, 94041
Tel +1 650 965 7772
Fax +1 650 965 7074
Email m.gupta@lgrinc.com

Aldo Ciambotti
Consiglio per la Ricerca e la Sperimentazione in Agricoltura, Centro di Ricerca per l'Enologia – via Pietro Micca 35, 14100 Asti, Italy
Email aldo.ciambotti@isenologia.it

is time-consuming and costly, usually requiring dedicated personnel to operate the IRMS and process the samples. Due in part to these limitations, the application of isotope analysis for wine authentication has been limited to select measurement laboratories that house the necessary expertise.

In this preliminary study, off-axis integrated cavity output spectroscopy (OA-ICOS) is used to quantify $\delta^{18}\text{O}$ in wines. This laser-based method has been extensively applied to the study of water isotopes for hydrological^{12–14} and medical¹⁵ applications. Recently, the development of a spectral contaminant identifier (SCI)¹⁶ has extended the application of these OA-ICOS analyzers to contaminated waters, including plant, stem, and leaf waters.¹⁷ Here, we utilize an OA-ICOS analyzer and the SCI to characterize wine samples containing 9%–15% ethanol, and show that the laser-based instrument provides a measurement precision of $\pm 0.07\text{\textperthousand}$ (1σ) and agrees with IRMS to within $\pm 0.63\text{\textperthousand}$ (1σ). Moreover, by training the SCI on isotopically-characterized wines, the agreement with IRMS improves to within $\pm 0.30\text{\textperthousand}$ (1σ). The utility of the instrument is demonstrated by measuring watered and mixed wines.

Materials and methods

A commercial, OA-ICOS liquid water isotope analyzer (LWIA, Los Gatos Research, Mountain View, CA, USA) was used to measure natural waters, prepared ethanol-in-water standards, prepared methanol-in-water standards, and wines. All measurements were made using three commercially-available (Los Gatos Research), internal water standards with isotope values ($\delta^2\text{H}$, $\delta^{18}\text{O}$) of ($-51.8\text{\textperthousand}$, $-8.02\text{\textperthousand}$), ($-9.6\text{\textperthousand}$, $-2.89\text{\textperthousand}$) and ($107.0\text{\textperthousand}$, $12.24\text{\textperthousand}$) as measured directly against VSMOW2 (Vienna Standard Mean Ocean Water 2) and SLAP2 (Standard Light Arctic Precipitation 2), and independently confirmed by IRMS. Measurement of sample unknowns included interspersed, periodic measurements of a fourth water standard which served as an internal control and confirmed that the analyzer was accurately measuring isotope ratios.

All samples (water, ethanol-in-water, methanol-in-water, and wines) were handled in an identical fashion. In order to remove a variety of organic compounds,¹⁸ 2 mL of each sample was placed in an Eppendorf tube, activated charcoal (~50 mg) was added to each tube, and the tube was agitated for 30 seconds. Subsequently, the tube was centrifuged for 2 minutes to settle the charcoal, and the top 1 mL of sample was transferred to an analyzer measurement vial. Six separate 1 μL injections from each vial (containing sample or standard) were placed into the LWIA for measurement.

The first two injections were discarded to remove any memory effects, and the final four were averaged to yield a measured isotope value. For every five sample unknowns measured, one standard was measured, yielding a net measurement frequency of 150 unknown samples/day.

The analyzer's post processing software (Version 2.2.0.14, Los Gatos Research, Mountain View, California, USA) was used to determine the measured values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ after calibration with the internal water standards. The analyzer's SCI software (Version 1.0.0.75, Los Gatos Research, Mountain View, California, USA) was then used to determine broadband (m_{BB}) and narrowband (m_{NB}) metrics for all of the measured samples. The m_{BB} and m_{NB} metrics are described in detail elsewhere,¹⁶ and reflect contamination due to hydroxyl compounds, with m_{BB} and m_{NB} serving as indicators of larger (eg, ethanol and higher alcohols) and smaller (eg, methanol) contaminants, respectively. Critically, previous work has shown that the values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ reported by the LWIA can be corrected for this contamination by using the measured values of the m_{BB} and m_{NB} metrics. The functional form of these corrections is shown below and has been validated in previous publications. Note that the exact composition of the contaminants is not important. For example, in previous studies of plant waters, there were several hundred trace contaminant compounds present (eg, acids, ketones).¹⁷ Regardless, the OA-ICOS analyzer was able to determine the correct isotope ratio as determined by IRMS. Thus, m_{BB} and m_{NB} are measures of total contamination due to broadband and narrowband spectral absorbers respectively, and the metrics can be used to correct the measured isotope values and yield accurate results, even in the presence of significant organic contamination. This is especially critical in wine studies, where there are numerous other compounds including organic acids, higher alcohols, and phenols.

