

Soft chemical depolymerization of polymers formed by oil and alkyd paints & their analysis by ultra-high resolution mass spectrometry

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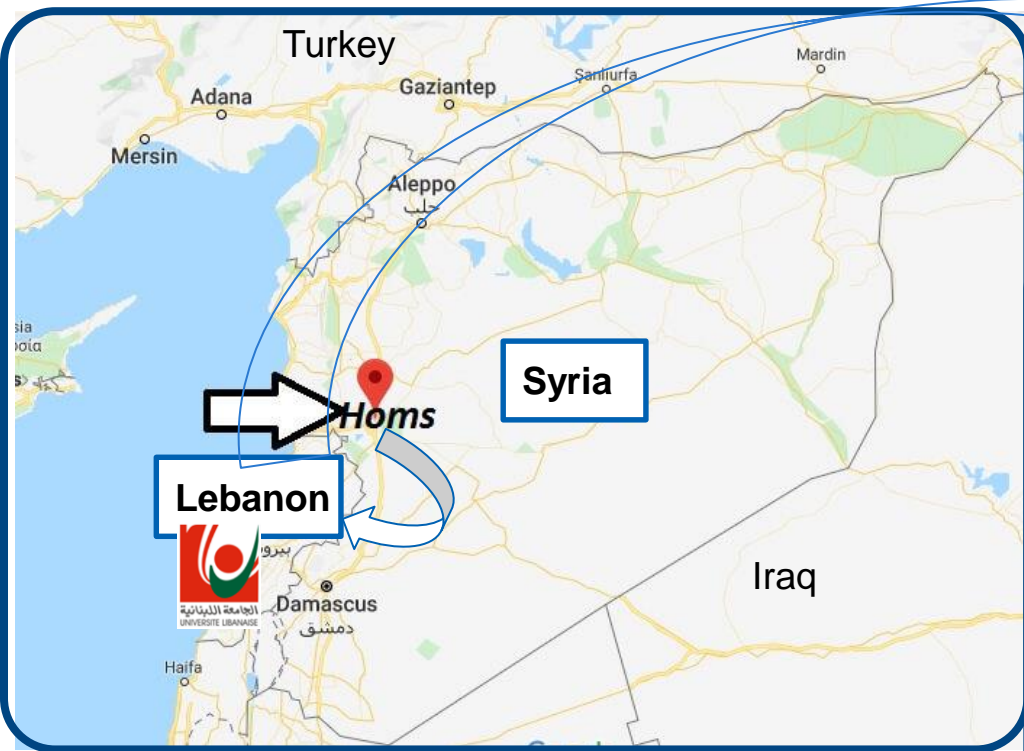
Miniaturization for Synthesis, Analysis & Proteomics UAR 3290

EU-FTICR-MS School, 12th December 2022

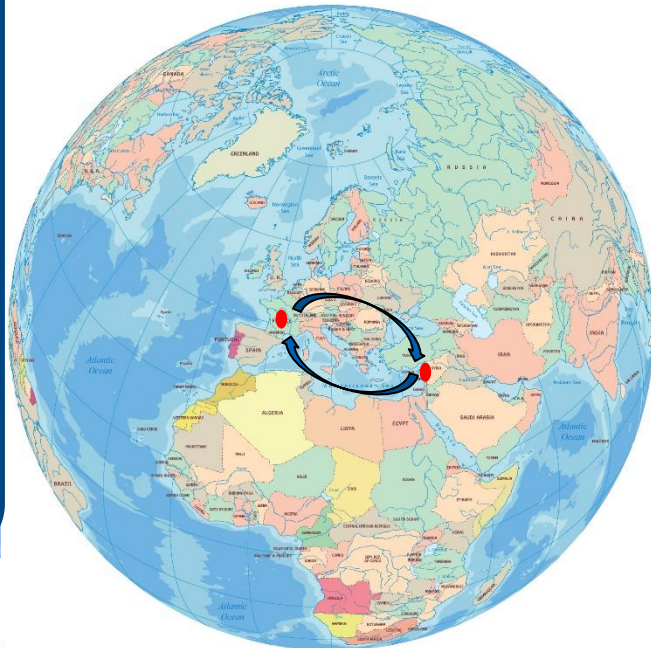
Lille, France



Syrian- PhD between Lebanon and France



PhD Co-tutelle:
Lebanese University-
University of Lille



Oil painting

Oil painting:

