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Research Article

Analytical Techniques for a Rapid Determination of Major Quality Parameters in Olive Oil

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2. Keywords

Olive oil; Traceability; CN; Xylella fastidiosa

1. Abstract

A more attention to agri-food products was increase from the consumers not only because of their nutritional value but also for their origin (location) and authenticity, in order to practice more conscious consumption and to safeguard their health. Analytical chemistry played an important role in traceability for all products in the food market. Olive oil is an important agricultural product for the economy of the Mediterranean area, but it has undergone major alterations in quality in recent years. In Italy, some farmers worked in the olive oil sector have been subjected to legal investigations due to manipulations through mixture with olive oils from other countries. The aim of this study was to verify and develop a fast screening method to characterize specific parameters of olive oil, such as acidity and nitrogen content, and to highlight correlations with infestations and / or parasites.

3. Introduction

Recently, food traceability is becoming an important factor to characterize the authenticity of agri-food products [1]. European Union established a legislation to guarantee the safety and quality of consumer products [2].

Olive Oil (OO) is one of the most representative products in southern Europe and has nutritional and organoleptic qualities that enable it to have a high commercial value. It is important to note that European Union is the first producer of OO in the world (75.4%), followed by Tunisia (5.9%), Syria (4.8%), Turkey (4.6%), and Morocco (3.1%) [3]. In the European Union, Spain (52.4%), Italy (27.7%) and Greece (17.3%) represent 97% of OO producers [3].

The traceability of OO allows characterizing the identity, history and origin of the product in order to strengthen its food safety [4]. As a matter of that, Extra Virgin Olive Oil (EVOO) must follow specific characteristics as chemical, physical, biological or sensory nature to be included in the commercial market but it is difficult to verify the authenticity of OO due to the wide range of categories, cultivations, pedoclimatic conditions and working methods.

With the use of rapid analytical methods, it is possible to verify the presence of pollutants in the OO with the aim of eliminating the risk of fraud. A typical chemical-physical characteristic of the OO is the acidity, conventionally expressed as a percentage of oleic acid. Acidity is useful to recognize extra virgin, virgin, lamp ante or refined olive oil. The Commission Implementing Regulation (EU) No 1348/2013 [5] describes the guidelines for a correct identification of OO, and the Regulation (EC) No 1989/2003 [6] and the International Olive Council (2015) [7] describe the values and the analytical technique of titration to define the characteristics of OO to be introduced into the economic market.

In the years 2013-2015, in the main Italian regions producing EVOO, olive trees suffered a dangerous attack by Xylella fastidiosa pathogen, and a new legislation was adopted, regarding the "measures to prevent the introduction into and the spread within the Union of Xylella fastidiosa" [8]. In 2014, the bacterium, which grows in the xilema of the plant [9], caused a reduction in the production of olives and consequently of EVOO. The impact of this pathogen on the productivity of olive groves was devastating, despite that, the economic market did not suffer any losses, leaving the doubt that more or less legal methods were used to have the same quality of EVOO.

Recent studies shown that the presence of nitrogen from fertilizers could implement the metabolism of nitrogen of the plant

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[10,11]. Massive use of fertilizers could be used to restore fertile activity in olive trees during these years in the Italian region affected by the Xylella fastiosa. For this reason, the presence of fertilizer could be a critical factor for the quality of OO and for the safety of the agro-food product, which is in contrast to the EU anti-fraud directives [12].

The object of this paper was to develop an analytical technique for determining traces of nitrogen in samples of EVOO from different Italian regions and several years (2013-2015). The analytical method was developed favoring quick analysis times, simple sample treatment procedures, and limited use of reagents. The analytical technique considered is based on an elemental combustor, which allows complete oxidation of the matrix (e.g. OO) by simultaneously separating species containing carbon and nitrogen.

4. Materials and Methods

4.1. Sampling

OO samples were collected in the period between 2013 and 2015 from small and medium Italian mills (**Figure 1**) with the exception of the samples from Albania (EVOO-006 and EVOO-010). The samples analyzed of Sun Flower Oil (SFO), Corn Seeds (CO) and Olive Oil (OO) were obtained from virgin and refined oils from industrial certified processes, and EVOO from different mills declared as extra virgin olive by the producer, with the exception of the samples of Albania (EVOO-006 and EVOO-010) and Perdifumo (SA) (EVOO-012) that were produced by farmers for strictly family use with handmade techniques.

Table 1 shows the list of the OO samples collected. After collection, all samples were transported to ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) laboratory in Bologna (Italy) and maintained at a constant conditions of temperature (laboratory room temperature: 22°C) until analyses were performed.

