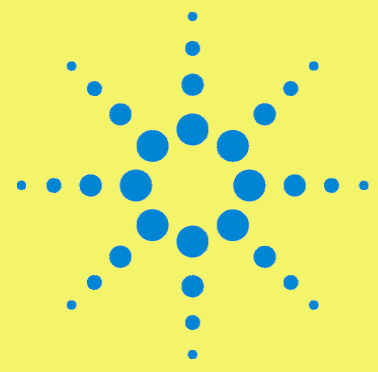


Dilute-and-Shoot GC/MS Analysis of Olive Oils for the Determination of Quality and Authenticity

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Agilent Technologies

Overview

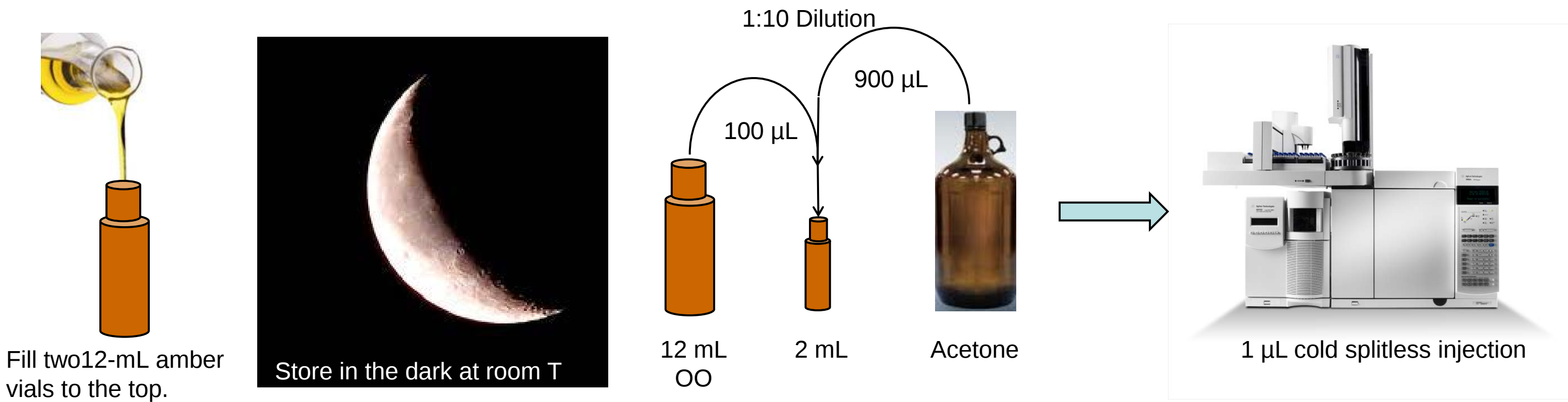
- Several reports indicate that extra virgin olive oil (EVOO) olive oil is one of the most adulterated foods on the market. Diluting the oil with cheaper seed oils or olive pumice oil has been reported. In some cases, seed oils have been colored with chlorophyll and sold as EVOO.
- There is a need for a simple test to differentiate EVOO from lesser quality or adulterated oils.
- The author has developed a rugged GC/MS method for the analysis of the olive oil fraction from nonanol through the sterols. Higher boiling components, e.g. mono-, di- and triglycerides are sent to waste or backflushed using a Deans switch.
- 12 Olive oils were purchased from two specialty markets, all labeled EVOO and from a single country of origin [Italy, Spain, Portugal, and the US (CA)]. 16 olive oils were purchased from a local grocery store with labels saying they were EVOO, pure olive oil (OO) or extra light OO.
- The data were analyzed using MassHunter Qual and Quant Software and with Mass Profiler Professional.
- 6 replicate injections were made of each OO, but only one sample had a biological replicate, which limits the significance of the statistical results.