application of pigments on a support using drying oil



Girl with the pearl earring



1655

Portrait of Dr. Gachet



1890

Nude Woman in a Red Armchair



1932

Painting techniques were used for centuries

Oil paint composition



Siccative vegetable oils

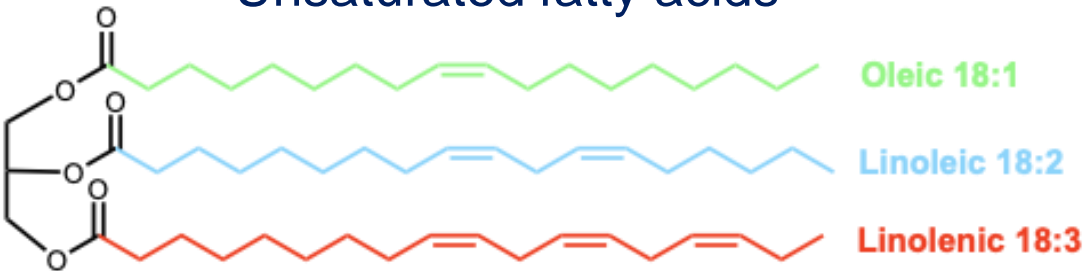


Traditional and modern oils

Fatty acid Oil	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Linseed	4-7 %	2-5 %	12-34 %	17-24 %	35-60 %
Poppy	10 %	2 %	11 %	72 %	5 %
Walnut	11 %	5 %	28 %	51 %	5 %

