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Determination of Olive Oil Oxidative Status by Selected Ion Flow Tube Mass Spectrometry

BRETT M. DAVIS AND MURRAY J. MCEWAN*

Department of Chemistry, University of Canterbury, and Syft Technologies Ltd., 3 Craft Place, Middleton, PB4800 Christchurch, New Zealand

The emergence of primary and secondary oxidation products in New Zealand extra virgin olive oil during accelerated thermal oxidation was measured and correlated with the concentrations of 13 headspace volatile compounds measured by selected ion flow tube mass spectrometry (SIFT-MS). SIFT-MS is a mass spectrometric technique that permits qualitative and absolute quantitative measurements to be made from whole air, headspace, or breath samples in real-time down to several parts per billion (ppb). It is well-suited to high-throughput analysis of headspace samples. Propanal, hexanal, and acetone were found at high concentrations in a rancid standard oil, while propanal, acetone, and acetic acid showed marked increases with oxidation time for the oils used in this study. A partial least-squares (PLS) regression model was constructed, which allowed the prediction of peroxide values (PV) for three separate oxidized oils. Sensory rancidity was also measured, although the correlations of headspace volatile compounds with sensory rancidity score were less satisfactory, and too few results were available for the construction of a PLS regression model. A fast (approximately 1 min), reliable method for prediction of olive oil PVs by SIFT-MS was developed.

INTRODUCTION

The assessment of defects in virgin olive oil is a necessity for all producers who wish to sell their oil to the public. For an olive oil to be labeled as extra virgin, the International Olive Oil Council (IOOC) regulations (*1*) state that it must meet rigorous chemical standards with respect to a list of factors including fatty acid and triglyceride composition, degree of triglyceride hydrolysis, and degree of undesired oxidation. These tests are all carried out according to official methods and are considered very reliable and reproducible. Yet, there is one essential test that is not based on objective instrumental testing: the sensory panel test.

The sensory panel test has been developed to be as robust and reproducible as possible, with rigorous selection and retention criteria for members of tasting panels and a precisely controlled environment where light levels and temperature are maintained according to IOOC regulations. Panelists are trained to recognize off-odors and flavors present in samples and to rate them according to their intensities. However, this form of testing is difficult and time-consuming to perform.

For several decades, researchers have attempted to explain the results of sensory panels by relating these to the volatile organic compounds (VOCs) present in olive oil as measured by instrumental techniques (*2*−*4*). This has produced promising results, with some researchers proposing markers for the detection of specific defects, the most widely studied being rancidity (*5*, *6*). Rancidity is the sensory defect associated with oil autoxidation. The sensory test is able to identify the rancid defect through the measurement of volatile secondary oxidation products. There are already established instrumental methods that can measure the oxidative status of oil. The most commonly employed of these is the peroxide value (PV) test, which measures lipid peroxides, primary oxidation products (*7*). However, this test cannot predict the sensory acceptability of the oil, as a taste test is still required to identify sensory defects. Morales et al. (*6*) monitored the gas chromatography−mass spectrometry (GC-MS) peak area ratios of hexanal to nonanal, as both are secondary products of lipid oxidation. Hexanal is also present in the headspace above fresh, faultless oil samples, due to the action of olive enzymes. As the oil becomes increasingly oxidized, the areas of both peaks increase and the ratio can approach one to one.

The most pronounced disadvantages of sensory panels are the low sample turnover rate and the expense of carrying out this type of analysis. The majority of instrumental studies has involved GC-MS analysis of olive oil VOCs. While this technique may ultimately decrease the cost associated with VOC analysis, it is not likely to provide a high sample turnover rate, as GC-MS is not a real-time technique. Aparicio et al. (*8*) addressed this issue by replacing their GC-MS-based method with one based on VOC detection by an electronic nose. The result was a relatively rapid method, involving no sample pretreatment, for detection of the rancid defect in virgin olive oil. The sample turnover time was approximately 5 min, and in that time, a reliable indication of the strength of the rancid defect was obtained for the sample set used.

