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Analysis of methanol and ethanol in virgin olive oil

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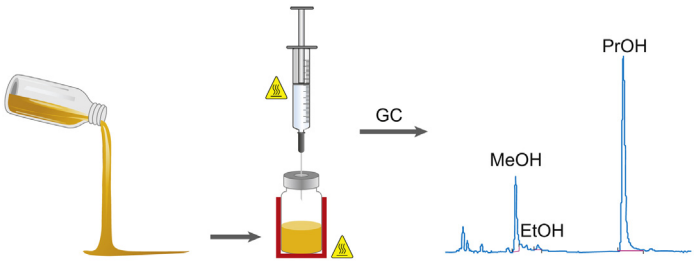
GRAPHICAL ABSTRACT



ABSTRACT

This work provides a short and easy protocol that allows the analysis of both methanol and ethanol in the static headspace of olive oil. The procedure avoids any kind of sample pre-treatment beyond that of heating the oil to allow a maximum volatile concentration in the headspace of the vials. The method's LOD is 0.55 mg kg^{-1} and its LOQ is 0.59 mg kg^{-1}. Advantages of this method are:

- Simultaneous determination of methanol and ethanol (the pre-existing Spanish specification UNE-EN 14110 only analyses methanol).
- No need of equipment modifications (standard split injectors work perfectly). Use of a highly polar capillary GC column, leading in most cases to chromatograms in which only three dominant peaks are present – methanol, ethanol, and propanol (that is extremely positive for easy interpretation of results).

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- Use of an internal standard (1-propanol) to determine the concentration of the analytes, reducing the presence of error sources.

ARTICLE INFO
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Method details

The presence of short chain alcohols in virgin olive oil could be closely related with oil quality. Actually low amounts of methanol (MeOH) and ethanol (EtOH) are accepted since small quantities of these alcohols may be formed during the maturation of olives. On the other hand, high volumes of EtOH appear during the fermentation processes occurred mainly throughout olive fruit storage. The role of these short-chain alcohols regarding olive oil quality is still unclear, although their influence on the presence of fatty acid alkyl esters (FAAE), a quality parameter, is well known [1,2].

Due to the high volatility of short-chain alcohols their determination is normally accomplished by static headspace extraction followed by gas chromatography (GC) analysis [3,4].

Reagents and samples

EtOH, MeOH, and 1-propanol (PrOH) used as reference materials were supplied by Romil Ltd. (Waterbeach, Cambridge, GB) and were of analytical quality.

Varietal virgin olive oils of Adramitini, Blanqueta, Bouteillan, Chemdal Kabilye, Cipresino, Coratina, Frantoio, Koroneiki, Leccino, Lechín de Granada, Manzanilla, Negral, Pendolino, Picual, Rapasayo, and Sigoise were directly prepared in the laboratory using the Abencor® system described elsewhere [5] to assure maximum oil quality. Olive fruits were obtained from an irrigated orchard (drip irrigation) in the southern part of Spain, under optimal cultivation parameters. They were handpicked and, according to their maturity index, belonged to the categories 0–4 (deep green to black skin olives with white flesh) [6].

Chemically refined olive-pomace oil was obtained directly from the producer. This oil, together with all reagents and samples was kept in the dark at 4 °C until use.

Concentrated solutions of PrOH (internal standard, IS) were prepared by dissolving PrOH (cooled down to 4 °C, density = 0.810 g mL^{-1}) in refined olive-pomace oil at proportions of 12.5 mL PrOH per kilo oil. From these concentrated solutions diluted IS solutions were prepared by mixing 1 g concentrated solution with 24 g refined olive-pomace oil. All critical volumes were measured with calibrated precision pipettes (0.6 μL systematic error). Both concentrated and diluted IS solutions were kept in the dark at −20 °C before use.

Samples were prepared just before the analysis in the following way: 3.00 g oil (room temperature) and 300 mg diluted IS solutions (room temperature) were introduced into a 9 mL vial (20 mm × 46 mm), which was immediately sealed with an aluminium crimp cap with silicone septa and with a PTFE face to eliminate bleed from the rubber portion. They were heated in a dry heat bath at 110 °C during 60 min. The vial headspace was then sampled via a thermostated stainless steel syringe (110 °C; sampling time = 30 s) and analysed by injecting the sample into the gas chromatograph.

After each injection the syringe was cleaned by blowing out air and then dry nitrogen. Blank injections were carried out after each analysis to check the absence of carry-over effects.

Instrumentation

Heating of the samples was carried out in a Tembloc thermostat dry-block (JP Selecta S.A., Barcelona, Spain).