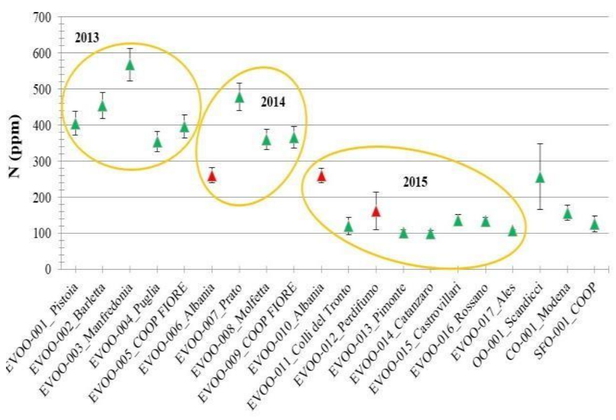

Figure 1: Map of the origin of the samples collected

Table 1: List of the samples collected (*industrial products, indicated the packaging area).

Sample	Location	Year
EVOO-001	Italy Toscana: Pistoia (PT)	2013
EVOO-002	Italy Puglia: Barletta (BAT)	2013
EVOO-003	Italy Puglia: Manfredonia (FG)	2013
EVOO-004	Italy Puglia	2013
EVOO-005	COOP FIORE	2013
EVOO-006	Albania	2014
EVOO-007	Italy Toscana: Prato (PO)	2014
EVOO-008	Italy Puglia: Molfetta (BA)	2014
EVOO-009	COOP FIORE	2014
EVOO-010	Albania	2015
EVOO-011	Italy Marche: Colli del Tronto (AP)	2015
EVOO-012	Italy Campania: Perdifumo (SA)	2015
EVOO-013	Italy Campania: Pimonte (NA)	2015
EVOO-014	Italy Calabria: Catanzaro (CZ)	2015
EVOO-015	Italy Castrovillari (CS)	2015
EVOO-016	Italy Rossano (CS)	2015
EVOO-017	Italy Sardegna: Ales (OR)	2015
OO-001	Italy Toscana: Scandicci (FI)*	/
CO-001	Italy Emilia-Romagna: Modena (MO)*	/
SFO-001	COOP*	/

4.2. Titration

Titration allows calculating the degree of acidity expressed in percentage of oleic acid, as described in the protocol of the International Olive Council (2015). The analytical method was based on a dilution of 0.1M titanium hydroxide solution (NaOH) starting from 1M ± 0.001 in a flask of 100.0 ml (± 0.1 ml). Diethyl ether / ethanol solution (95% v / v) was mixed in equal volume (100 ml) to which 0.3 ml of phenolphthalein was added. The procedure involved the use of an OO matrix of about 10 g. To reduce waste and environmental impact, a small amount of OO was analyzed reducing the volume of alcohol / ether mixture, since it was noticed that the result did not change. The matrixes were determined by weighing in a 250 ml flask the OO using an electronic balance KERN ABT (ARW Balance, Vicenza, Italy). The mixture of alcohol and ether (50 ml) was combined and titration with 0.1M NaOH was carried out. When the solution has been reached, the mixture seemed to have an orange color due to the phenolphthalein presence. The titrated volume is recorded and the degree of acidity is calculated as the percentage of the weight of the oleic acid (equation 1):

$$\frac{V \cdot M \cdot MW_{oleic\ acid} \cdot 100}{1000 \cdot w} = \frac{V \cdot M \cdot MW_{oleic\ acid}}{w \cdot 10} \quad \text{(equation 1)}$$

V= sample volume;

M= molarity of the titrant (NaOH);

$MW_{oleic\ acid}$ = molecular weight = 282.46 g/mol;

w = sample weight.

4.3. CN vario max cube

Elemental analysis was carried out by an elemental combustor (Vario Max Cube, Elementar Gmbh, Frankfurt, Germany), based on the Dumas combustion reaction, in order to determine the content of carbon and nitrogen and its ratio. The samples were prepared by weighing 250 ml of OO in stainless steel crucibles using the electronic balance KERN ABT.

The automatic sampler inserts the crucible into the combustion zone, where oxygen is injected directly on the sample. A second post combustion reactor converts possible byproducts of the combustion to carbon dioxide. Excess oxygen removal, conversion of nitrogen oxides to N2 and removal of Sulphur is achieved in the tungsten reduction system. The analytical gases N2 and CO2 are completely separated by the purge & trap separation system. The gases are sent to the high performance Thermal Conductivity Detector (TCD) [13]. At the beginning of the analysis, standard samples (aspartic acid) were analyzed for the calibration of the instrument.