Triglycerides in oils

Unsaturated fatty acids

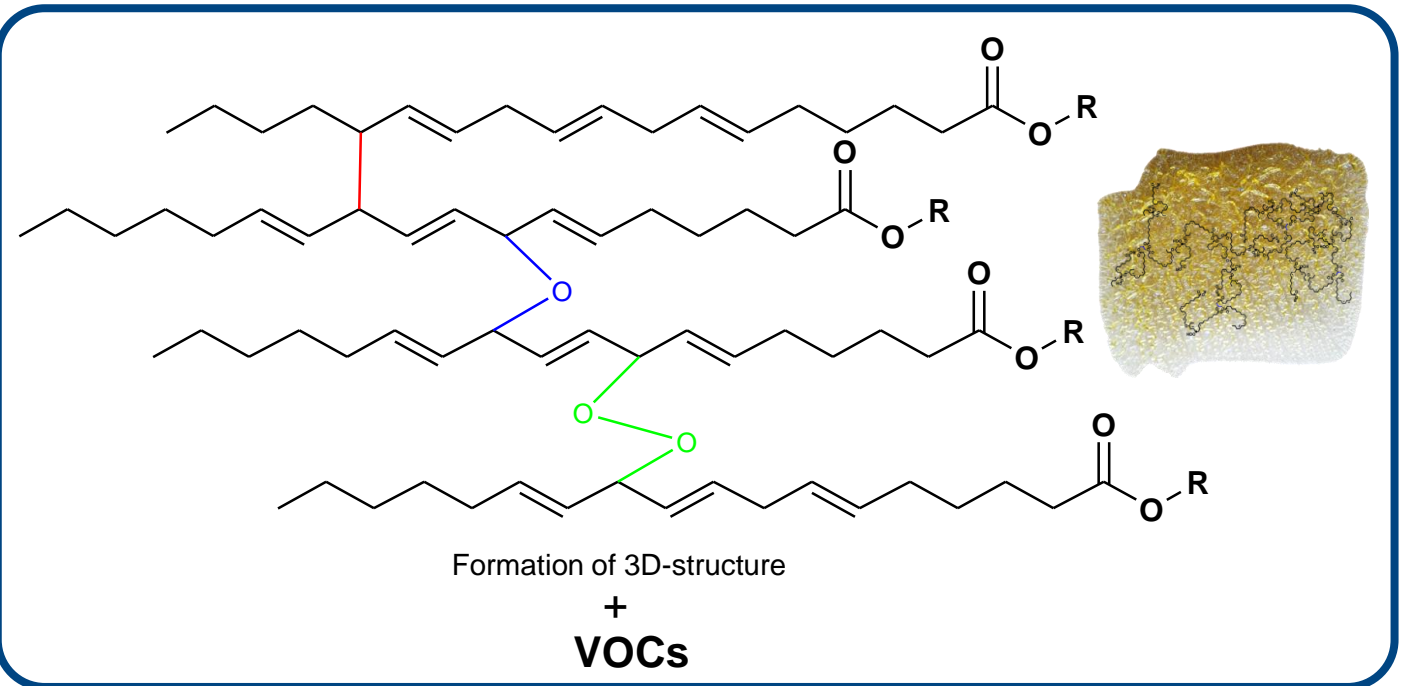
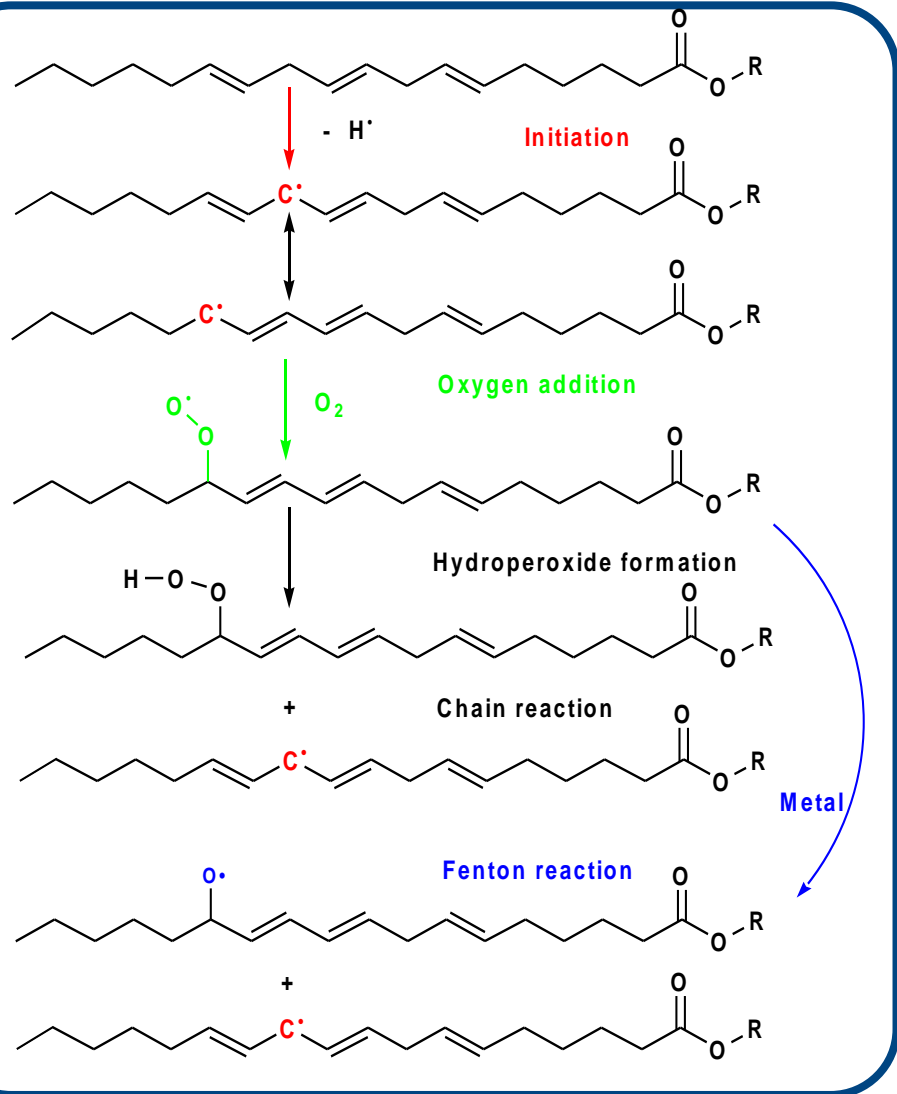


Saturated fatty acids



Drying depends on unsaturated fatty acids content

Siccative or autoxidation mechanism

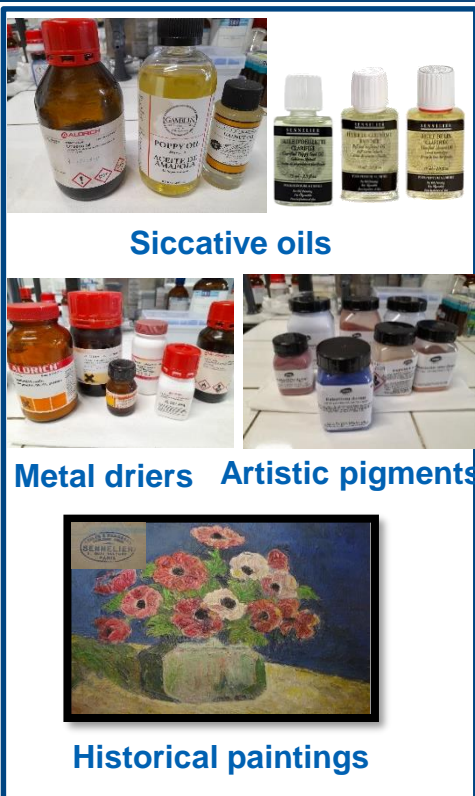


Siccative

The ability of oil to form a solid film upon exposition to light and air.

