

Detection of Vinegary Defect in Virgin Olive Oils by Metal Oxide Sensors

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An array of metal oxide sensors has been set up for detecting the vinegary defect in virgin olive oil. The optimization process was carried out evaluating the variables affecting the process by three desirability functions. Repeatability studies for 6 months and within day were done to evaluate the sensor responses and remove those with high relative standard deviation. The sensor responses were preprocessed applying five weight functions previously to build a regression model. Samples of Spanish Arbequina and Picual virgin olive oil varieties spiked with different amounts of acetic acid (15–200 mg/L) were used as a training set for the regression model. The test set was composed of samples of Italian Coratina virgin olive oil spiked with the vinegary standard at five percentages (10, 25, 40, 50, and 75). A fine-adjusted regression coefficient ($R_{adj}^2 = 0.98$) was computed with the test set.

KEYWORDS: Olive oil; electronic nose; vinegary defect; regression

INTRODUCTION

Aroma is a fundamental parameter in the sensory quality assessment procedures for virgin olive oil (VOO). To date, the sensory evaluation of VOO is determined by standardized panel tests described in the European Union regulation (1) and trade standards of the International Olive Oil Council (IOOC) (2). Panels of trained assessors are used in both cases to evaluate a set of sensory descriptors. Sensory descriptors of VOO can be classified into “positive” and “negative”. The latter describes defects of VOO, and they are mainly fusty, musty, muddy sediment, vinegary, metallic, and rancid. Chemical compounds, mainly volatiles, are responsible for these defects, and they are formed through biogenic pathways of olives, during the oxidation process of the unsaturated fatty acids, by the attack by molds and bacteria, or when olives are overripe (3). In the case of the vinegary defect, the volatile compounds are produced by acetic bacteria, which grow during the storage of olives. Ethyl acetate and acetic acid are the main metabolites responsible for this defect (4).

The identification of the vinegary defect is usually carried out by two procedures, the panel test (5) and the analysis of volatile compounds (3). The former procedure is slow and costly, and small cooperative societies cannot afford it. The alternative solution is based on the quantification of volatile compounds by dynamic headspace high-resolution gas chromatography (GC) (6). This procedure, though easy and rapid, cannot be applied online in the processes of storage and bottling of the VOOs.

A second alternative to a panel test is based on the use of sensors that have been widely adopted in many fields of

analytical chemistry (7). The electronic nose, usually called the array of sensors, is an emergent technology in the quality assessment of foodstuffs (8–10). Previous papers have reported the application of sensors in the detection of VOO defects (11), classification of edible oils (12), volatile compounds (13), and edible oil shelf life (14, 15).

This paper analyzes the possibilities of three arrays of metal oxide sensors (MOS) in the detection of the vinegary attribute and their potential application in the sensory assessment of VOO. For this purpose, the variables of the electronic nose were optimized and modeled before the regression analyses.

MATERIALS AND METHODS

Materials. A Spanish VOO cv. Arbequina spiked with 60 mg/kg of acetic acid was the standard used in the repeatability studies. This standard was kept frozen between analytical runs and remained stable over the course of the experiments. An Italian VOO sample (Coratina var.) was used for optimizing the procedure. The training set was composed of two Spanish VOOs (Picual and Arbequina varieties) spiked with various amounts of acetic acid (15, 30, 60, 90, 120, and 200 mg/L). The test set was composed of an Italian VOO (Coratina var.) that was spiked with the standard of vinegary VOO at 10, 25, 40, 50, and 75%. The standard, supplied by the IOOC, had an intensity of vinegary attribute 9 out of 10. The objective of the test set was not only to verify the results of the training set but also to check the detection of vinegary perception in VOO as the calibration of sensors (training set) was done by simply adding various amounts of acetic acid.

Equipment. A Fox 4000 with ACU500 humidifier supplied by AlphaMOS SA (Toulouse, France) was used. This instrument is equipped with 18 MOS inside three chambers, six of which are undoped MOS and 12 that are MOS-doped with noble catalytic metals to shift the selectivity spectrum toward different chemical compounds. The temporary and reversible adsorption of volatile reducing compounds at the sensor surface changes its electrical resistance in a nonlinear

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manner (8). The response is characteristic of each sensor and depends on the concentration and the profile of the volatile compounds in the sample.