The present study involves the application of direct headspace sampling by selected ion flow tube mass spectrometry (SIFT-MS) to the determination of olive oil oxidative status. SIFT-

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MS is a direct mass spectrometric technique that allows qualitative and quantitative analysis of a number of VOCs in real time (*9*), with a sample turnover time that depends ultimately on both the number of analytes being monitored and the desired analytical precision. The present method has a turnover time of approximately 1 min, permitting high-throughput analysis of headspace samples. Very few other techniques offer such a simple and rapid method of sample analysis. The SIFT-MS technique does not involve temporal separation of analyte VOCs, but instead, selective chemical ionization is used. The headspace above an olive oil is sucked through a flow-limiting orifice into a flow tube. Mass-selected reagent ions are introduced into the flow tube where ion−molecule reactions of the reagent ion with the VOCs in the headspace occur. The product ions of the reaction are monitored by a mass spectrometer located at the downstream end of the flow tube. The amplitude of the product ion signal arising from the ion−molecule reactions of the reagent ion and analyte provides a quantitative measure of the amount of analyte in the headspace. These product ions are characterized by their masses using a quadrupole mass spectrometer. The analysis of mixtures is possible because the reaction of each analyte molecule with a selected reagent ion has a small number of possible products, and there is normally little fragmentation. SIFT-MS is currently finding application in many areas (*10*), including detection of human breath VOCs (*11*, *12*) and bacterial metabolites (*13*).

MATERIALS AND METHODS

Oil Oxidation. Three olive oils from New Zealand were obtained for use in this study. For each oil, 50 ± 0.5 mL oil was added to each of 29 glass vials of volume 125 mL, which were then sealed with septa and placed in a water bath heated at 60 ± 1°C. The remaining oil was analyzed by SIFT-MS, submitted for a peroxide test, and subjected to a taste test. One vial was removed from the water bath daily for SIFT-MS analysis. Every second sample vial was also submitted for a peroxide test after SIFT-MS analysis. In addition, every fourth day, five extra vials were removed and the oil from these vials was combined and submitted for taste testing by an accredited panel of tasters. On occasions, the timing of this procedure was extended from sequential days to an interval of 2 days to achieve a higher degree of rancidity.

SIFT-MS Analysis. A 5 ± 0.1 mL amount of olive oil was placed in a 500 mL clear glass bottle (Schott Glass, Mainz, Germany), full capacity 632 ± 0.5 mL, with a silicone rubber septum cap, and was left to stand for 20 min at 25 ± 0.2 °C to allow a good partition of volatiles between the liquid and the gas phases. All SIFT-MS analyses were performed using an instrument, which has been described previously (*10*). The vial headspace was sampled via a needle into the SIFT-MS flow tube through a calibrated, heated stainless steel flow limiter at a rate of 1.69 ± 0.1 Torr L s^{-1} (133 ± 8 mL min^{-1} under standard conditions). The flow tube contained He flowing at 57.6 ± 0.1 Torr L s^{-1} (4547 ± 8 mL min^{-1}) and Ar flowing at 9.3 ± 0.2 Torr L s^{-1} (730 ± 10 mL min^{-1}), with a total internal tube pressure of 0.80 ± 0.05 Torr (106 ± 7 Pa).

Analysis was performed using selected ion mode (SIM) scans, analyzing 14 compounds using known kinetic parameters (*14*−*17*): methanol, ethanol, propanol, pentanol, propanal, acetone, hexanal, (*Z*)-3-hexenal, (*E*)-2-hexenal, ethyl acetate, acetic acid, propanoic acid, (*E*)-2-pentenal, and nonanal. We have previously shown that the major volatiles of olive oil are methanol followed by ethanol followed by *trans*-2-hexenal (*10*).

PV Determination. The PVs were determined by AgriQuality in Auckland, New Zealand. AgriQuality is the official laboratory used by Olives New Zealand for chemical tests on olive oil. The assay was performed according to AOCS method Cd 8b-90, and results were expressed as mequiv of O_2/kg.

Sensory Analysis. Olive oil samples were analyzed for the rancid defect by the sensory panel at Hort Research in Auckland, New Zealand. This panel was awarded full accreditation for the tasting of olive oil by the IOOC part way through the present study but held at least provisional accreditation at all times during the study. The Hort Research panel is used by Olives New Zealand for extra virgin certification of oils. Defects were scored according to the IOOC-recommended procedure (*18*), where each panel member rated the strength of the defect by a mark on a continuous line 10 cm in length. The left end of the line denoted no perceptible defect, and the right end denoted full strength defect. The distance of the mark from the left end of the line was measured, with the median and robust standard deviation of the entire panel reported.