Catalyzed by driers (historically Pb, now Co, Cr, Fe, Mn) and pigments.

Oil paint analytical methodology

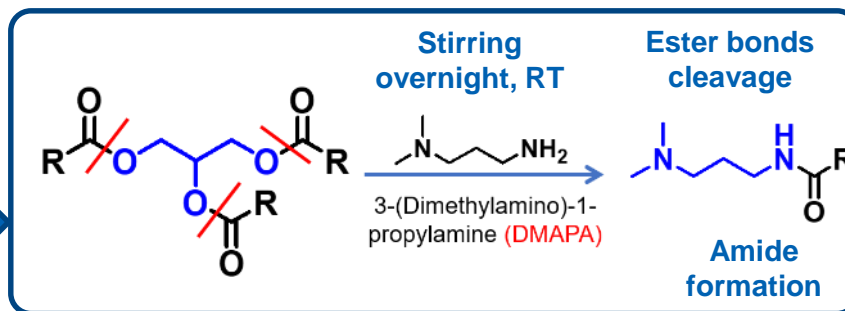


Polymerization
or drying

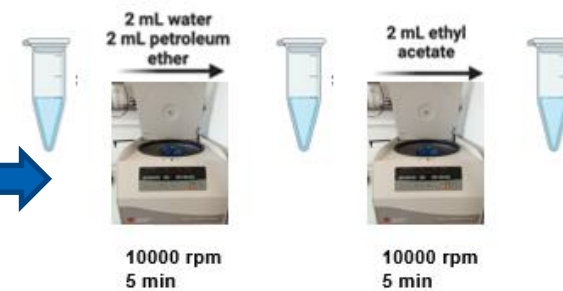


Painting

Chemical depolymerization by transamidation



Quenching
Liquid-liquid extraction



MS analysis

MALDI-TOF- MS



LC- Orbitrap



Ultra high resolution
MALDI FT-ICR MS



Evaporation



Solubilization
dilution

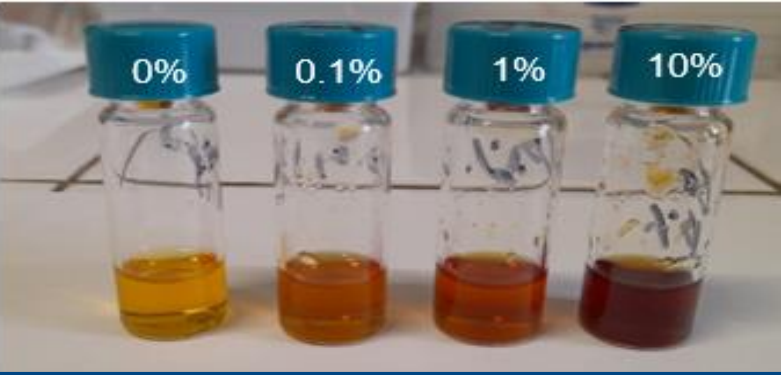
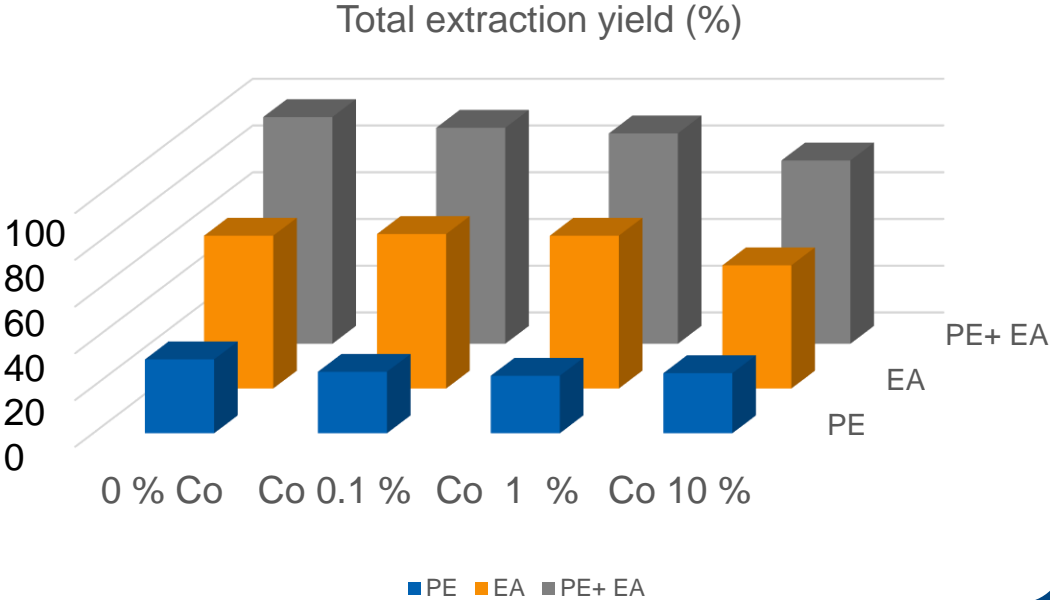


