ADVANCING MOSH/MOAH ANALYSIS TOWARDS SPECIATION AND CONTAMINANT IDENTIFICATION

SRA INSTRUMENTS
ANALYTICAL SOLUTIONS

UNIVERSITÀ DEGLI STUDI DI UDINE
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INTRODUCTION

Mineral oil hydrocarbons (MOH) are well-known food contaminants. They are generally divided in saturated (MOSH) and aromatic (MOAH) fractions, which are of different toxicological concern [1]. MOH contamination in olive oil can be either of environmental origin or occur due to harvesting operations, processing, or packaging. Capability of identifying contamination source would be valuable to minimize its occurrence and preserve consumers' health, as well as complying with current legislation [2].

Nowadays, the reference methodology is based on HPLC-GC-FID hyphenation [3]. FID detection provides quantitative results but does allow to obtain qualitative information about the type of MOSH or MOAH present or to accurately discriminate interferences. In this regard, GC×GC-FID/MS is a useful tool to confirm the petrogenic origin of contamination and to characterize more in detail hydrocarbon profiles [4].

GOALS

- In this study the impact of olive harvesting operations on mineral oil contamination of EVOOs was investigated.
- HPLC-GC-FID was used as standard method of analysis for EVOOs and lubricants employed in harvesting machinery.
- A GC×GC-FID/MS platform was developed and assessed as additional analytical tool for confirmation and further investigation of oil samples found positive to contamination.
- Highly informative GC×GC chromatograms were exploited to advance analysis towards speciation of hydrocarbons' classes.

EXPERIMENTAL

Sampling and sample treatment

Selected olive samples collected in various olive groves in Italy directly from the tree (hand-picked) and after different harvesting operation, and corresponding mineral oil products (lubricants, greases, hydraulic oils) used during harvesting operations.

The oil was physically extracted and subjected to saponification and epoxidation [5]. Olive oils and lubricants were fractionated by HPLC into MOSH and MOAH and individually analyzed by GC-FID (on-line) and the optimized **GC×GC-FID/MS** platform (off-line).

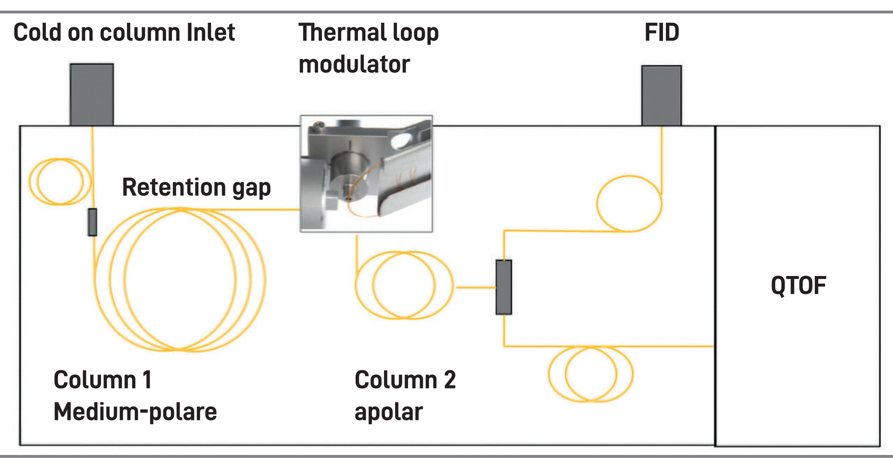
GC×GC-FID/MS platform

Agilent Technologies 8890 GC with cold on-column inlet, FID detector and 7250 QTOF Mass Spectrometer.

Zoex ZX2 Cryogen-free loop thermal modulator controlled by an Optimode v2.0 unit (SRA Instruments).

2D data were processed by GC Image software package.