The air conditioning unit (ACU 500) consists of a thermostated tank containing distilled water where the carrier gas bubbles continually. In that way, dry and humid air streams are obtained. A controlled mixture of dry and humid synthetic airs sweeps the headspace of the sampling chamber whose temperature is controlled automatically. When a valve is opened in the injection phase, the gas sweeps the headspace of the sampling chamber and flows successively to the three sensor chambers. Inside each chamber, two sensors measure the temperature and the relative humidity; there is not any automatic control.

Industrial air, from an air compressor, was used as a carrier gas after it was filtered through two columns. The first column was filled with molecular sieve 8/12 mesh (Supelco, Bellefonte, PA) to remove the moisture, while the second column was filled with activated carbon (Supelco, Bellefonte, PA) to remove hydrocarbons and other undesirable volatile compounds. No significant differences in the baseline were found when synthetic air and this purified industrial air were compared.

Procedure after Optimizing the Conditions. Aliquots of 5 g of each sample—enough to cover the bottom of the 100 mL flasks—were heated at 34 °C inside a controlled thermostat sampling chamber for 10 min. After this headspace generation time, the carrier gas (air) pumped the volatile compounds into the sensor chambers at a flow rate of 100 mL/min for 90 s, the so-called injection time. After the injection time, a valve was switched and only carrier gas was blown into the sensor chambers to return to the baseline of the sensor signals as soon as possible. The computer starts to collect data immediately after the headspace generation time for 600 s, 90 s of the injection time and 510 s of desorption time. The time between subsequent analyses was 900 s. The flow rate was kept at 500 mL/min during the first 10 min of this nonmeasurement time. These conditions ensured that the baseline had indeed been recovered before performing the next analysis. Samples were analyzed in duplicate.

Standards for calibration of the sensor array were measured at programmed times to control the aging of sensors that did not affect the measurements.

Optimizing Electronic Nose Conditions. In the optimization process, the main goal was to extract the maximum amount of unbiased information regarding the factors affecting the procedure from as few observations as possible.

A Hyper Greco Latin-square design was used because the factors of interest had more than two levels, and we previously knew that there were no interactions between them (12). Numerous input variables have a possible influence upon the electronic nose though some of them are insignificant or nonpertinent, and they have been rejected. Sample amount, headspace generation time, sample temperature during the headspace generation, flow rate sweeping the volatile compounds, and injection time were identified as the most significant variables, and they were used in the experimental design.

In previous papers about the analysis of VOO volatile compounds, the authors had established that sample temperature in headspace studies should not be above 50 °C in order to avoid degradation of volatiles (16). At higher temperatures, olive oil becomes rancid; hence, it has high concentrations of aldehydes and acids (17) that will certainly mask the results (14). On the other hand, previous experience had shown that sample temperatures lower than 25 °C require a too-long headspace generation time (6).

The authors' experience working on dynamic headspace, for the concentration of VOO volatile compounds, was used to delimit the minimum amount of sample in relation to the volume of the flasks (18). The minimum was 5 g, an amount that was enough to cover the bottom of the flask, while the maximum was selected arbitrarily at 30 g.

The maximum and minimum generation times were selected according to the literature, with the only condition being that the minimum time was sufficient to allow sensors to reach equilibrium. From a mathematical viewpoint, the equilibrium is reached when the sensor response is asymptote to a value. The minimum value was fixed at 10 min while the maximum was 30 min. The maximum and minimum flow rates were also taken from the literature (400 and 100

Table 1. Hyper Greco Latin-Square Experiments^a

E	S	W	F	T	I	E	S	W	F	T	I
1	30	5	400	25	30	9	15	5	175	50	60
2	30	15	250	34	60	10	15	15	100	42	30
3	30	25	175	42	90	11	15	25	400	34	120
4	30	30	100	50	120	12	15	30	250	25	90
5	20	5	250	42	120	13	10	5	100	34	90
6	20	15	400	50	90	14	10	15	175	25	120
7	20	25	100	25	60	15	10	25	250	50	30
8	20	30	175	34	30	16	10	30	400	42	60

^a Values of the variables affecting sensor responses. Figures in bold represent the best conditions. Legend: E, order number of the experiments; S, generation time (min) of the static headspace; W, sample weight (g); F, carrier gas flow rate (mL/min) sweeping volatiles; T, sample temperature (°C); and I, injection time (s).

mL/min, respectively) since the authors had no previous experience. The minimum and maximum injection times were 30 and 120 s, periods of time that were enough to reach the equilibrium with any sample of VOO.

