ASSESMENT OF VIRGIN OLIVE OIL THERMAL OXIDATION BY DIFFERENTIAL SCANNING CALORIMETRY AND ELECTRON SPIN RESONANCE

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INTRODUCTION

Extra virgin olive oil (EVOO), a pillar of the Mediterranean diet, is resistant to oxidative deterioration due to its triacylglycerol composition and high antioxidant content. On the other hand, the free fatty acids and photosensitizers present may act as prooxidants and reduce its stability. Both effects influence the shelf life of EVVO, i.e., the time during which EVOO remains free of off-flavors or defects and its quality parameters remain within limits (Vittadini et al., 2003). Since real-time determination of shelf life is not possible and existing accelerated testing methods are limited by expensive and highly specialized equipment, innovative techniques to develop accurate shelf life prediction models are being investigated (Koprivnjak et al., 2008; Cerretani et al., 2012). Therefore, the objective of this study was to evaluate the feasibility of using differential scanning calorimetry (DSC) and electron spin resonance (ESR) in assessing the deterioration of EVOO during accelerated oxidation in the oven.

MATERIALS AND METHODS

Heated at 98 °C for 24 hours

0, 2, 4, 8, 16, 24 h

K values (ISO 3656:2011)
Peroxide value (ISO 3960:2017)

Electron spin resonance spectroscopy
(Koprivnjak et al., 2008)
Bruker Magnettech ESR5000
DPPH 0.15 mM
frequency 9.27 GHz; field sweep 10 mT; microwave power 4.9 mW; modulation amplitude 0.11 mT

ELECTRON SPIN RESONANCE

DIFERENTIAL SCANNING CALORIMETRY

DSC 214 Polyma Differential Scanning Calorimeter, NETZSCH-Gerätebau GmbH a nitrogen flow rate of 40 ml/min, normal pressure. Oil samples heated to 80 °C (heating rate 10 °C/min); held for 10 min, then cooled to -75 °C at 10 °C/min (held at -75 °C for 30 min). Then the melting profiles were obtained by heating the samples to 80 °C at a heating rate of 15 °C/min. The second part of the curve (cooling) is recorded (Ostrowska-Ligenza et al., 2021).

RESULTS

Table 1. Peroxide value and K-values in EVOO samples during heating at 98 °C for 24 hours (means ± st. dev., n=3). Values with different letters are statistically different at p≤0.05.

Sample	Peroxide value (mg O_2/kg)	K_{230}	K_{270}
EVOO_0h	4.74^{a}±0.07	1.79^{a}±0.00	0.15^{a}±0.00
EVOO_2h	5.92^{b}±0.22	1.85^{b}±0.05	0.16^{a}±0.01
EVOO_4h	6.70^{c}±0.01	1.95^{c}±0.04	0.20^{b}±0.02
EVOO_8h	7.80^{d}±0.00	2.08^{d}±0.06	0.21^{b}±0.01
EVOO_16h	9.54^{e}±0.07	2.33^{e}±0.15	0.26^{d}±0.01
EVOO_24h	12.20^{f}±0.01	2.36^{e}±0.01	0.23^{c}±0.01

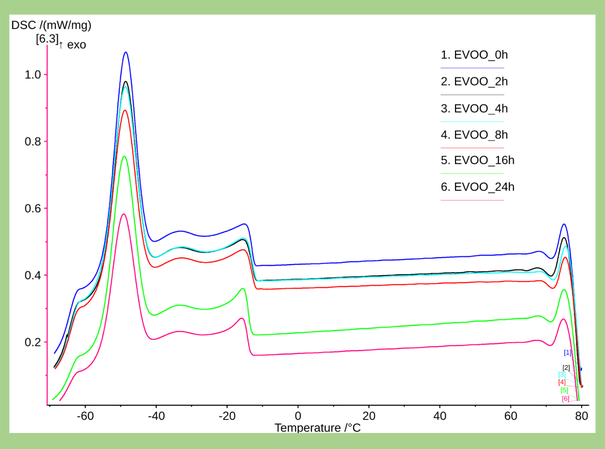

Fig 1. DSC thermogram of EVOO samples heated at 98 °C for 24 hours during cooling from 80 °C to −75°C at a rate of 10 °C/min.

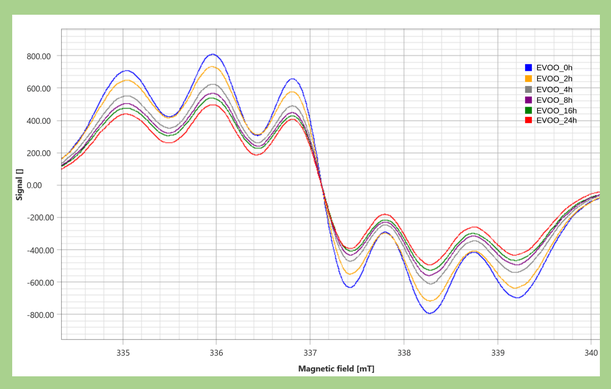

Fig 2. DPPH radical-scavenging activity determined by ESR of EVOO samples heated at 98 °C for 24 hours.

Table 2. Heat flux (DSC) and DPPH radical-scavenging activity (ESR) of EVOO samples heated at 98 °C for 24 hours (means ± st. dev., n=3). Values with different letters are statistically different at p≤0.05.

Sample	Heat flux (mW/mg)	DPPH reduction (%)
EVOO_0h	0.938^{a}±0.009	72.6^{a}±0.5
EVOO_2h	0.892^{b}±0.011	70.4^{b}±0.5
EVOO_4h	0.876^{b}±0.006	68.8^{b}±0.4
EVOO_8h	0.794^{c}±0.007	65.6^{c}±0.4
EVOO_16h	0.733^{d}±0.006	60.0^{d}±0.3
EVOO_24h	0.583^{e}±0.004	55.4^{e}±0.2

DISCUSSION

Heating EVOO at 98 °C for 24 h resulted in a slight shift of the DSC crystallisation peak to lower temperatures, i.e. from -48.6 °C to -49.1 °C, and also in a significant decrease of the heat flux. This finding is in agreement with the previously published results of Vittadini et al. (2003), who suggested that this behaviour could be caused by the degradation of triacylglycerols and the increase in viscosity during oxidation. ESR measurements of DPPH radical scavenging activity showed that it also decreased during heating. The observed changes caused by thermal degradation correlated with the increase in peroxide values and ultraviolet spectrophotometric parameters. The peroxide, K_{232} and K_{270} values were positively correlated with DSC heat flux (r=0.990, r=0.886 and r=0.610, respectively) and also with DPPH radical scavenging activity (ESR) (r=0.988, r=0.962 and r=0.740, respectively). These results confirm the great potential of DSC and ESR techniques in evaluating the deterioration of EVOO during oxidation and provide a basis for developing accurate models to predict its shelf-life.

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