Results and discussion

The analyzer was first tested on natural waters to gauge its precision and accuracy. Note that there was no measured change in the isotope ratio due to sample handling. A single water sample was independently measured 45 times in less than 8 hours to gauge the instrument's accuracy and precision. The instrument measured the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the water sample (average of four injections) with a precision of $\pm 0.37\text{\textperthousand}$ (1σ) and $\pm 0.10\text{\textperthousand}$ (1σ) respectively. This precision improved to better than $\pm 0.25\text{\textperthousand}$ (1σ) and $\pm 0.05\text{\textperthousand}$ (1σ) respectively by averaging five measurements (eg, an average of 20 injections). Moreover, the measured

mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope values of the water sample were accurate to within 0.2‰ and 0.16‰, respectively, relative to IRMS measurements.

The analyzer was then used to measure twelve ethanol-in-water samples ranging from 0%–17.2% by volume. The samples were made by adding ethanol to water of a known isotope ratio. Since there is minimal exchange between oxygen atoms in ethanol and water, the $\delta^{18}\text{O}$ values of the ethanol-in-water mixtures are considered identical to that of the water alone. Thus, the difference between the actual and measured $\delta^{18}\text{O}$ values ($\Delta\delta^{18}\text{O} = \delta^{18}\text{O}_{\text{actual}} - \delta^{18}\text{O}_{\text{measured}}$), was determined as a function of m_{BB} and fit to function of the form:

$$\Delta\delta^{18}\text{O} = a_0 e^{a_1(m_{\text{BB}} - 1)} - a_1 \quad (1)$$

yielding fitted values of $a_0 = -12.537 \pm 4.18$ and $a_1 = -0.689 \pm 0.31$. All precisions are expressed as 1-sigma standard deviations. Using this correction, the actual and measured values of $\delta^{18}\text{O}$ agree to within $\pm 0.42\text{‰}$ (1σ). Note that previous work^{16,17} has used a linear relationship between $\Delta\delta^{18}\text{O}$ and m_{BB} ; however, for the large m_{BB} values measured in wines, an exponential function is better suited. Moreover, m_{BB} scales linearly with ethanol content (P, by volume):

$$P = b_0 + b_1 \cdot m_{\text{BB}} \quad (2)$$

where $b_0 = -13.31 \pm 0.37$ and $b_1 = 13.72 \pm 0.20$. Note that the analyzer measures m_{BB} with a precision of ± 0.017 (1σ), indicating that it can accurately quantify ethanol levels to within $\pm 0.23\%$ (1σ). For the wine samples measured in this study, ethanol concentrations and m_{BB} values ranged from 9.3%–14.8% and 1.64–2.03, respectively.

The dependence of the reported $\delta^{18}\text{O}$ values on the narrowband metric, m_{NB} , was determined by measuring five methanol-in-water samples ranging from 0–130 ppm by volume, three times each in a manner identical to that used for ethanol. Again, there is minimal exchange between oxygen atoms in methanol and water, and the $\delta^{18}\text{O}$ values of the methanol-in-water mixtures are identical to that of the water alone. The $\Delta\delta^{18}\text{O}$ values were determined as a function of m_{NB} and fit to a function of the form:¹⁶

$$\Delta\delta^{18}\text{O} = \frac{-\ln\left(\frac{m_{\text{NB}}}{C_0} + 1\right)}{C_1} \quad (3)$$

yielding fitted values of $C_0 = 0.756 \pm 0.037$ and $C_1 = 1.0438 \pm 0.0135$. Using this correction factor, the actual and measured $\delta^{18}\text{O}$ values agree to within $\pm 0.43\text{‰}$ (1σ).

The method was first tested on 14 wine samples that were not isotopically-characterized. They spanned both red and white wines from major wine growing regions in North and South America, Europe, and Australia. These tests were used to prove that the analyzer was capable of measuring wines with adequate precision and minimal effects due to sample memory and contamination. Additionally, these measurements showed that the reported m_{BB} could be used to determine ethanol concentration. By comparing the labeled ethanol content (accurate to $\pm 1.5\%$) to the measured ethanol content calculated from m_{BB} (Figure 1), the analyzer was found to be capable of determining the alcohol content of both wines and ethanol-in-water standards to within the error on the known values. Although not the primary focus of this work, accurate measurements of the wine ethanol