Conceptually speaking, optimizing implies that the variable to be maximized has been selected and that the response of the sensors contains enough information for this purpose. The problem is to decide which characteristics would be useful in determining the quality of the sensor responses. These characteristics, a mixture of objective and subjective factors, are called desirabilities, and they will be the set of output variables to be optimized. Three desirability variables were evaluated as follows: the slope of the sensor adsorption, the dynamic equilibrium of the sensors, and the output balance.

It is well-known that the sensors need a certain period of time to produce a stable response to the excitation produced by the volatile compounds. Thus, the slope of the sensor adsorption indirectly measures the time that each sensor needs to reach equilibrium. The lower the slope angle, the greater the range for distinguishing oils.

The sensors exhibit interactions when volatile compounds flow over them. A dynamic equilibrium develops as volatile compounds are constantly adsorbed and desorbed at the sensor surface (19). The evaluation of this desirability variable was based on the equilibrium and recovery time. They are the times that the sensor needs to reach either equilibrium or recovery.

The response intensity of each sensor depends on the sensitivity to the food product, but the response can be increased or decreased, acting properly on the variables to be optimized. The increase of the response of some sensors can take others to saturation, or on the contrary, medium response of the most sensitive can generate a very low signal of less sensitive sensors. This desirability represents a balance between these extreme cases by measuring the response intensities of the whole set of sensors.

A Hyper Greco Latin-square experimental design (20) was applied as it is recommended when factors have more than two levels and there are no interactions between factors. Sixteen experiments (Table 1) were automatically programmed (20), and the results were evaluated, in terms of the described desirability functions, by three assessors.

The results of the experimental design, in terms of the three desirability functions, involve a certain degree of uncertainty and fuzziness. Assessors analyzed the same process from three different criteria, and we needed a single function (implication function) that clusters the three desirability functions. Taking into account both aspects (subjectivity and the three criteria), it seems reasonable that the implication functions to calculate the overall desirability should derive from fuzzy logic rather than classical arithmetic. We have applied the fuzzy algorithm Luckasiewicz $T_{1.5}$ -conorm (21) formulated as

$$T_{1.5}(w_1, w_2, w_3) = w_1 w_2 w_3 / [4 - 2(w_1 + w_2 + w_3) + w_1 w_2 + w_1 w_3 + w_2 w_3]$$

where w_1 , w_2 , and w_3 are the values associated with the three desirability functions.

Applying the implication function, the conditions of the thirteenth experiment (weight, 5 g; temperature, 34 °C; generation time, 10 min;

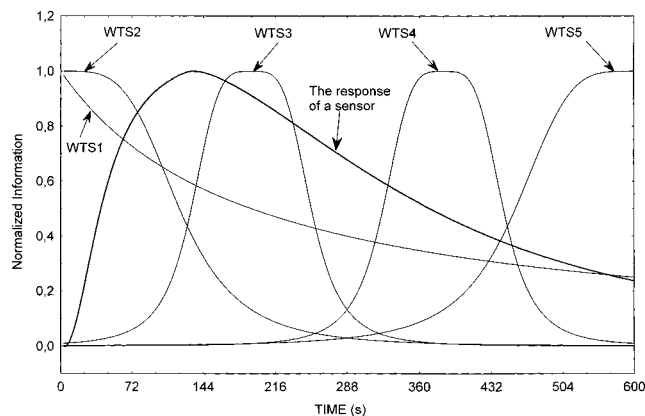


Figure 1. WTS functions for reducing the information of each sensor to five data. The response of a sensor (curve in bold) has been superimposed to show the regions where information is collected.

flow rate, 100 mL/min; and injection time, 90 s) were the best evaluated and hence selected for the next experiments. Modified simplex (22) was also used, and after successive expansions and contractions (23), the results were very similar to the conditions attained by the Hyper Greco Latin-square design.