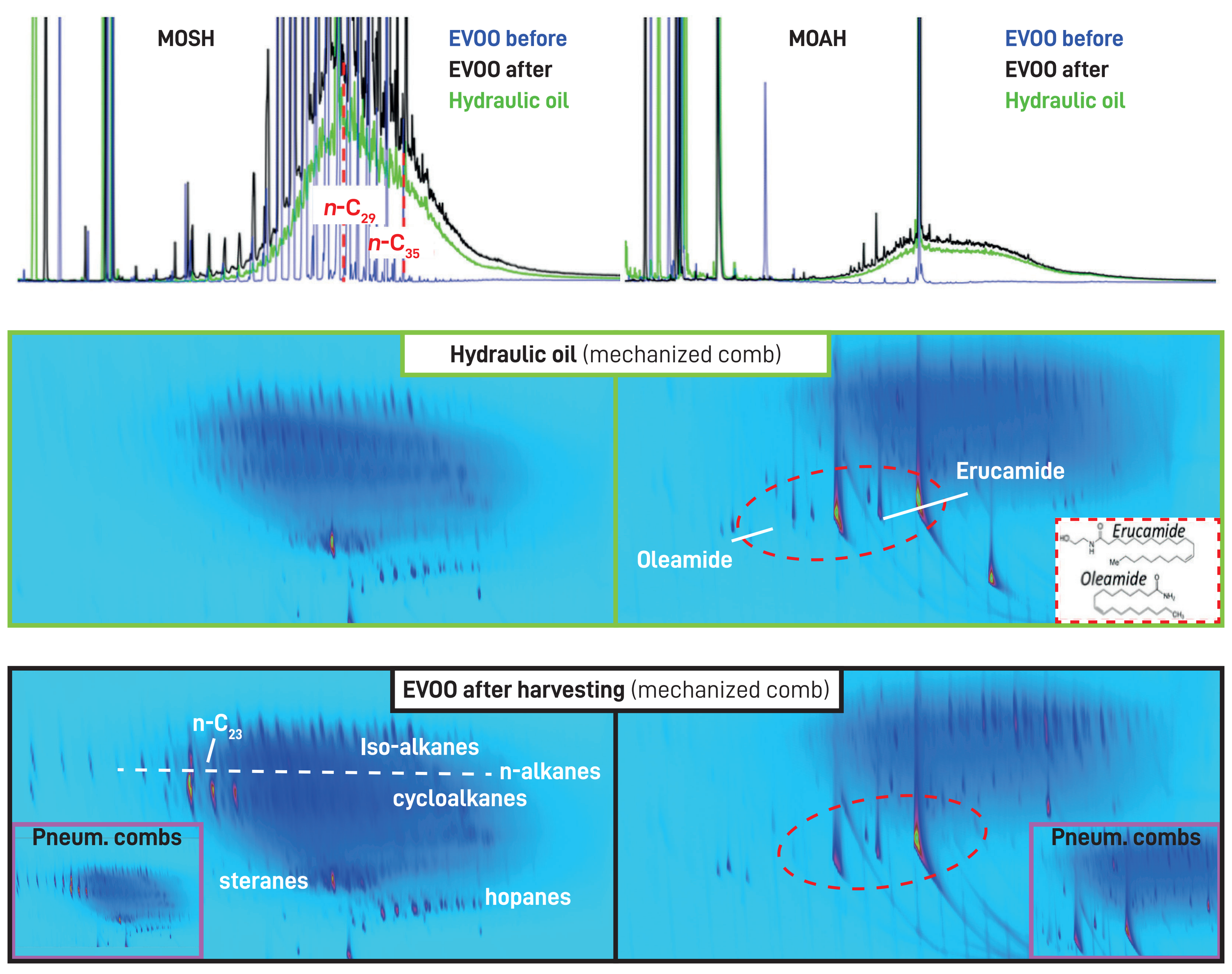
- Injection volume up to 25 μL.
- Parallel detection: quali-/quantitative output.
- High Resolution MS with accurate mass.