Linseed oil polymerization- depolymerization



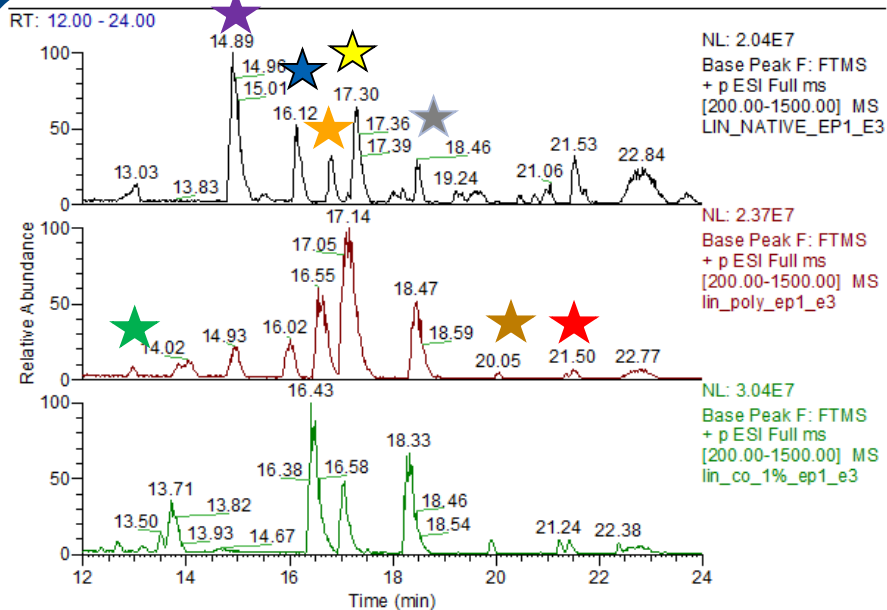
Linseed oil with Co (II)2-ethylhexanoate
Film thickness = 0.04 cm

Polymerization 1 week



Depolymerization

Linseed oil polymerized 1 week: depolymerization & LC MS

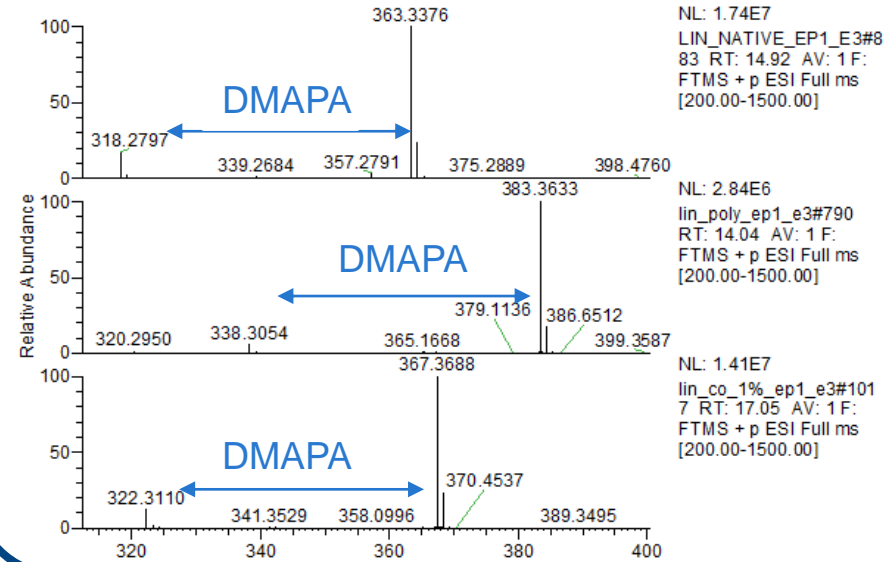


Native

Without drier

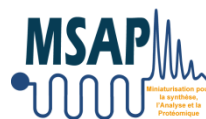
With Co 1 %

- ★ Oleic10
- ★ Linolenic
- ★ Linoleic
- ★ Palmitic
- ★ Oleic
- ★ Stearic
- ★ Eicosanoic
- ★ Docosanoic