Data Preprocessing. The response of sensors presents an exponential-like shape, but not all of this information is useful. The data preprocessing operates on the response in a way that allows reduction of the effect of sensor drift, diminishment of the whole set of data to a reasonable number, and normalization of the information (24). After different methods of data preprocessing (raw data, differential transform, and subtracting the baseline of each sensor) were tested, the fractional resistance change $(R_0 - R)/R_0$ (R is steady state resistance, and R_0 is baseline resistance) was selected since it showed the optimum differential properties. Weighting time slicing (WTS) functions have been used to reduce the information of the sensor array to a reasonable dataset. The number of WTS was five. The first function was applied to the whole sensor response while the other four functions were applied to specific regions defined along the response curve, **Figure 1**. The first function allows balancing of the sensor response (adsorption vs desorption) by giving more weight to the adsorption slope. The other four functions, also called windowing time slicing (24), are almost a precise selection of values in the adsorption slope, in the vicinity of the equilibrium stage or steady state (where adsorption and desorption occur at the same velocity), at the middle of the desorption slope, and at the end of the desorption slope. Schaak et al. (25) also reported these selected regions. When WTS functions were performed, vector autoscaling was used to normalize the information from the array of sensors.

Measurements of Repeatability. The study of the repeatability, either between days or within day, was investigated by consecutively collecting the sensor results of the same sample of olive oil (VOO cv. Arbequina spiked with 60 ppm of acetic acid). The within day repeatability was studied by collecting the sensor responses of the same sample 10 times during a day. The between days repeatability was studied by analyzing the results of the samples collected for 6 months. The relative standard deviation (%RSD) was the parameter used to analyze the repeatability, RSD is defined as the ratio between the standard deviation (STD) and the mean.

Mathematical Procedure. Stepwise multiple regression analysis (SMRA) was used to build a predictive linear model that explains the dependent variable (i.e., acetic acid concentration) by the set of independent variables (data after applying WTS functions). SMRA includes in, or excludes from, the equation independent variables at each step of the analysis. When no further variable adds to the prediction equation, the analysis stops. Assumptions of linearity and normality, problems of multicollinearity and outliers, the number of variables and samples, and importance of residual analysis were taken into account when applying the procedure. The F distribution statistical table was used to determine F values, either F -to-enter or F -to-remove, to select the independent variables. The degrees of freedom of these F -values

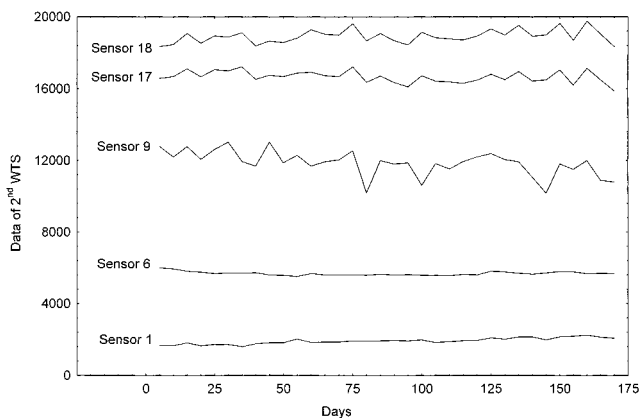


Figure 2. Values of the second WTS of various sensors for 6 months.

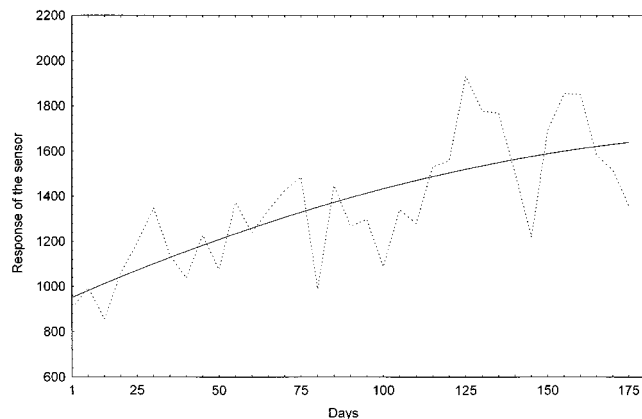


Figure 3. Values of the second WTS of sensor 12 for 6 months.

were “1” and “ $N-p-1$ ”, where N is the number of sample and “ p ” is the number of independent variables in the regression equation. F values were selected from the F distribution table for $F(F) = 0.999$ in all cases. Adjusted R^2 (R_{adj}^2) was chosen as the regression coefficient to avoid the fact that a sensor could be selected because it diminishes or removes irrelevant variance and not because it predicts the dependent variable (26). The Durbin–Watson test (27) was applied to ensure that there was nonautocorrelation among residuals. Statistica (20) was used to perform the data processing and to implement multivariate data analyses.