Statistical Analysis. The method of partial least-squares (PLS) regression was used to obtain a model for prediction of PV. PLS regression is a confirmatory technique, which generates new variables (called latent variables) designed to efficiently predict a set of dependent values from a set of independent values. The latent variables are created in such a way as to best represent the correlations between the independent and the dependent variables. This is achieved by reducing the dimensionality of the data and producing a model that includes the lowest possible number of variables. PLS regression was performed using Matlab 6.5, Release 13, via the nonlinear iterative partial least-squares algorithm presented by Haaland and Thomas (*19*). The number of latent variables to include was evaluated using the root-mean-square error of cross-validation [RMSECV, suggested in the Matlab PLS Toolbox 3.5 Reference Manual (*20*)]. Evaluation of the model's prediction was achieved by the "leave-one-out" cross-validation method suggested by Martens and Dardenne (*21*). Essentially, cross-validation (determining the optimum number of latent variables to include) was conducted by extracting one sample, building a model using the remaining samples, and predicting the result for the extracted sample. This was repeated for all samples to obtain residual values that permitted the evaluation and comparison of models with different numbers of latent variables. This is considered to be the best method when only a small sample size is available.

RESULTS AND DISCUSSION

The sensitivity of the SIFT-MS technique is determined by the amount of product ion detected for a given amount of corresponding analyte. This is dependent on the amount of reagent ion and the rate of reaction of the analyte concerned with the reagent ion. Typical reagent ion counts for the H_3O^+ reagent ion were 2.5×10^5 s^{-1}, while NO^+ counts were typically 3.7×10^5 s^{-1}. This, combined with rate constants for the analytes between 0.9 and 4.0×10^{-9} cm^3 s^{-1}, gives sensitivities of between 0.7 and 3.0 counts per second of product ion per ppb analyte.

The precision of SIFT-MS is dependent on the ion count for each product ion species. Obviously, this depends on the sensitivity, but it depends also on the time spent counting each product ion. This time may be in two forms: dwell time—the time spent counting ions of a given mass during each SIM cycle—and the number of times the cycle is repeated (the number of sampling points used). The dwell time for all product ions in this study was 100 ms, while 6−8 sampling points were taken for each product ion, from which the counts were averaged to form one measurement.

Accepting 20% standard deviation, the theoretical limits of quantitation for the analytes observed in this study are between 7 and 30 ppb. The experimental values of precision are frequently observed to be very similar to the calculated values.

A mass scan of a rancid olive oil standard using the NO^+ reagent ion for chemical ionization is shown in **Figure 1**. Note the dominant peaks corresponding to propanal, acetone, and hexanal. The ion chemistry relevant to the VOCs monitored is known (*15*). The advantage of NO^+ here over H_3O^+ is that it allows the differentiation of acetone (eq 1) and propanal (eq 2), as each undergoes a different reaction with the NO^+ ion and forms product ions with different masses.

$$NO^+ + CH_3COCH_3 + M \rightarrow CH_3COCH_3 \cdot NO^+ + M^* \quad (1)$$

$$NO^+ + CH_3CH_2CHO + M \rightarrow C_3H_5O^+ + HNO + M^* \quad (2)$$

where M is an inert species found in the flow tube (e.g., helium or argon) to which internal energy is transferred, stabilizing the products formed. Reaction with H_3O^+ yields product ions from acetone and propanal that are identical in mass. Results for the three VOCs, which showed significant correlations with oil PV, are shown in **Figure 2a**−**c**. The R^2 values for the correlations of PV with propanal, acetone, and acetic acid are 0.79, 0.35, and 0.39, respectively. Propanal gives an R^2 value of 0.85 with a logarithmic fit to PV, although it is not known why a logarithmic relationship should give a better fit than a linear one. Acetone has been observed in olive oil samples displaying many different defects (unpublished data), so it is not considered specific to thermal oxidation. Acetic acid did not show a large increase in concentration (no increase was observed for oil B). Although acetic acid is regarded as a fermentation product (*22*, *23*), it is also found at elevated concentration in rancid olive oils (*8*).