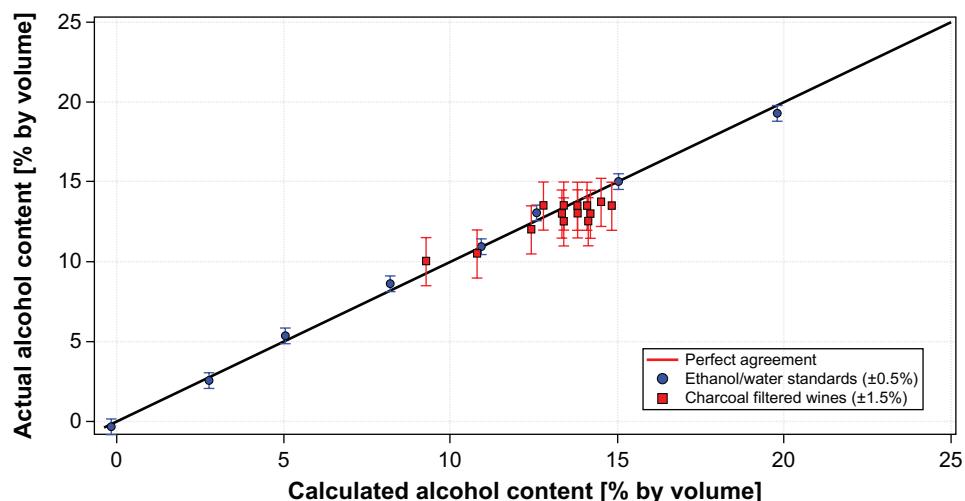


Figure 1 Alcohol content (% by volume) calculated from the analyzer's measured m_{BB} values agree with the actual, labeled alcohol content to within the error of the known values.

content can also be used to detect fraudulent activity (eg, watering).

The analytical method was then tested on eight isotopically-characterized wine samples obtained from the Centro di Ricerca per l'Enologia (CRA-ENO) in Asti, Italy. The IRMS $\delta^{18}\text{O}$ values of the wine samples were measured against local internal water standards by the CRA-ENO using the Organisation Internationale de la Vigne et du Vin (OIV) Method OIV-MA-AS2-12.¹⁰

Aliquots of the wines were then shipped to Mountain View, California and characterized using the OA-ICOS analyzer. The $\delta^{18}\text{O}$ precision for multiple measurements of the same sample (ie, four different analyses of the same sample, each of which consisted of four averaged injections) during a run was $\pm 0.07\text{\%}$ (1σ), exceeding the OIV repeatability requirement of $\pm 0.24\text{\%}$ (1σ). Likewise, $\delta^{18}\text{O}$ measurements conducted over 2 days agreed to within $\pm 0.22\text{\%}$ (1σ), exceeding the OIV reproducibility requirement of 0.5\% . Additionally, the LWIA and SCI provided measurements of m_{BB} and m_{NB} with a precision of ± 0.0054 (1σ) and ± 0.067 (1σ) respectively.

The measured $\delta^{18}\text{O}$ readings are plotted against the IRMS values in Figure 2. The uncorrected data (ie, LWIA readings calibrated against the internal waters standards, but not corrected for m_{BB} or m_{NB}) is offset from the IRMS values by -2.11\% and, even after taking this offset into account, is spread around the IRMS readings by $\pm 1.10\text{\%}$ (1σ). The corrected data (ie, LWIA readings calibrated against the

internal water standards and corrected for the m_{BB} and m_{NB} values using the previous equations) is offset from the IRMS values by $+1.39\text{\%}$. After taking this offset into account, the two values agree to within $\pm 0.63\text{\%}$ (1σ). Note that a single sample of rose wine has a relatively high m_{NB} value of 6.19 and is a clear outlier in the corrected data. Removing this sample from the analysis improves the agreement between the LWIA and IRMS to $\pm 0.42\text{\%}$ (1σ), which is within the convoluted precisions of the two instruments. The rose wine sample is particular in that it has a high sugar concentration relative to the other wine samples. Sugars do not absorb light in this spectral region; however, they readily ferment to produce alcohols. These alcohols may then lead to erroneous m_{BB} and m_{NB} values, which result in erroneous $\delta^{18}\text{O}$ values. Future studies should focus on sugar-rich samples, including sweeter wines and fruit juices.

There are several possible reasons for the offset and imperfect agreement between the corrected LWIA data and IRMS values. First, the two analyzers were calibrated on different water standards; second, the IRMS sample handling method may induce a slight shift in the $\delta^{18}\text{O}$ values (akin to the well-known salinity effect).¹⁹ Third, the correction curves for m_{BB} and m_{NB} are made by independently varying the two parameters using ethanol-in-water and methanol-in-water mixtures. At high ethanol levels (large m_{BB} values), these two parameters are not truly independent and the correction curves may be slightly incorrect. Finally, other compounds