Samples

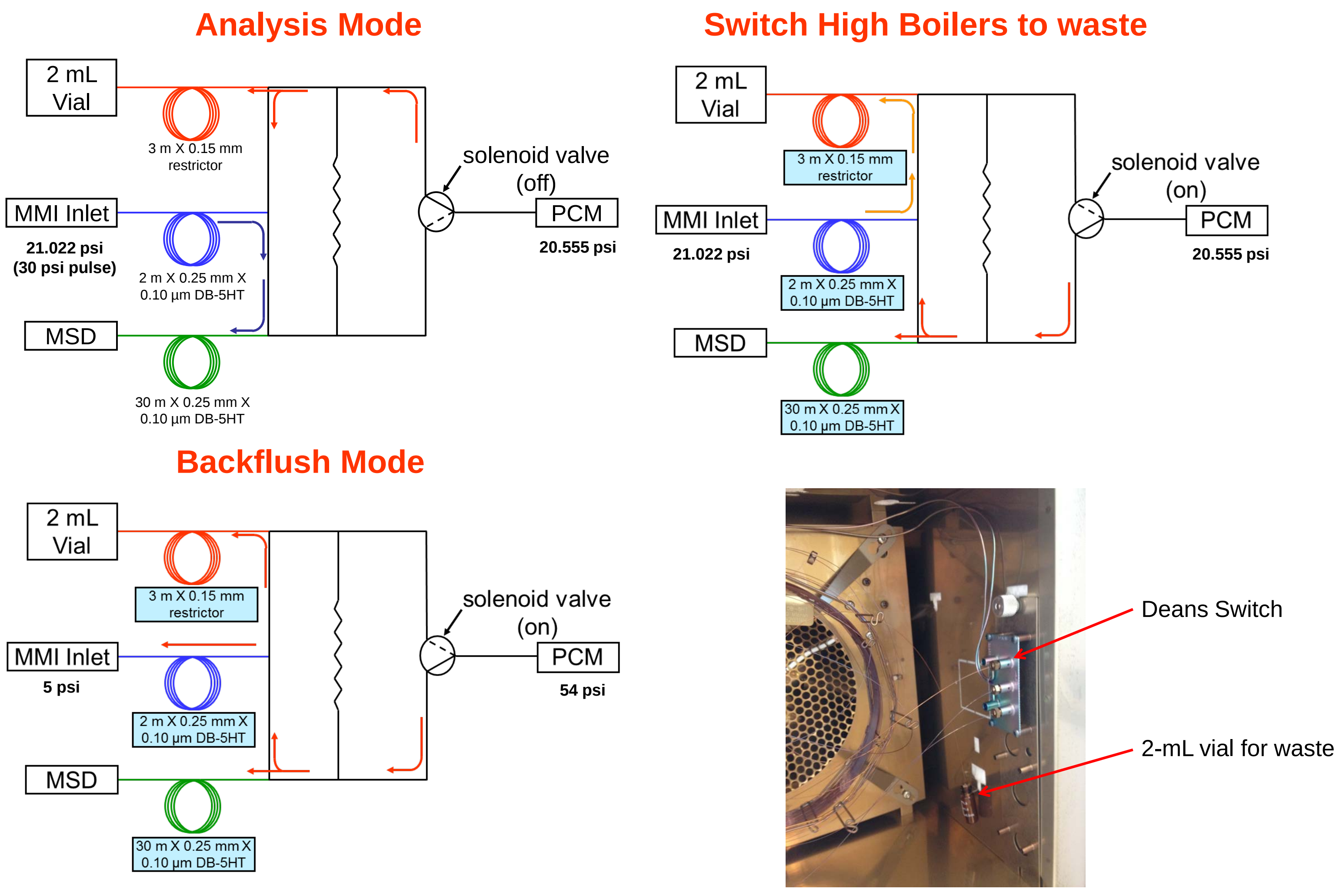
OO #	Brand	Label Information	Country of Origin	Cost/mL (cents)	Olive Varieties
1	Unio 100% Organic	Arbequina Variety; 1st cold pressed EVOO;	Sp	3.898	Arbequina
2	Lucini Estate Select EVOO	Made from 100% hand-picked olives grown on select Italian Estates; 1st cold press; 0.3 - 0.5% acidity; Olives picked and crushed within 24 hrs. Lighter in body and flavor, ideally suited for high heat cooking	It	2.699	
3	Olio carli EVOO	Produced and Packed in Italy; Fratelli Carli	It	2.598	
4	Da Morgada EVOO	Alentejo, Portugal; Early harvest First Cold Press	Po	3.598	Galega and Verdeal
5	Ranise Olio Extra Vergine di Oliva	"Taggiasca"; Imported by Italian Harvest, San Francisco; Crop 2010/11;	It	8.396	
6	Alhema d Queiles EVOO	Estate bottled; Max acidity 0.2%, Peroxides <20, Waxes <250 mg/Kg; Made by Hacienda Queiles mainly with arbequina olives	Sp	4.2	"Mainly" arbequina
7	Pasolivo EVOO	Made in Paso Robles, CA; grown sustainably and organically; crushed within hours; Handpicked & unfiltered cold pressed & certivied EVOO. Named a top ten oil in the World in Europe's largest tasting.	USA	7	"Tuscan Olives"
8	Distributed by Bella Cucina Artful Food, Atlanta GA	Slightly peppery and grassy, this oil was harvested in the hills of Tuscany, Italy	It	6.4	
9	Bulk EVOO re-bottled by store	No information.	?	3.733	
10	Unio EVOO	1st cold pressed EVOO; Not labeled as organic; Superior category olive oil obtained directly from olives and solely by mechanical means;	Sp	3.6	Arbequina
11	Rustichella d'Abruzzo EVOO	Made exclusively from Dritta Francavillese olives grown in the coastal hills of Abruzzo, near the Adriatic Sea.	It	5.2	Dritta Francavillese