5. Results

Table 2 shows the results of titration analysis to compare the acidity on that expressed on the Regulation (EC) No 1989/2003. EVOO from 2014 have high percentage of oleic acid, respect the previous (2013) and next (2015), except for the red spots representing samples EVOO-006, EVOO-010 and EVOO-012 produced by farmers for strictly family use. Samples EVOO-006, EVOO-010 and EVOO-012 show the highest acidity, especially in the year 2015 (> 2%). This value not classify these types of oil as EVOO respect the Regulation (EC) No 1989/2003, but we remember that EVOO from Albania and Perdifumo were produced by farmers for strictly family use with handmade techniques. For this reason, we exclude the presence of pollutants or risk of fraud.

Table 2 also shows the average concentrations of carbon and nitrogen analyzed by CN Vario Max Cube. Carbon concentration is expressed in percentage, instead of nitrogen is expressed in parts per million (ppm) in order to observe quantifiable nitrogen values. The results underline that carbon value is constant in all the samples, whereas nitrogen value is variable.

Figure 2 shows that nitrogen concentration is higher in the samples from 2013-2014, period characterized by the Xylella fastidiosa pathogen. In red, the Albania and Perdifumo samples show nitrogen concentration comparable to each other but lower respect to the Italian samples. SFO and CO show a similar nitrogen concentration of the EVOOs, whereas OO shows higher nitrogen concentration than EVOOs.

Table 2: Acidity analyzed by titration and carbon (expressed in %) and nitrogen concentration (expressed in ppm) analyzed by CN.

	Acidity ($\%_{oleic acid}$)	C (%)	C (dev std)	N (ppm)	N (dev std)
EVOO-001	0.28	77.38	0.08	405.5	32.44
EVOO-002	0.65	77.16	0.12	454.3	36.35
EVOO-003	0.54	77.20	0.08	568.1	45.45
EVOO-004	0.31	77.43	0.15	354.1	28.33
EVOO-005	0.42	77.32	0.18	396.0	31.68
EVOO-006	1.20	77.36	0.12	260.6	20.85
EVOO-007	1.30	77.05	0.08	478.2	38.26
EVOO-008	1.00	77.10	0.11	360.3	28.82
EVOO-009	0.64	77.33	0.14	366.7	29.34
EVOO-010	7.20	76.92	0.23	260.5	19.80
EVOO-011	0.34	77.06	0.14	120.0	24.56
EVOO-012	2.70	77.07	0.33	162.4	52.29
EVOO-013	0.92	77.01	0.14	101.2	8.10
EVOO-014	0.48	77.08	0.08	100.8	8.06
EVOO-015	0.45	77.09	0.02	136.7	15.28
EVOO-016	3.10	77.51	0.41	133.3	10.67
EVOO-017	0.56	77.05	0.18	108.1	1.13
OO-001	0.17	77.14	0.11	256.9	90.69
CO-001	0.17	77.28	0.08	156.8	21.31
SFO-001	0.22	77.22	0.12	126.7	21.58

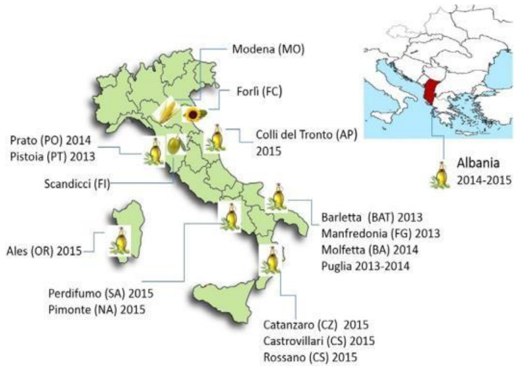

Figure 2: Nitrogen concentration (expressed in ppm) in the samples analyzed by CN Vario Max Cube

6. Discussion

6.1. Xylella fastidiosa contribution

In 2013, the pathogen Xylella fastidiosa caused severe damage to all the olive trees in the Mediterranean area. In Puglia (south of Italy), Xylella fastidiosa infected 74,000 acres causing a major decrease in OO production during the years 2014 and 2015. This may cause a massive use of fertilizers by farmers. Vossen et al [14] indicated that an excessive use of nitrogen fertilizers on olive trees leads to a slow deterioration of sensory qualities.

The high nitrogen concentration analyzed by CN could be related to the massive use of nitrogen fertilizer on olive trees.

7. Conclusion

The determination of the percentage of oleic acid by titration is a useful method for a quick selection of oil samples. Titration shows that two EVOO samples, obtained with handmade methods, have a very high quantity of acidity; this anomaly could be related to the type of extraction.

CN analysis proved to be a fast and accurate technique to characterize nitrogen and carbon concentration in EVOO samples. EVOO samples produced in 2013 and 2014 years show higher nitrogen concentration compared to 2015.

This could be related to the use of nitrogen-based fertilizers, in order to increase the yield of the olive oil product, strongly down because of the infestation due to Xylella fastidiosa pathogen.

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