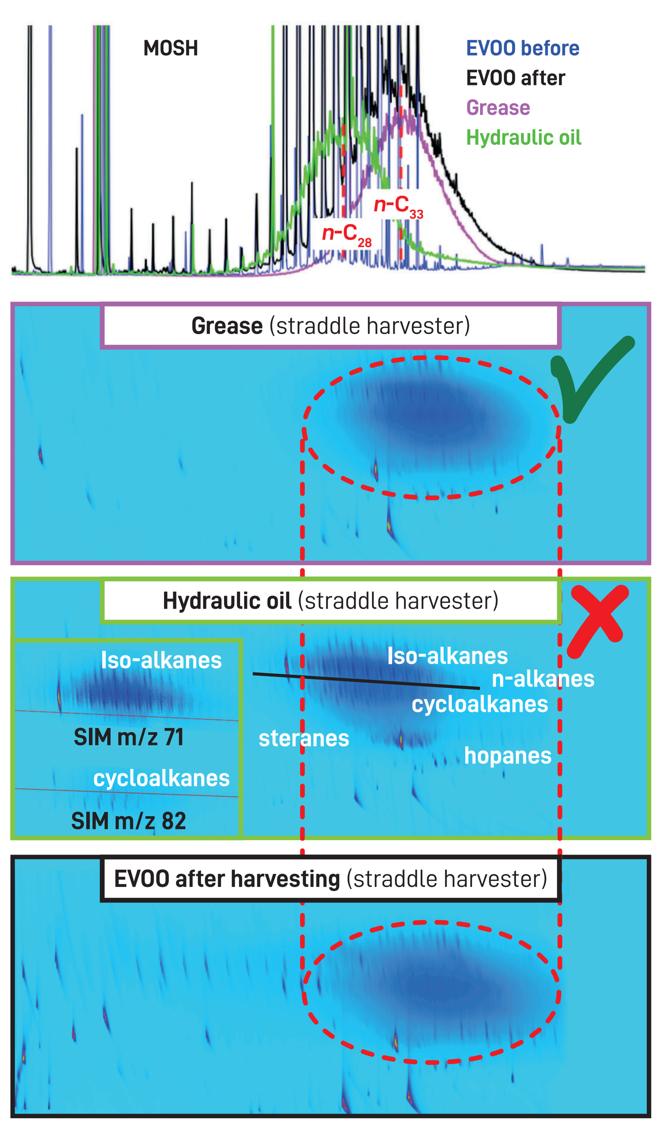
RESULTS

- Comparison of GC-FID traces of EVOOs and lubricants used during harvesting, together with MOSH/MOAH ratio, allowed identification of contamination source.
- Comparison of GC-FID and GC×GC-FID traces confirmed contaminant identity assignment with good confidence.
- Quantitative results on lubricants showed reasonable agreement between 1D and 2D data.
- GC×GC-MS delivered insightful characterization of hydrocarbon fractions. Individual components and chemical classes and sub-classes could be mapped.

Example 1: Olives harvested with vibrating comb. Leak of hydraulic oil contaminated the nets and consequently olives harvested with this machinery.

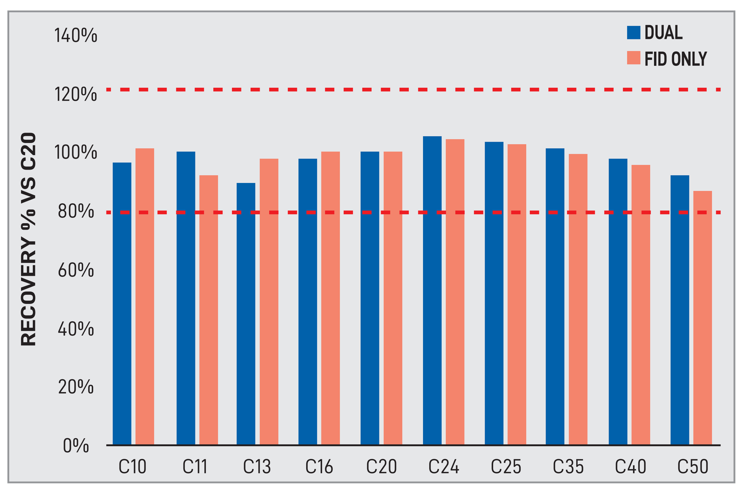


Example 2: Olives harvested with a straddle harvester. Mechanical parts were lubricated with grease and hydraulic oil flowed inside the hydraulic circuits.