12	Da Morgada EVOO	Alentejo, Portugal; Early harvest First Cold Press	Po	3.598	Galega and Verdeal
13	Filippo Berio Extra Light Tasting Olive Oil	Extra light tasting for frying and baking. High smoke point. Subtle taste & light bouquet	It Sp Gr Tun	1.798	
14	Filippo Berio EVOO	Rich flavor.	It Sp Gr Tun	1.798	
15	Rosa EVOO	US Grade A. Only Italian olives.	It	2.076	
16	Cento Pure OO	100 % pure olive oil	Packed in Italy	1.796	
17	Bellino Organic 100% Italian EVOO	Organic. Proprietary brand of Cento Fine Foods	It	2.398	
18	Cento EVOO	First cold press. 100% EVOO	It Gr Sp	1.996	
19	Colavita EVOO	First cold press. Exclusively from olives harvested & pressed in Italy. Certified Authentic 100% Italian	It	4.116	
20	Botticelli Premium EVOO	Imported from Italy	It Gr Sp	1.698	
21	Carapelli Extra Light (in taste) OO	Best for baking and sauteing. Imported from Italy	It Sp	1.678	
22	Terra Medi EVOO	rich, full flavoured, acidity 0-0.5%. Olives grown on Greece's Peloponnesian Peninsula. Cold-pressing of hand-picked olives. Solely by mechanical means	Gr	3.198	Koroneiki
23	Rosa OO	Cold press. Packed in Italy. 100% pure Italian olive oil	It	1.676	
24	Bellino First Cold Pressed EVOO	First cold pressed. A proprietary brand of Cento	It	1.998	
25	Wild harvest organic EVOO	First cold pressed. Estate grown 100% organic. Product of Italy	It	1.796	
26	Bellino EVOO	Pressed from the finest selection of Italian olives. First cold pressed.	It	4.796	
27	Ferrara	First cold pressed. Product of Italy		1.499	
28	Acme EVOO	First cold pressed. Imported from Italy. Sold in clear plastic bottle	It Sp Gr Tun	1.398	
29	DiUbaldo Italian	Family made in Italy	It		
30	Filippo Bario EVOO	Provided by a colleague – purchased at Costco		0.7	
31	?	Provided by a colleague – purchased at Costco		1.05	