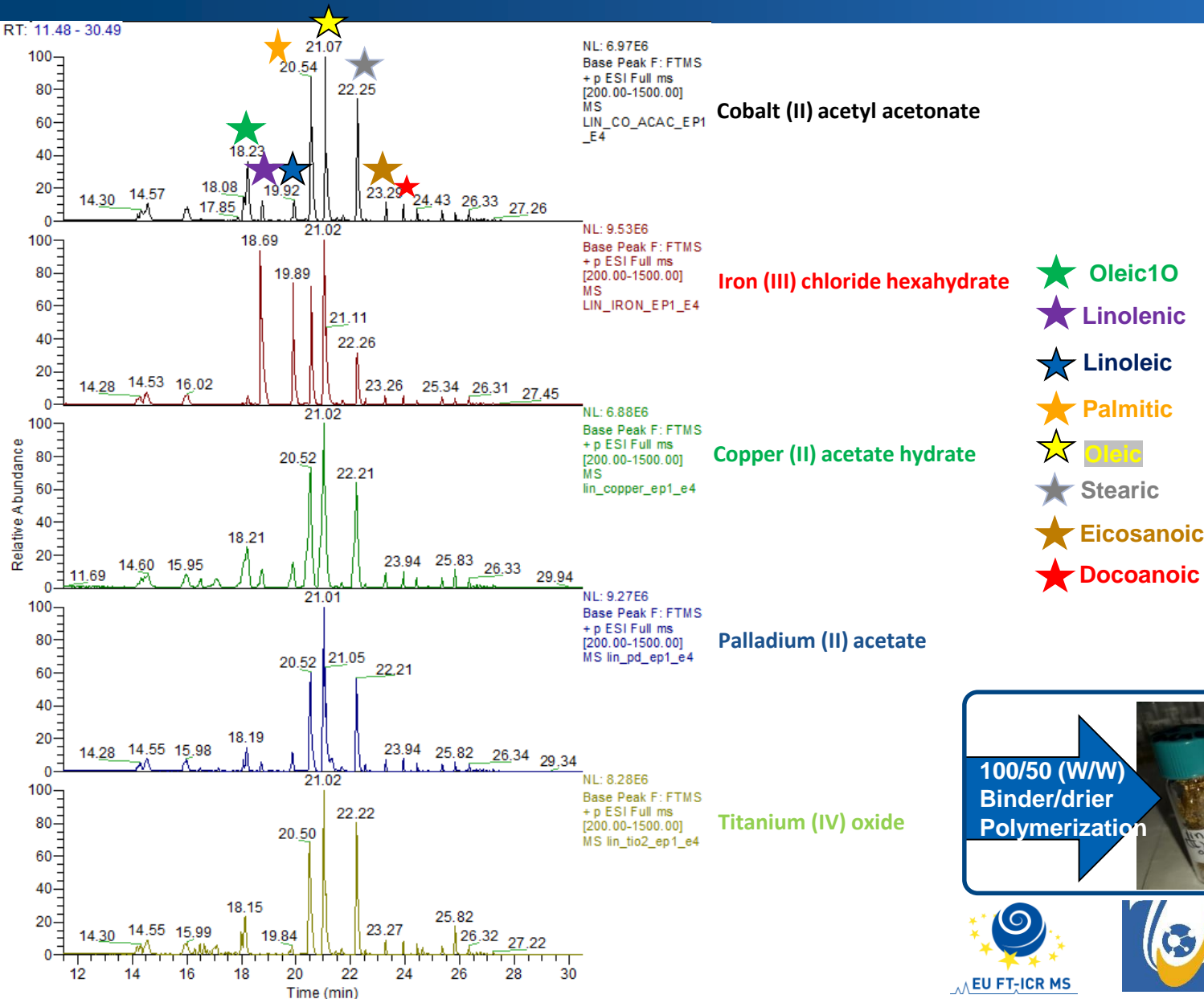


Percentage of fatty acid vs unsaturated fatty acids

	Native	Without drier	Co 0.1 %	Co 1 %
C18:1	36 %	67 %	86 %	95 %
C18:2	25 %	18 %	9 %	3 %
C18:3	38 %	15 %	6 %	1 %
C16:0	49 %	53 %	53 %	56 %
C18:0	49 %	44 %	43 %	38 %
C20:0	1 %	4 %	4 %	5 %