The VOCs chosen to monitor oxidative status in this study differ from those reported by other researchers investigating olive oil oxidation. Propanal is often used by researchers investigating oils with a higher linolenic acid content than olive oil (*24*, *25*), while nonanal and hexanal are reported as major secondary oxidation products in many studies performed on olive oil (*22*, *26*). Belitz and Grosch (*27*) report propanal as the major product of autoxidation arising from linolenic acid, pentane the major product of the autoxidation of linoleic acid, and nonanal from oleic acid. Hexanal, octanal, and various other aliphatic aldehydes are listed as significant, yet lesser, products. However, Belitz and Grosch state that hexanal is the major oxidative product in vegetable oil headspace.

SIFT-MS is a technique that gives a quantitative measure of the VOCs in the headspace above the substrate. The superior volatility of propanal as compared with hexanal and nonanal is possibly responsible for the sensitive response to oil oxidation by propanal that is observed in this study. The fact that no large increase in hexanal was detected is difficult to explain given the high degree of rancidity reached, especially as the IOOC defective standard oil showed a significant hexanal concentration. It is clear that the hexanal concentration in the headspace did not exhibit the same increase that propanal did. The lack of appreciable nonanal in the headspace is considered to be a feature of its low volatility. Pentane, as with other similar hydrocarbons, is difficult to distinguish in a complex mixture

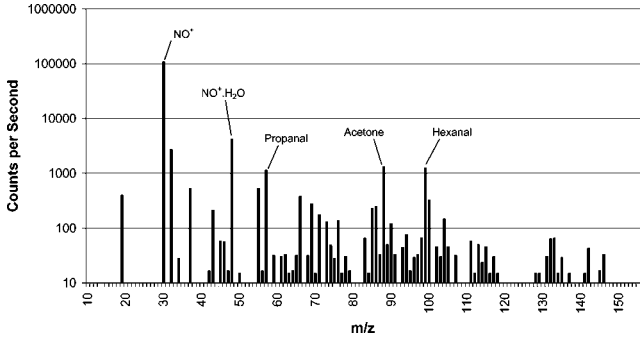

Figure 1. Mass scan of a rancid standard olive oil using the NO^+ reagent ion. Characteristic products of propanal, acetone, and hexanal can clearly be seen. Pentane is not observed because it does not react with the NO^+ reagent ion.

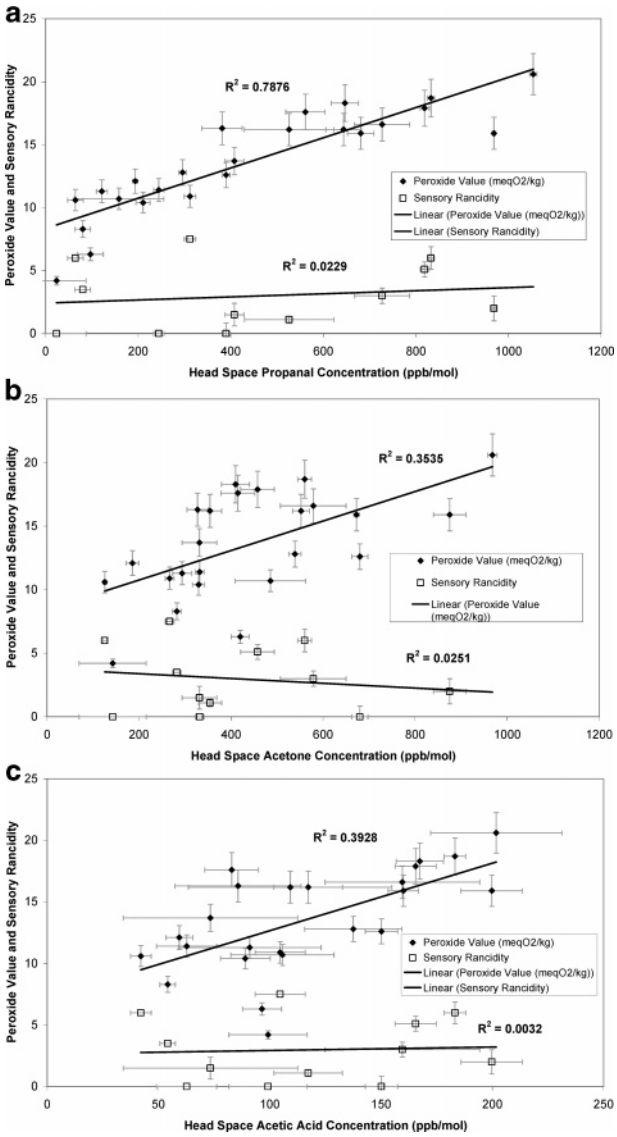

Figure 2. (**a**) Correlation of head space propanal concentration with PV and sensory rancidity for all three olive oils oxidized at 60 °C. SIFT-MS and PV data are means ± standard deviations, while sensory panel results are medians ± robust standard deviations. (**b**) Correlation of head space acetone concentration with PV and sensory rancidity. (**c**) Correlation of head space acetic acid concentration with PV and sensory rancidity.

using the reagent ions employed for this study (*28*). For that reason, it was decided to concentrate on the other autoxidation products.