Abbreviations used in table: It = Italy, Sp = Spain, Gr = Greece, Po = Portugal, Tun = Tunisia, USA = United States

Olive Oil Storage & Dilution



Deans Switch



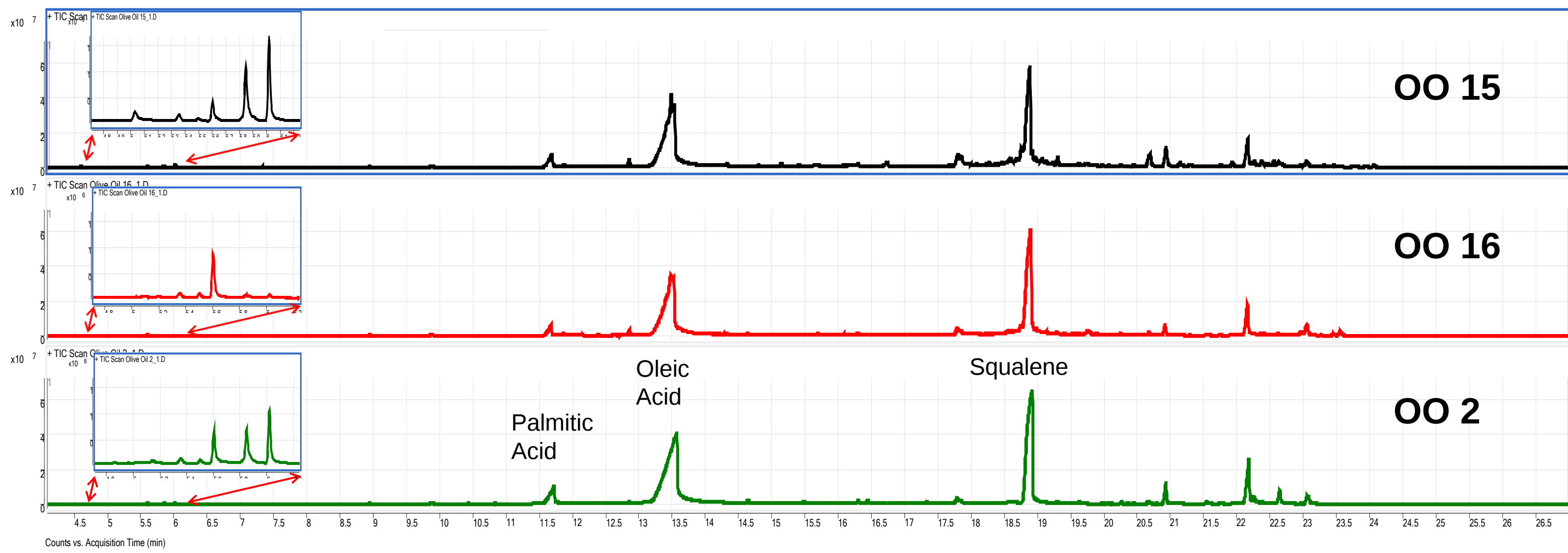
MMI Inlet Program

60 °C (0.1 min), 900 °C/min to 350 °C (hold)
Pulsed Splitless (30 psi pulse for 0.6 min)