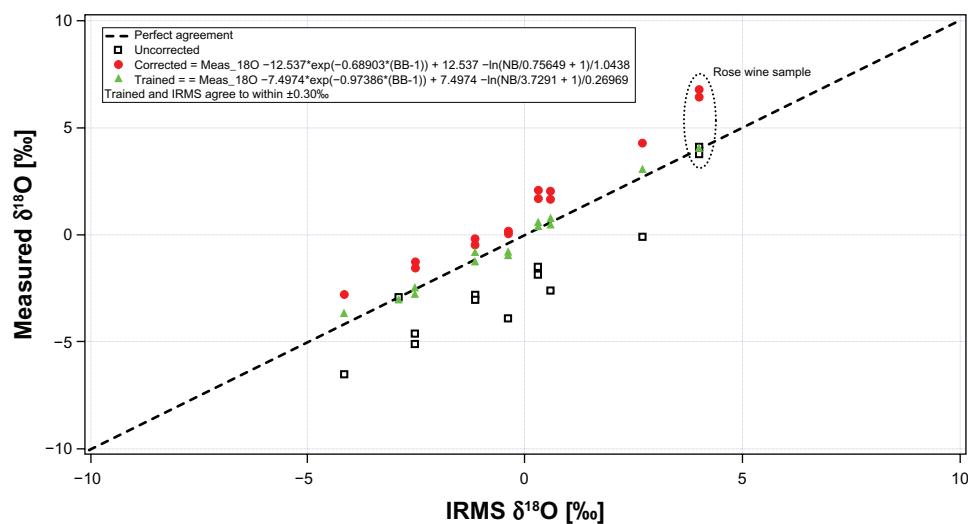


Figure 2 OA-ICOS measurements of the $\delta^{18}\text{O}$ values in wine compared to IRMS readings.

Notes: The uncorrected data set has a large offset (-2.11\%) and poor agreement even when the offset is shifted to be mean-centered around perfect agreement ($\pm 1.10\text{\%}$). By correcting for the broadband and narrowband spectral metrics (m_{BB} and m_{NB}), the offset and agreement improve to $+1.39\text{\%}$ and $\pm 0.63\text{\%}$, respectively, with the high m_{NB} rose wine sample as a clear outlier. Finally, by training the LWIA on all of the IRMS measurements, the offset is eliminated and the data sets agree to $\pm 0.30\text{\%}$.

Abbreviations: OA-ICOS, off-axis integrated cavity output spectroscopy; IRMS, isotope ratio mass spectrometer; LWIA, liquid water isotope analyzer.

in the wine samples may have small absorption features in the probed spectral region, giving erroneous values for the correction factors, particularly m_{NB} .

Because of the residual offset of $+1.39\text{\textperthousand}$, a third, alternate approach was also utilized to correct the LWIA data. In this approach, the IRMS values are assumed to be accurate, and the m_{BB} and m_{NB} correction coefficients (a_0 , a_1 , c_0 , and c_1) are fit to obtain the best agreement between the LWIA and IRMS data sets. This allows the LWIA to be “trained” on a wine set of known isotope ratios to determine a_0 , a_1 , c_0 , and c_1 , and then subsequently used to measure unknown wines. Using this methodology on all of the IRMS samples, the fitted metric coefficients are $a_0 = -7.5 \pm 3.9$, $a_1 = -0.97 \pm 0.76$, $c_0 = 3.7 \pm 5.0$, and $c_1 = 0.27 \pm 0.21$. Note that the large uncertainty in the m_{NB} coefficients (c_0 and c_1) is due to the limited number of wines with high m_{NB} values and would improve with a larger training set. The results of the “trained” LWIA are not offset from the IRMS values and the two instruments agree to within $\pm 0.30\text{\textperthousand}$ (Figure 2), limited by the convoluted precisions of the two instruments.

In practice, this training methodology would involve using a set of “known wines” that have been characterized by IRMS and a set of “unknown wines” whose isotope ratios need to be determined. In order to mimic this method, the wines (wine #1 through wine #8) were reanalyzed as follows. First, wine #1 was removed from the training set (ie, seven known wines, one unknown wine) and the fitted metric coefficients were recalculated for the seven known wines (wines #2 through wine #8). The isotope ratio of wine #1 was determined from the coefficients and compared to its IRMS value to provide a measurement error for wine #1.

The process was then repeated by treating, in sequence, each of wines (wine #2 through wine #8) as the unknown and determining measurement errors for each wine. The average of these errors for wine #1 to wine #8 was termed the average error for the measurement of one unknown wine using seven wines in the training set. The process was then repeated by removing two wines from the training set (ie, six known wines, two unknown wines), training on the six remaining wines, and determining the measurement errors for the two wines. Again all permutations were analyzed to determine the average error (and associated standard deviation) for the measurement of two unknown wines using six wines in the training set. Finally, the method was repeated for three and four unknown wines with five and four known wines in the training set respectively.