All three oils exceeded the maximum allowed PV of 15 mequiv O_2/kg for "extra virgin" designation by Olives New Zealand (*29*) by the end of the study. However, only two of the three oils (A and C) exceeded the IOOC limit of 18 mequiv O_2/kg for "extra virgin" designation. To predict the PV of future samples, the multivariate statistical technique of PLS regression was employed. A model involving 13 VOCs was constructed. The rate constants and product ions of all VOCs from reaction with the relevant reagent ions have been previously characterized by SIFT-MS and published (*14*−*17*). Latent variable loadings for all 13 VOCs on the first three latent variables are shown in **Figure 3a**,**b**. As expected, propanal, acetone, and acetic acid display the highest loadings on the first latent variable. Predicted PVs by the PLS regression model including three latent variables are plotted in **Figure 4**, along with the corresponding measured values. The fit of the model is displayed graphically in **Figure**

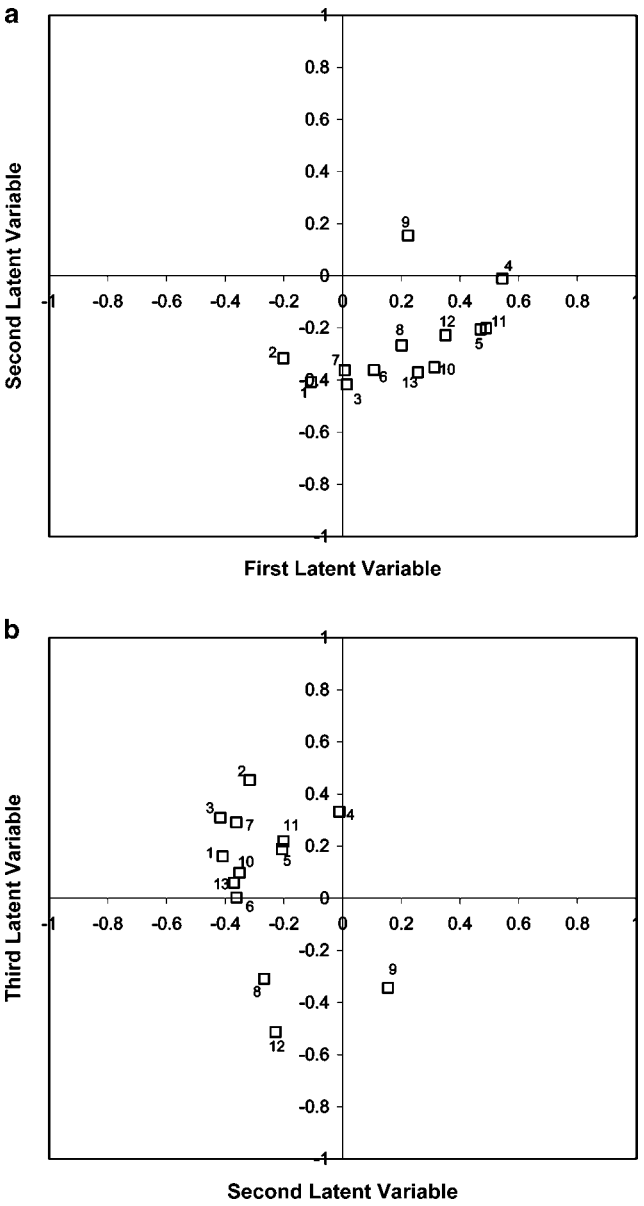

Figure 3. (**a**) Latent variable loadings of the measured VOCs on the first and second latent variables of the PLS model generated to predict PV from head space VOC concentrations. VOCs included are as follows: 1, methanol; 2, ethanol; 3, propanol isomers; 4, propanal; 5, acetone; 6, hexanal; 7, (*Z*)-3-hexenal; 8, (*E*)-2-hexenal; 9, ethyl acetate; 10, (*E*)-2-pentenal; 11, acetic acid; 12, propanoic acid; and 13, pentanol isomers. (**b**) Latent variable loadings of the measured VOCs on the second and third latent variables of the PLS model.