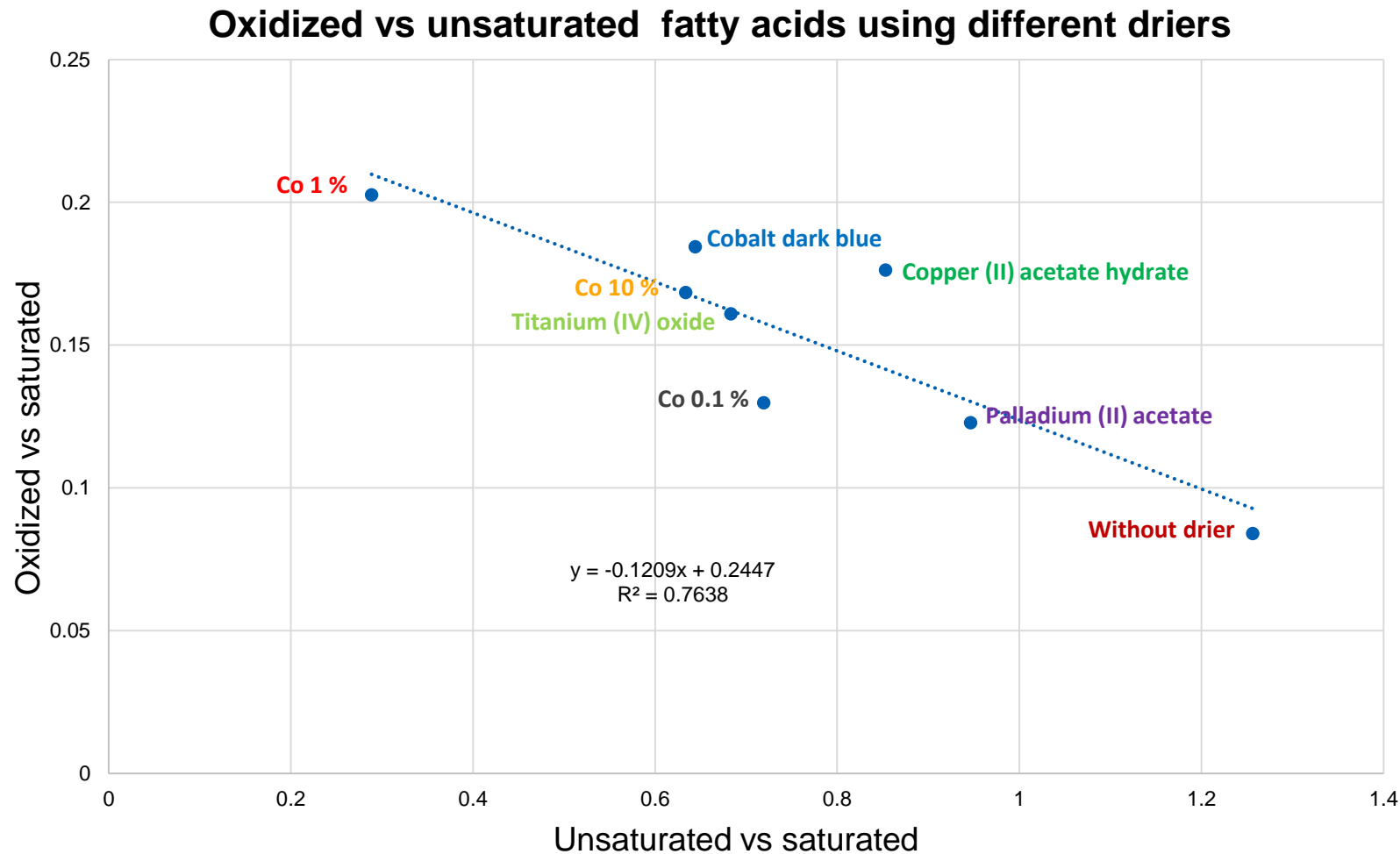
Linseed oil polymerized 1 week: influence of metal driers