The results are shown in Figure 3. As expected, the 1σ measurement error increases from $\pm 0.30\text{\textperthousand}$ to $\pm 0.56\text{\textperthousand}$ as the training set is reduced from eight wines (zero unknowns) to four wines (four unknowns). Regardless, these results illustrate that the training methodology can be successfully used to characterize unknown wine samples. Note that the relatively large standard deviations of the measurement error suggest that it is important to select the correct wines in the training set correct wines in the training set, such that the training set spans the $\delta^{18}\text{O}$, m_{BB} , and m_{NB} measurement ranges of the unknown wines, similar to the IRMS and LWIA requirements for calibration measurements of natural waters.

In order to demonstrate the efficacy of using the OA-ICOS analyzer to identify wine fraud, wine samples were intentionally watered and mixed. First, a single wine sample was watered by adding 0%–20% water of known isotopic composition.

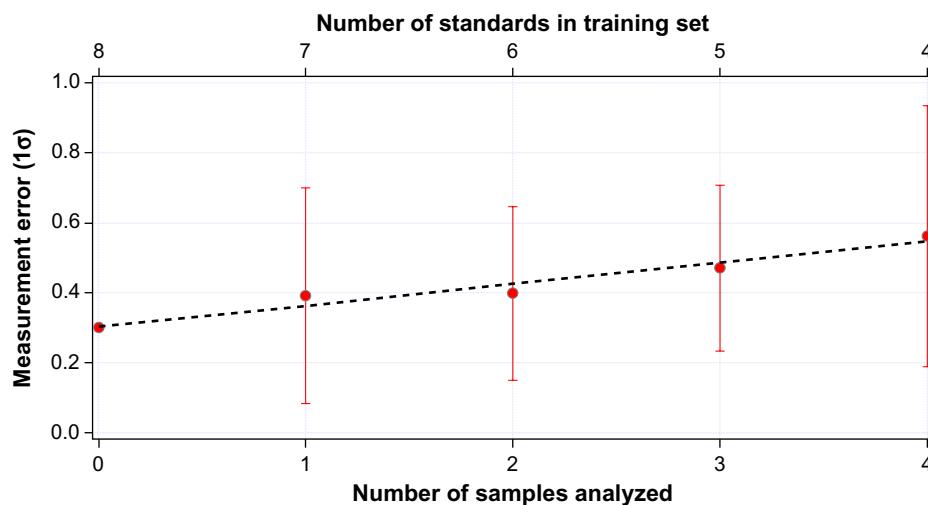


Figure 3 Scaling of the measurement error with the number of “unknown wine” samples analyzed and number of “known wine” standards in the training set.