5 (RMSECV = 0.39), where the measured values are plotted against the predicted values.

A median score greater than zero for rancidity from the panel test exceeds both the Olives New Zealand and IOOC limits for "extra virgin" designation. No VOC monitored in this study showed a significant direct correlation with the panel test. This behavior was unexpected and suggests that rancidity as measured by the panel test, unlike PV, does not display a simple correlation with secondary oil oxidation products. The limited number of samples available prohibited the use of PLS regression for the tasting data, as the resultant model would be expected to suffer from overfitting, displaying very good descriptive power for the data used, yet very poor predictive power for new data.

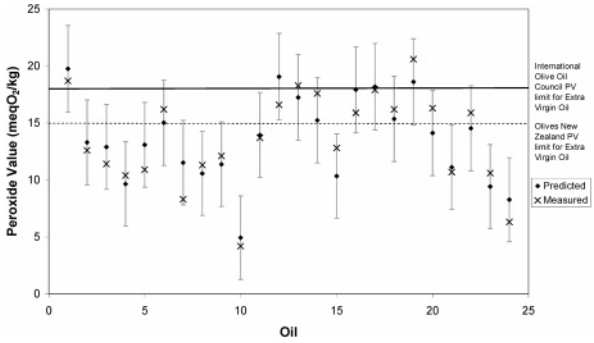

Figure 4. Predicted PVs of the test set for the PLS regression model. The maximum allowed limits of PV for Olives New Zealand (15 mequiv O_2/kg) and the IOOC (18 mequiv O_2/kg) are shown.

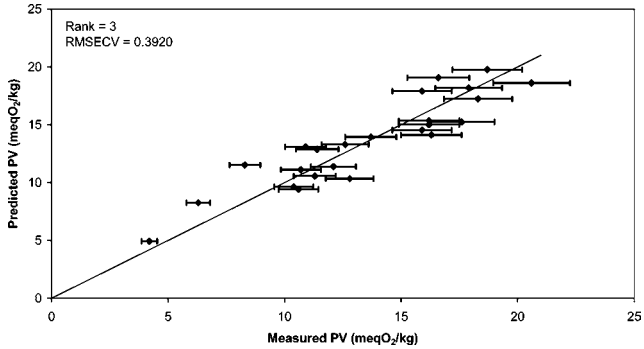

Figure 5. Plot showing the predictive power of the PLS regression model for the test set. Values are means ± standard deviations of triplicate SIFT-MS head space measurements.

Even though no increase in hexanal was observed for the olive oils oxidized in this study, the rancid standard did display a high concentration of hexanal. The analysis of hexanal appears to present a somewhat more coarse route for the determination of olive oil oxidative status—so coarse that no direct correlation between the hexanal concentration and the desired properties was observed in this study. We also note that measurements made of many bulk supply olive oils sold in New Zealand supermarkets had high levels of propanal as compared to freshly produced oils. Nonanal was not detected in any of the samples, reflecting its low vapor pressure. Chromatographic techniques consistently uncover the presence of hexanal and nonanal in oxidized olive and similar oils (*5*, *6*, *8*, *30*−*32*). These compounds may have higher volatility in other techniques due to higher sampling temperatures, as all SIFT-MS analyses are conducted at room temperature. GC-MS, especially when coupled to solid-phase microextraction (SPME), can achieve a lower detection limit as a consequence of preconcentration of the VOC on the SPME fiber. This process is, however, time-consuming. The advantages of SIFT-MS in its rapid real-time analysis and the absence of sample preparation make it well-suited to the rapid appraisal of oxidative status of olive oil.

The technique of SIFT-MS has been shown to provide a useful indication of olive oil oxidative status. Headspace propanal, acetone, and acetic acid concentrations were observed to rise with increasing PV in this study, and a PLS regression model including 13 VOCs was constructed to predict oil PV. Rancidity as found by the sensory panel test did not correlate well with headspace VOC concentrations or PV. Sensory rancidity is likely conveyed by a much larger group of compounds (not all of which are necessarily volatile) than was included in this study and, therefore, was difficult to characterize on the basis of the chosen VOCs.

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