RESULTS AND DISCUSSION

Study of Repeatability. Because sensor signal drifts are often observed when analyzing from day to day, it is important to understand whether any signal variation is due to sample change or inherent signal drift. Thus, the use of reference standards seems very important when carrying out any electronic nose analyses (15). We selected a VOO spiked with acetic acid because the best material for monitoring performance and providing data for recalibration should be similar to the product that is being tested (12, 15).

Figure 2 shows the response of some sensors (WTS 2) over a period of 6 months to study their aging (28, 29). The fact that the signals of those sensors do not decrease or increase continuously leads to the assumption that a significant part of the measurement of sensors during the experiences with the training and test sets does not arise from a change of sensor sensitivity (30). **Figure 3**, on the contrary, shows how the results of the second WTS of sensor 12 (%RSD = 21.0) increase over time, and the graph clearly points out a drift effect that disqualifies this sensor information for further studies. **Table 2** shows the %RSD of all sensors for a day to day study over a

Table 2. Mean Values of RSD (%)^a

sensor	A	B	sensor	A	B
1	9.2 (1)	1.9 (1)	10	12.1 (3)	7.9 (1)
2	22.2 (1)	3.9 (2)	11	12.5 (1)	9.1 (1)
3	13.6 (4)	3.1 (2)	12	24.7 (1)	12.0 (1)
4	11.2 (1)	3.5 (2)	13	16.2 (3)	11.0 (1)
5	16.4 (1)	2.7 (1)	14	12.2 (2)	9.3 (3)
6	2.2 (1)	1.4 (1)	15	12.1 (4)	7.2 (2)
7	13.1 (1)	9.6 (1)	16	6.9 (3)	9.1 (3)
8	14.9 (1)	9.3 (1)	17	1.9 (2, 3)	1.3 (1, 2, 3)
9	6.9 (3)	6.4 (1)	18	2.1 (3)	1.2 (1, 2, 3)

^a Repeatability study for 6 months (A) and within day (10 analyses) (B). Figures in parentheses represent the WTS whose results have the highest %RSD.

period of 6 months. Those values are the mean of the five WTS, and sensors with values higher than 10% (sensors: 2–5, 7, 8, and 10–15) were not used in the following studies. Concerning the rest of the sensors (1, 6, 9, and 16–18), any WTS with a %RSD higher than 10% was not used in the next studies either. **Table 2** also shows the %RSD of the within day study; the number between brackets corresponds to the WTS where the maximum %RSD was detected. %RSD values of the within day repeatability study were low enough; the mean was 6.1%, with the highest value at 12.0% (sensor 12). In the 6 month study, the mean was slightly higher (11.7%) with the highest value 22.2% (sensor 2). The kind of sensor dope does not seem to affect the behavior of sensors in these studies. Sensors of the first chamber (undoped sensors) have shown only a slightly worse behavior (higher %RSD) in the 6 month study (12.5% of undoped vs 11.3% of doped sensors).

With regard to the WTS, the data of the fifth WTS showed the lower values of %RSD either in within day or between days

studies. These data are related to the end of the sensor desorption slope, when volatile compounds are desorbed from the sensor surface. Nevertheless, data from the first WTS have the highest values of %RSD; these data correspond to the balance between the adsorption and the desorption of the volatile compounds onto the sensor surface.