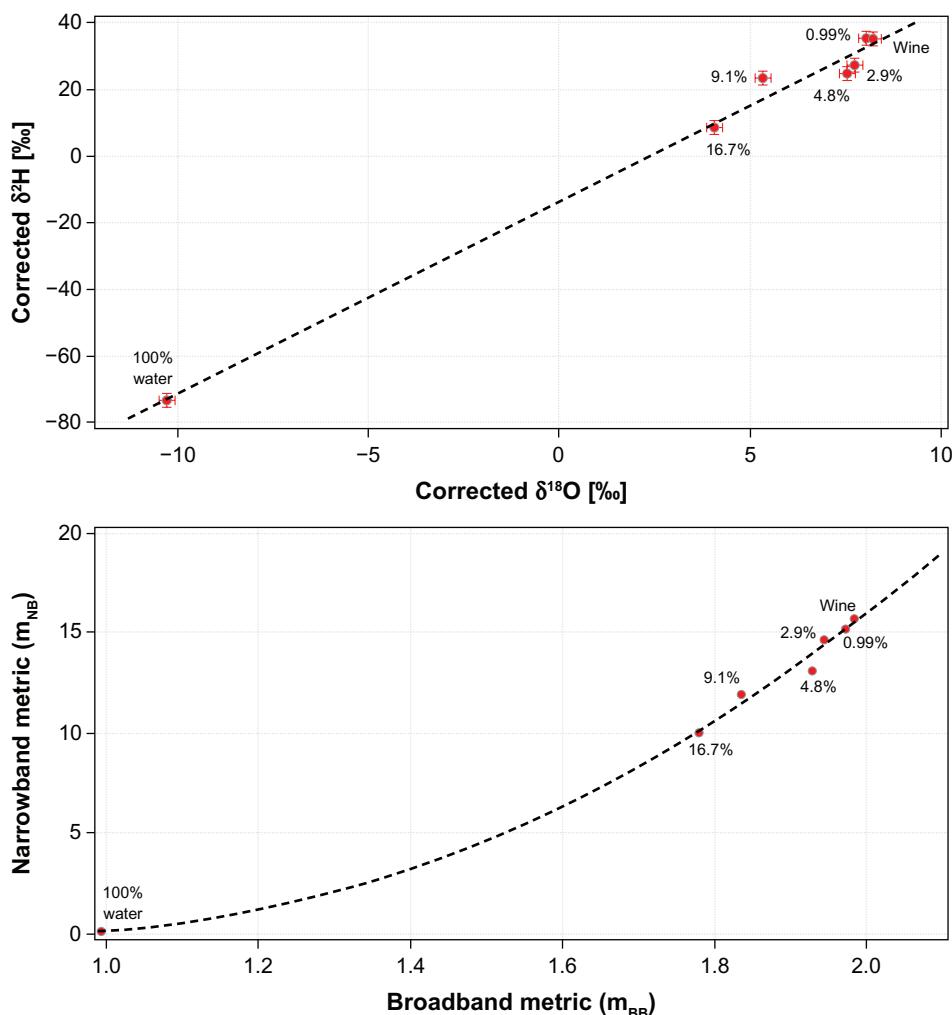


Figure 4 Identifying watering of a wine sample.

Note: Watering of a wine sample was readily identified using both the calculated isotope values (top) and the spectral metrics (bottom).

The resulting measurements of $\delta^2\text{H}$, $\delta^{18}\text{O}$, m_{BB} , and m_{NB} are shown in Figure 4. Note that only the corrected values are shown and the samples were not measured via IRMS.

The plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ (Figure 4 top) clearly shows that, if the wine and water have substantially different isotope ratios, the calculated isotope measurements can be used to identify wine watering. This assumption is justified as wine samples usually have enriched $\delta^{18}\text{O}$ isotope ratios relative to naturally-occurring, meteoric waters. For example, German, Italian, and French wines have $\delta^{18}\text{O}$ values ranging from approximately $-3\text{\textperthousand}$ to $+7\text{\textperthousand}$,⁵ whereas the corresponding $\delta^{18}\text{O}$ isotope ratios of the groundwater in these countries range from $-6\text{\textperthousand}$ to $-12\text{\textperthousand}$. Moreover, a plot of m_{NB} versus m_{BB} also shows that wine watering changes these metric values primarily by diluting the ethanol and methanol concentrations in the wine. A 3% addition of water ($\delta^2\text{H} = -73\text{\textperthousand}$, $\delta^{18}\text{O} = -10.3\text{\textperthousand}$, $m_{\text{NB}} = 0.15$,

$m_{\text{BB}} = 0.99$) to wine ($\delta^2\text{H} = +45\text{\textperthousand}$, $\delta^{18}\text{O} = +8.0\text{\textperthousand}$, $m_{\text{NB}} = 15.7$, $m_{\text{BB}} = 1.983$) results in a change in the isotope ratios and spectral metrics of $\Delta\delta^2\text{H} = 7.9\text{\textperthousand}$, $\Delta\delta^{18}\text{O} = 0.32$, $\Delta m_{\text{NB}} = 1.1$, and $\Delta m_{\text{BB}} = 0.039$. Taking into account that $\delta^2\text{H}$, $\delta^{18}\text{O}$, m_{NB} , and m_{BB} are measured with a precision (1σ) of $\pm 0.95\text{\textperthousand}$, $\pm 0.07\text{\textperthousand}$, ± 0.067 , and ± 0.0054 , respectively, the data suggests that the LWIA can be used to identify watering levels of 1%, the target for many wine authentication studies.

The analyzer was then used to measure the isotope ratios and spectral metrics for mixed wines (Figure 5). Two wines (Wine 1 and Wine 2) were mixed to produce samples varying from 0%–100% Wine 2. Wine 1 and Wine 2 had isotope values $\delta^2\text{H}/\delta^{18}\text{O}$ of $18.9\text{\textperthousand}/5.63\text{\textperthousand}$ and $2.6\text{\textperthousand}/0.68\text{\textperthousand}$, respectively. The wine mixtures had corrected isotope values that fell between the two wines, and the analyzer could identify samples that contained more than 10% Wine 2. Note that the spectral metrics