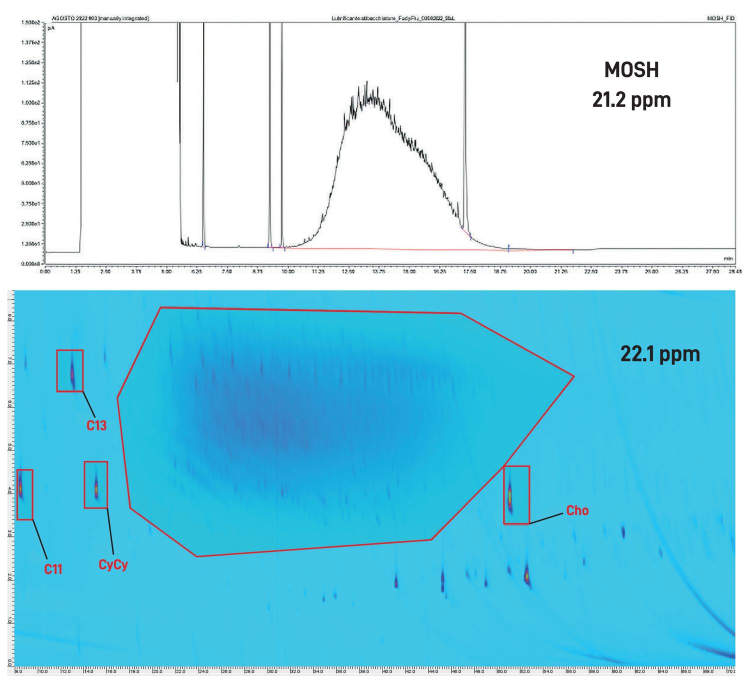
Discrimination

- Recovery: FID signal relative to reference – n-C_{20}.
- Well within limits (80-120%) [6] for all compounds.
- Good agreement between FID only and parallel detection



Quantification: comparison 1D vs 2D for lubricants.

Sample	MOSH (ppm)		MOAH (ppm)	
	LC-GC-FID	GC×GC-FID	LC-GC-FID	GC×GC-FID
Lubricant 1	21.2	22.1	7.0	6.9
Lubricant 2	21.3	23.5	5.3	3.6
Lubricant 3	20.7	21.0	7.7	6.7
Lubricant 4	18.6	20.3	5.2	4.7



CONCLUSIONS

- Harvesting operations are an important source of contamination due to contact of the food matrix with machinery lubricants. Adoption of good harvesting practices and use of food-grade lubricants can help to mitigate the risk of MOH contamination.
- GC×GC-FID/MS demonstrated to be a useful for confirming sources of contamination and therefore act as confirmatory tool next the reference LC-GC-FID platform.
- GC×GC chromatograms bring additional value in terms of characterization of MOSH and MOAH fractions, as well as to identify contamination origin (fingerprinting).

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Acknowledgements This research was financed by the following Italian associations of the olive oil supply chain: Associazione Italiana Frantoiani Oleari (AIFO), Associazione Italiana dell'Industria Olearia (ASSITOL), Associazione Frantoi Oleari Italiani (ASSOFRANTOI), Federazione Nazionale del Commercio Oleario (FEDEROLIO), Filiera Olivicola-Olearia Italiana (FOOI), Italia Olivicola Società Consortile, Unione Nazionale Associazioni Produttori Olivicoli (UNAPOL), and by SRA Instruments S.p.A., Chelab S.r.l. and ALS Italia S.r.l.

This work has been published: L. Menegoz Ursol et al. (2023). Food Chemistry, 406, 135032.