Regression Model. As said, sensory attributes of VOO aroma have been traditionally determined by a panel test (1) and perceived by assessors through volatile compounds. Aparicio et al. (16) have identified the volatile compounds responsible for some of those sensory attributes, while Morales et al. (4) have found several volatile compounds that explain the vinegary attribute. Volatiles were concentrated by dynamic headspace, desorbed thermally, and quantified by GC. From the set of 16 chemical compounds explaining the vinegary attribute, acetic acid and ethyl acetate showed the highest correlations. Acetic acid contributed more to vinegary attribute than other volatiles when assessors perceived the attribute with intensities around or above 2 (structure scale of 0–5), while ethyl acetate was also an important contributor when that value was greater than 4 (4).

On the other hand, VOOs do not have the same profile of volatile compounds (18, 31); hence, the level of perception of sensory defects depends on the inherent matrix of volatiles characterizing the oil. Assessors can perceive identical concentrations of acetic acid in different VOOs with different scores due to the effect of masking by other volatile compounds. Two Spanish varieties, Arbequina and Picual, characterized with quite different sensory attributes (18), were used in the training set. Arbequina is characterized by a sweet–fruity sensory attribute, while a strong fruity odor characterizes the Picual variety (18). These samples, spiked with acetic acid at various concentrations,