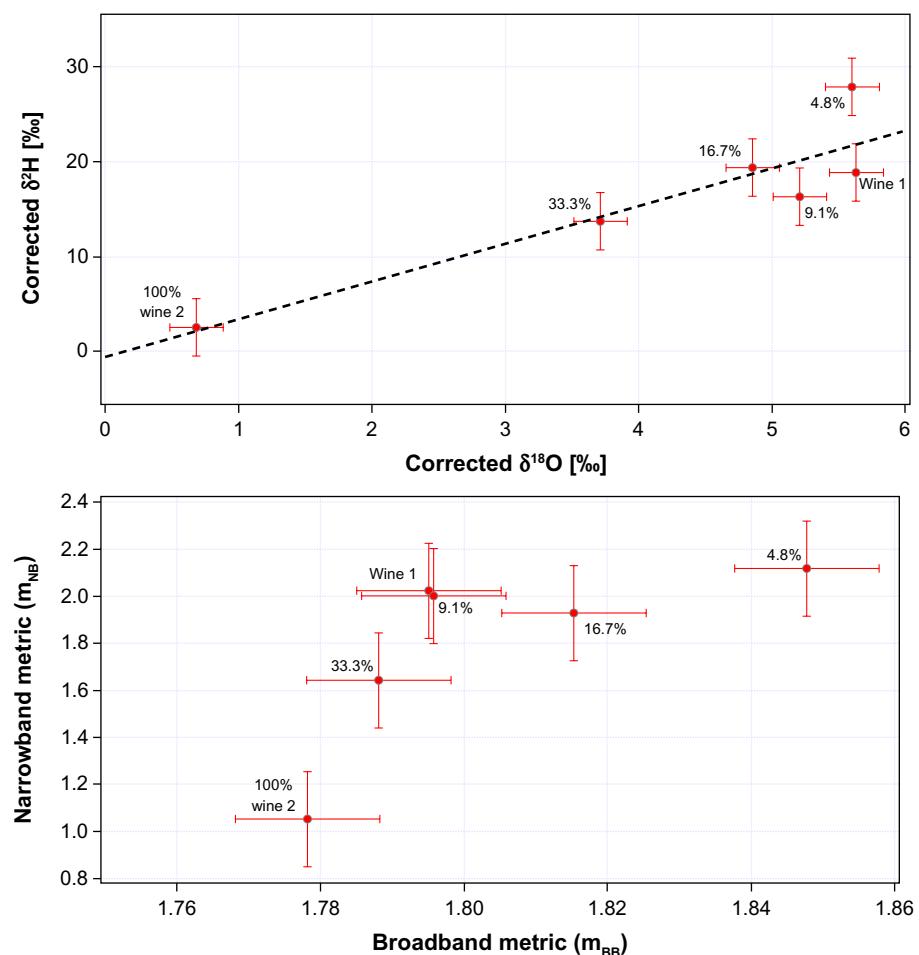


Figure 5 Analyzing the mixing of two wine samples with disparate isotope ratios.

Notes: Mixing of two wine samples with disparate isotope ratios could be identified by measuring the isotope ratio of the resulting mixture (top). The spectral metrics (bottom) did not provide additional information, since both wine samples contained similar levels of ethanol and methanol.

could not easily distinguish between the samples as they had comparable m_{BB} values and relatively small m_{NB} values.

Conclusion

A commercial, laser-based, OA-ICOS LWIA was used in conjunction with spectral contaminant identification software to make preliminary measurements of wine samples. The instrument was able to determine the ethanol content and $\delta^{18}\text{O}$ isotope ratios of the samples. By training the analyzer on the IRMS values, the LWIA and IRMS agreed to within $\pm 0.30\text{\%}$. The analyzer was then used to identify watered and mixed wine samples using both isotope values and spectral metrics. Based on these results, we conclude that the instrument may be used to verify wine authentication and address other applications of wine isotopes.²⁰ Future work will involve further validating the methodology by measuring a larger set of characterized wine samples that span a greater range of wine types and isotope ratios.

As noted above, the technique also reports correct $\delta^2\text{H}$ values for the water in the wine. Currently, these values cannot be readily confirmed by IRMS, since IRMS analysis of $\delta^2\text{H}$ in wines involves measuring the isotope ratio of all of the hydrogen in the wine sample (ie, water, ethanol, methanol) via thermal conversion elemental analysis (TCEA). Similarly, OIV Method OIV-MA-AS311-05 involves using NMR to measure $\delta^2\text{H}$ of the ethanol in the wine.¹¹ Thus, it may be possible to combine these techniques to determine the $\delta^2\text{H}$ isotope ratio of both water and ethanol in wines. Furthermore, isotopic analysis with the OA-ICOS analyzer can be extended to address fruit juice extracts, concentrated spirits, and other food authentication applications.

Acknowledgments

Los Gatos Research would like to gratefully acknowledge Encotech SAGL for their support and help in procuring the isotopically-characterized wine samples. Los Gatos

Research would also like to acknowledge Ketav Shah for preparing the wine samples for OA-ICOS analysis. Partial funding for this effort was provided through the Department of Energy's Small Business Innovative Research Program grant DE-FG02-07ER8496.

Disclosure

The authors report no conflicts of interest in this work. MG, JBL, and ESFB are employees of Los Gatos Research.