GC Oven Program

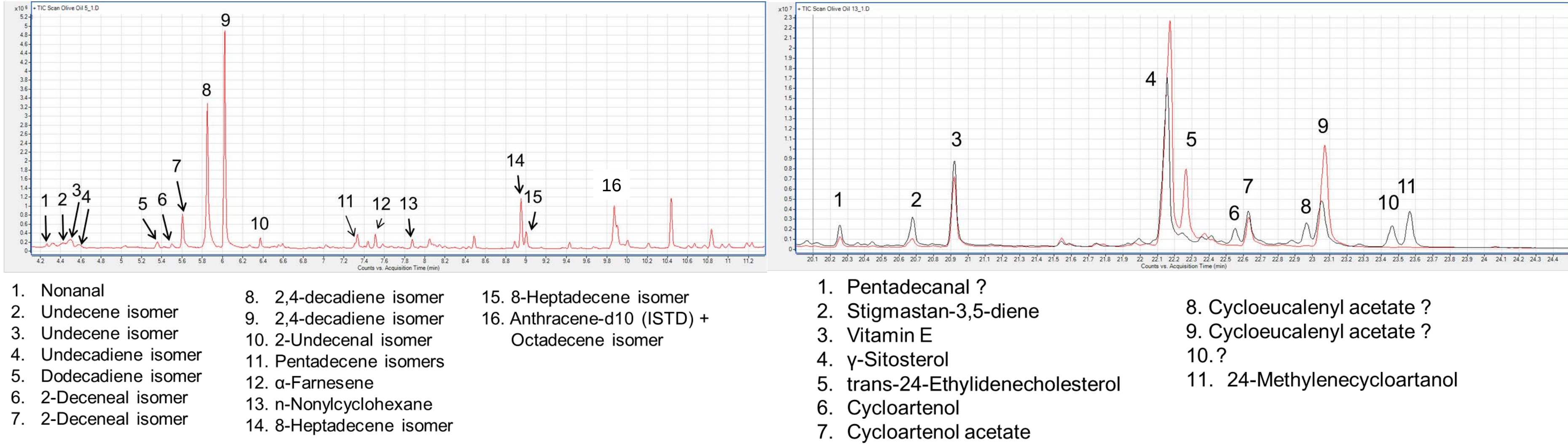
50 °C (1 min), 20 °C/min to 150 °C (0 min)
10 °C/min to 310 °C (5 min)
5 min post-run backflush @ 340 °C