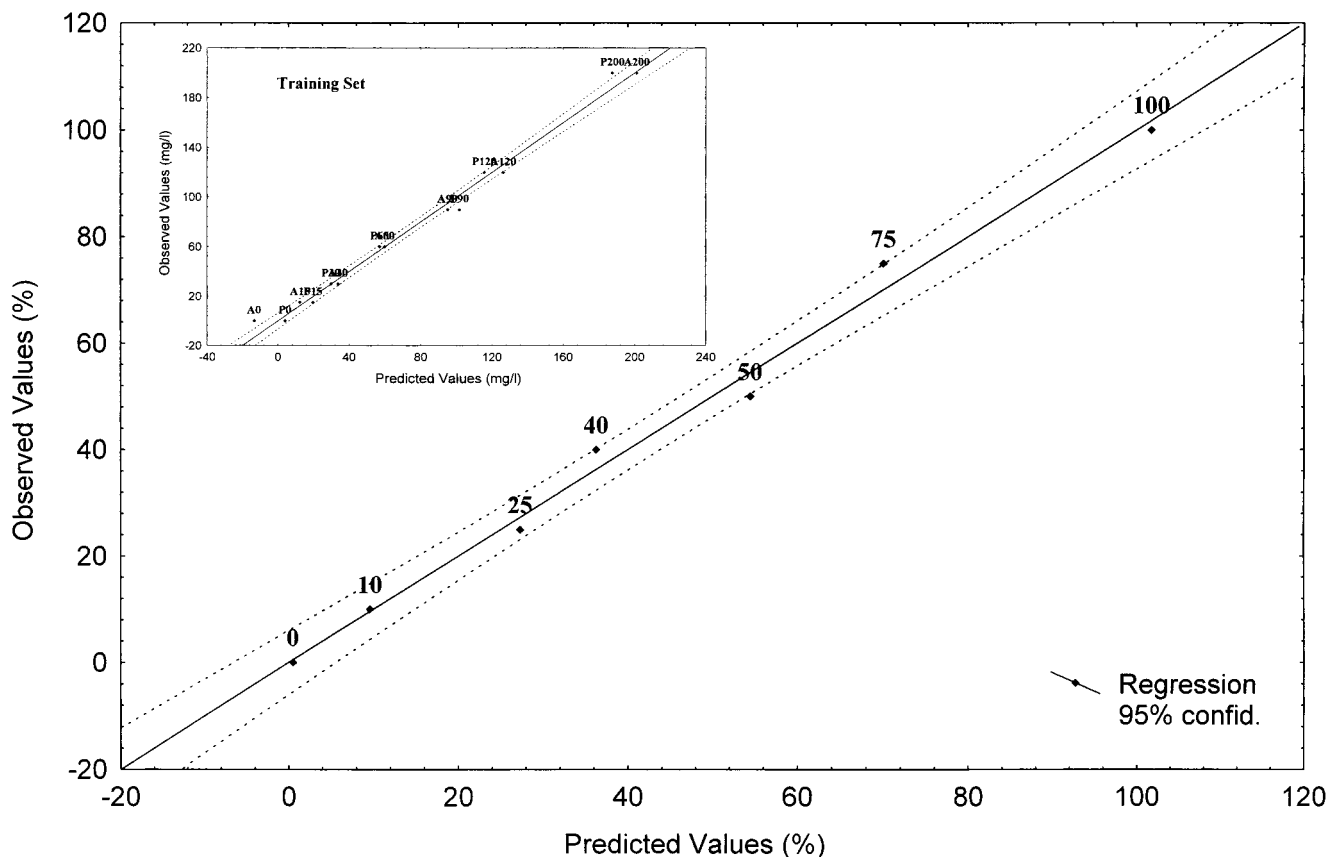


Figure 4. Predicted vs observed values plot obtained for either training (smaller figure) or test sets of samples. Legend: A is the Arbequina variety, and P is the Picual variety.

were used to calibrate the sensors, since acetic acid contributes more to a vinegary flavor than other compounds present in olive oil. In fact, Harper and Kleinhenz (32) have established that the minimum detection threshold of some sensors for acetic acid in oil can be slightly lower than the orthonasal human threshold level: 124 ppb for human vs 100 ppb for sensors.

Morales et al. (4) have determined the odor activity value (OAV)—the ratio between concentration and odor threshold—of acetic acid (9.7) as the highest found for volatile compounds characterizing vinegary attribute, while its correlation coefficient was 0.92. In our case, when SMRA was applied to the Arbequina variety, the adjusted regression coefficient (R_{adj}^2) was 0.96 (F -to-enter = 47.18) while this value was slightly higher ($R_{adj}^2 = 0.97$; F -to-enter = 47.18) for the Picual variety. Sensor 6 was selected in both cases.

A regression model was designed with a training set with samples of both varieties, Arbequina and Picual. The adjusted regression coefficient was $R_{adj}^2 = 0.97$ for the following equation:

$$y = 37\,432 + 1674 \times \text{sensor 1 (WTS 3)} + 1267 \times \text{sensor 6 (WTS 3)} - 106\,670 \times \text{sensor 6 (WTS 5)}$$

The next objective was to check the regression model with another varietal VOO (cv. Coratina from Italy) qualified with other sensory attributes, mostly a bitter—pungent perception. This oil was spiked with IOOC standard of vinegary VOO, so emulating the authentic vinegary marked samples of VOO. Thus, the test set was composed of samples that were supplemented not only with acetic acid (the amount in the IOOC standard was 4.84 mg/kg) but also with other chemical compounds (4) such as, for example, pentan-1-ol, octane, hexyl acetate, butyric acid, etc. The regression coefficient of SMRA on the test set was even higher than the training set ($R_{adj}^2 = 0.98$; $F = 47.18$). **Figure 4** shows the results of applying the regression equation to the training set (samples of Picual and Arbequina spiked with different concentrations of acetic acid) and test set (samples of Coratina variety spiked with different percentages of IOOC winey/vinegary standard).

It is well-known that the measures are not exact, and they are subjected to imprecision. However, the statistical procedures are mostly applied on the mean of the repetitions without taking into account that it is a measure that should be reported along with its confidence intervals. The confidence intervals for the mean give us a range around the mean where we expect that the value of any hypothetical measure is located. Thus, a measure can be represented by a normal distribution (i.e., a bell shape or a triangular function) whose peak point is the mean, and its bandwidth is the product of the STD for the t -Student (t) at $p = 0.05$. This implies that a set of n data should be a set of n distributions of data or at least a set of $k \times n$ data; k represents the two values of the equation $x \pm \text{STD} \times t$, where x is the mean. A regression analysis based on this premise would mean that the regression equation would have been checked with any predictable data.

We have calculated the confidence limits using the Student's t distribution at $p = 0.05$ while the STD was that of the 6 month repeatability study. The objective was to take into account the imprecision that was possible or, in other words, to check the regression equation against the worst variability of sensors that can be predicted. Each one of the data of the test set (Coratina var.) was supplemented with the confidence limits for the first (third WTS) and sixth (third and fifth WTS) sensor described in the regression equation. The good regression coefficient ($R_{adj}^2 = 0.92$) points out that the nonlinear nature of MOS sensor

responses (33) does not seem to have a negative effect on the result and the degradation of sensors over time does not mean there is a problem with the regression equation either.

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