References

1. No author Château Lafake: the fine-wine boom is attracting forgers. *The Economist*. June 16, 2011; Sect Business.
2. Chambery A, del Monaco G, Di Maro A, Parente A. Peptide fingerprint of high quality Campania white wines by MALDI-TOF mass spectrometry. *Food Chem*. 2009;113(4):1283–1289.
3. Cordella C, Moussa I, Martel AC, Sbirrazzuoli N, Lizzani-Cuvelier L. Recent developments in food characterization and adulteration detection: technique-oriented perspectives. *J Agric Food Chem*. 2002;50(7):1751–1764.
4. Martin GJ, Guillou C, Martin ML, Cabanis MT, Tep Y, Aerny J. Natural factors of isotope fractionation and the characterization of wines. *J Agricul Food Chem*. 1988;36(2):316–322.
5. Rossmann A, Reniero F, Moussa I, Schmidt HL, Versini G, Merle MH. Stable oxygen isotope content of water of EU data-bank wines from Italy, France and Germany. *Z Lebensm Unters Forsch A*. 1999;208(5): 400–407.
6. Christoph N, Rossmann A, Voerkelius S. Possibilities and limitations of wine authentication using stable isotope and meteorological data, data banks and statistical tests. Part 1: Wines from Franconia and Lake Constance 1992 to 2001. *Mitt Klosterneuburg*. 2003;53(1–2): 23–40.
7. Bréas O, Reniero F, Serrini G, Martin GJ, Rossmann A. Isotope ratio mass spectrometry: analysis of wines from different European countries. *Rapid Commun Mass Spec*. 2005;8(12):967–970.
8. Jamin E, Guérin R, Rétif M, Lees M, Martin GJ. Improved detection of added water in orange juice by simultaneous determination of the oxygen-18/oxygen-16 isotope ratios of water and ethanol derived from sugars. *J Agric Food Chem*. 2003;51(18):5202–5206.
9. Meier-Augenstein W, Kemp HF, Hardie SML. Detection of counterfeit Scotch whisky by ^2H and ^{18}O stable isotope analysis. *Food Chem*. 2012;133(3):1070–1074.
10. Sven A, Michaud AL, Brenna JT. Sourcing organic compounds based on natural isotopic variations measured by high precision isotope ratio mass spectrometry. *Curr Organic Chem*. 2003;7(15):1527–1543.
11. Guyon F, Douet C, Colas S, Salagoity MH, Medina B. Effects of must concentration techniques on wine isotopic parameters. *J Agric Food Chem*. 2006;54(26):9918–9923.
12. Lis G, Wassenaar LI, Hendry MJ. High-precision laser spectroscopy D/H and $^{18}\text{O}/^{16}\text{O}$ measurements of microliter natural water samples. *Anal Chem*. 2008;80(1):287–293.
13. Wassenaar LI, Van Wilgenburg SL, Larson K, Hobson KA. A groundwater isoscape (δD , $\delta^{18}\text{O}$) for Mexico. *J Geochem Explor*. 2009;102(3):123–136.
14. Berman ESF, Gupta M, Gabrielli C, Garland T, McDonnell JJ. High-frequency field-deployable isotope analyzer for hydrological applications. *Water Resour Res*. 2009;45:W10201.
15. Berman ES, Fortson SL, Snaith SP, et al. Direct analysis of δH and $\delta^{18}\text{O}$ in natural and enriched human urine using laser-based, off-axis integrated cavity output spectroscopy. *Anal Chem*. 2012;84(22): 9768–9773.
16. Brian Leen J, Berman ES, Liebsson L, Gupta M. Spectral contaminant identifier for off-axis integrated cavity output spectroscopy measurements of liquid water isotopes. *Rev Sci Instrum*. 2012;83(4):0444305.
17. Schultz NM, Griffis TJ, Lee X, Baker JM. Identification and correction of spectral contamination in $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ measured in leaf, stem, and soil water. *Rapid Commun Mass Spectrom*. 2011;25(21): 3360–3368.
18. López S, Castro R, García E, Pazo JAS, Barroso CG. The use of activated charcoal in combination with other fining agents and its influence on the organoleptic properties of sherry wine. *Eur Food Res Technol*. 2001;212(6):671–675.
19. O'Neil JR, Truesdell AH. Oxygen isotope fractionation studies of solute-water interactions. A Tribute to Samuel Epstein. The Geochemical Society, Special Publication No 3. *Stable Isotope Geochem*. 1991;3:17.
20. West JB, Ehleringer JR, Cerling TE. Geography and vintage predicted by a novel GIS model of wine delta ^{18}O . *J Agric Food Chem*. 2007;55(17):7075–7083.

International Journal of Wine Research

Publish your work in this journal

The International Journal of Wine Research is an international, peer-reviewed open-access, online journal focusing on all scientific aspects of wine, including: vine growing; wine elaboration; human interaction with wine; and health aspects of wine. The journal provides an open access platform for the reporting

Submit your manuscript here: <http://www.dovepress.com/international-journal-of-wine-research-journal>

Dovepress

of evidence based studies on these topics. The manuscript management system is completely online and includes a very quick and fair peer-review system, which is all easy to use. Visit <http://www.dovepress.com/testimonials.php> to read real quotes from some of our published authors.