Results

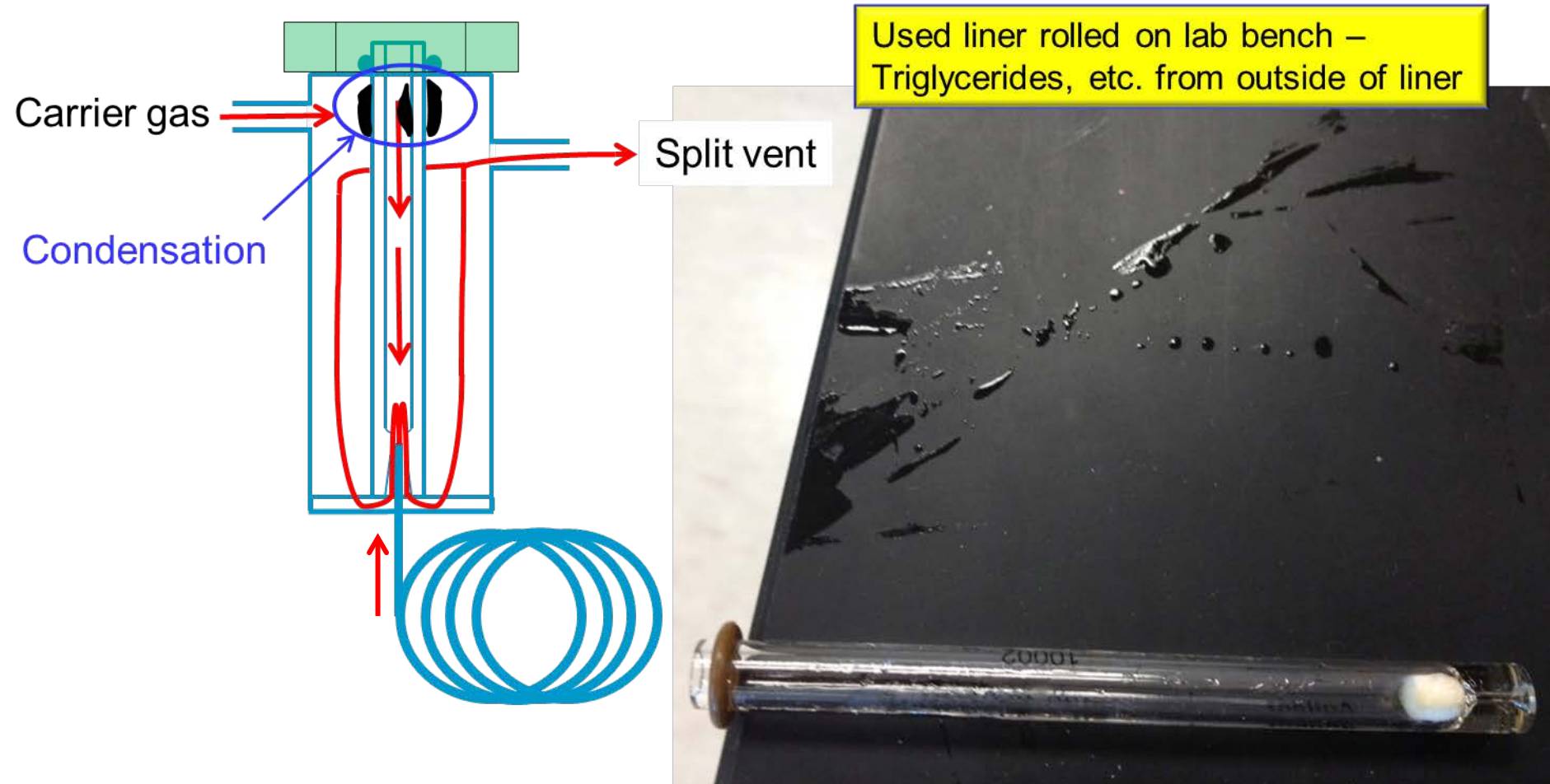


Three different olive oils. OO #2 & 15 are labeled EVOO. OO #16 is labeled "Pure OO." Note: The large peaks are very much overloaded on this thin film GC column.

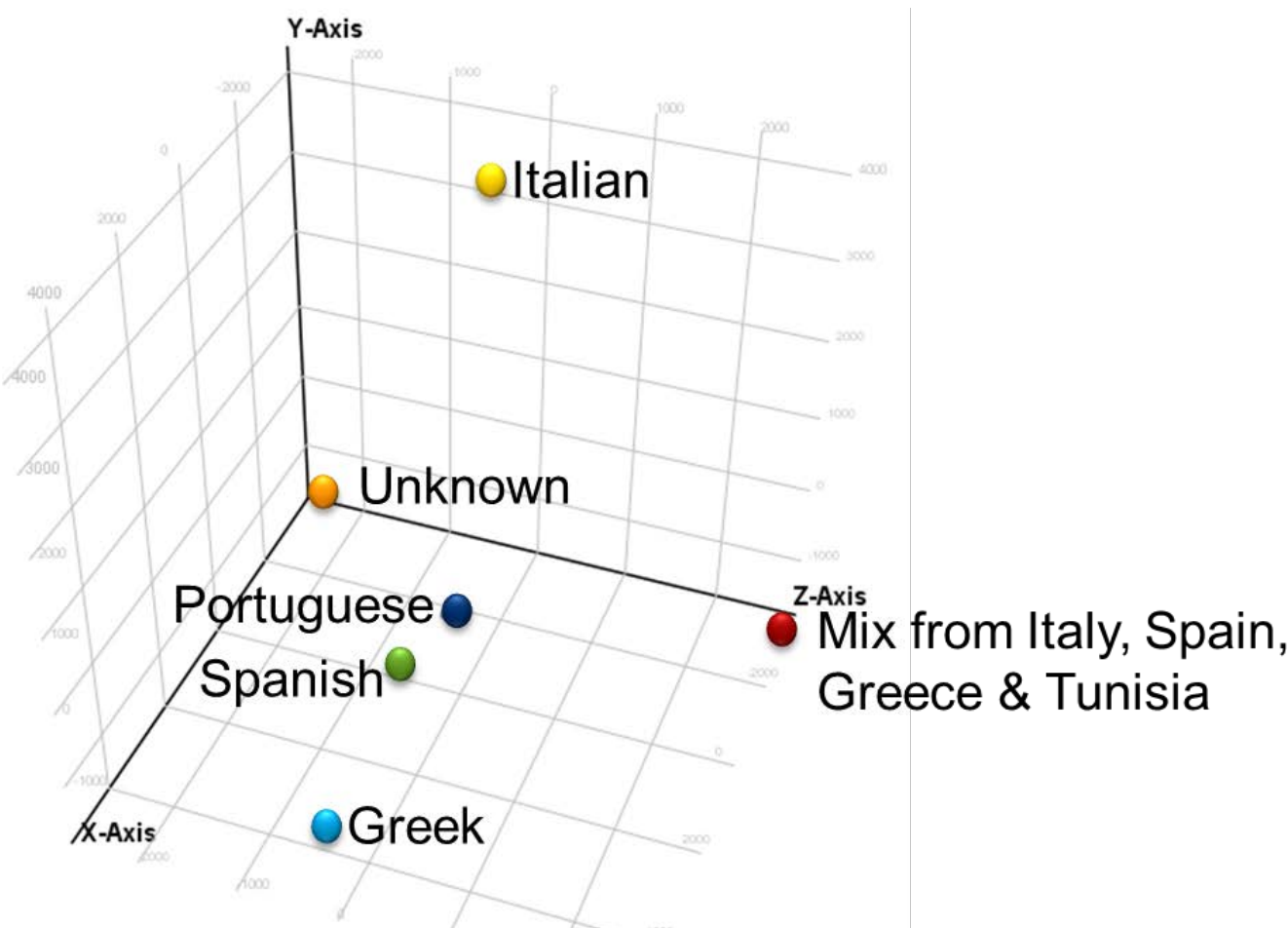
Tentatively Identified Compounds



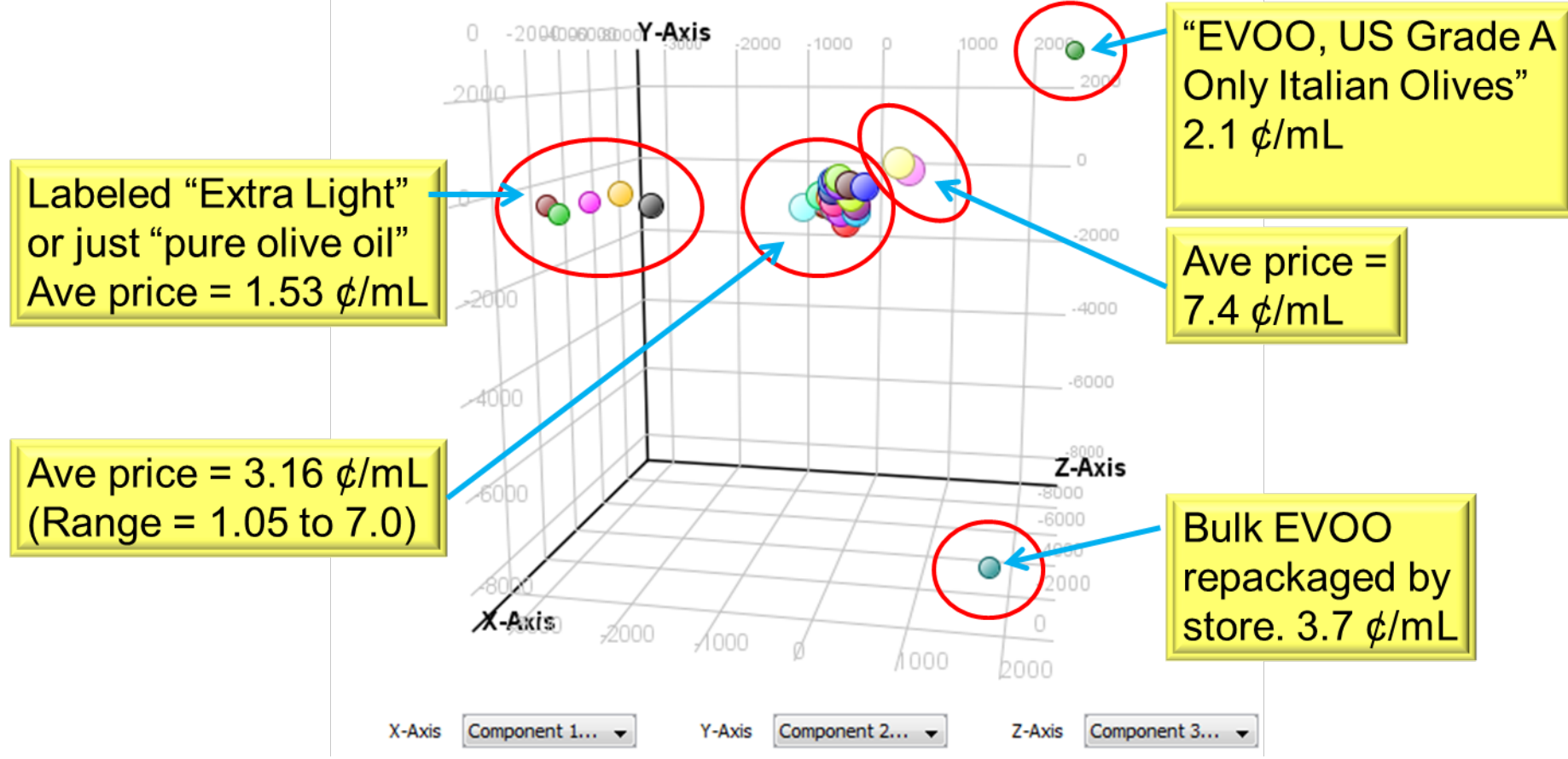
High boilers are backflushed from column and condense on the outside of the inlet liner



PCA scores plot of the OO origin. The one US OO was classified as Unknown



PCA scores plot of the OO by brand. Note: There was only one brand replicate. Each dot represents the average of 6 injections.



The amount of free fatty acids and squalene vary considerably among these OOs.

Olive Oil #	Price (¢/mL)	Label Origin	Label Info
1	3.89	Sp	EVOO
2	2.70	It	EVOO
5	8.40	It	EVOO
10	3.60	Sp	EVOO
13	1.80	It Sp Gr Tun	Extra Light
15	2.08	It	US Grade A
21	1.68	It Sp	Baking Sautéing

Conclusions

- There are no EVOO standards that one can purchase.
- Method developed for the direct GC/MS analysis of olive oils after a 1:10 dilution in acetone
- A Deans switch was used to divert some high boiling components to waste
- The Deans switch was used to backflush the 2-m section of GC column.
- Backflushing at 340 °C may have been a mistake. Due to column bleed, retention times shifted by up to 5 s over the course of about 300 injections.
- PCA could differentiate samples labeled EVOO from those labeled Light or just OO.
- One OO (15) stood out from the rest because of the number & abundance of minor GC/MS peaks.
- Sensory evaluation would have been extremely useful but I had no access to a sensory panel.
- More biological replicates are needed for proper statistical analysis.
- Future plans: analyze seed oils, and mixtures of EVOO adulterated with seed oils and olive pumice oil.