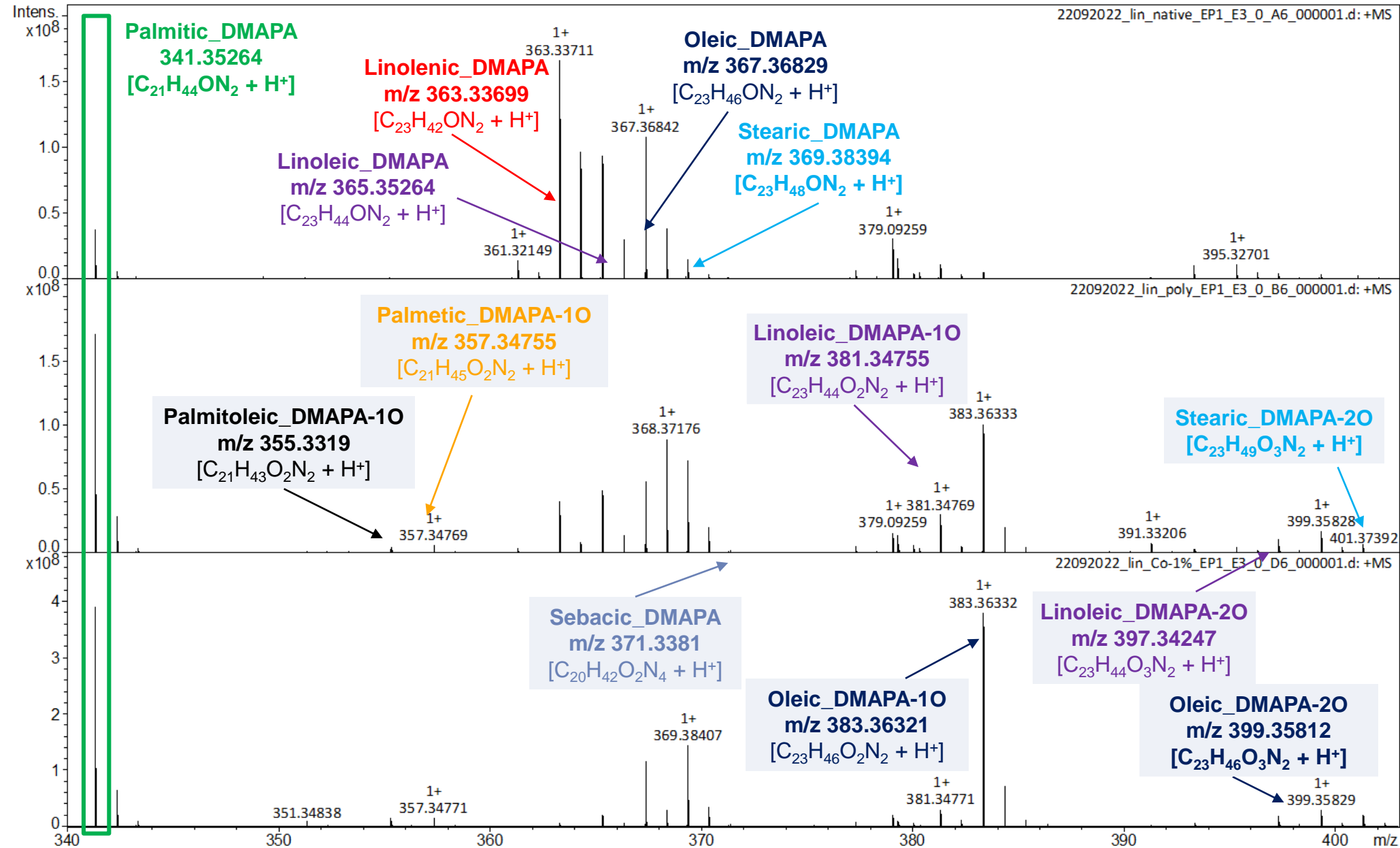
Percentage of fatty acid vs unsaturated fatty acids					
	Co	Fe	Pd	Cu	TiO ₂
C18:1	84 %	38 %	85 %	80 %	94 %
C18:2	11 %	27 %	10 %	12 %	5 %
C18:3	5 %	35 %	5 %	8 %	1 %
C16:0	34 %	29 %	46 %	44 %	51 %
C18:0	62 %	66 %	49 %	50 %	43 %
C20:0	5 %	5 %	6 %	6 %	6 %



Linseed oil polymerized 1 week: oxidized vs unsaturated fatty acids



Linseed oil polymerized 1 week: MALDI-FTICR MS, petroleum ether fraction

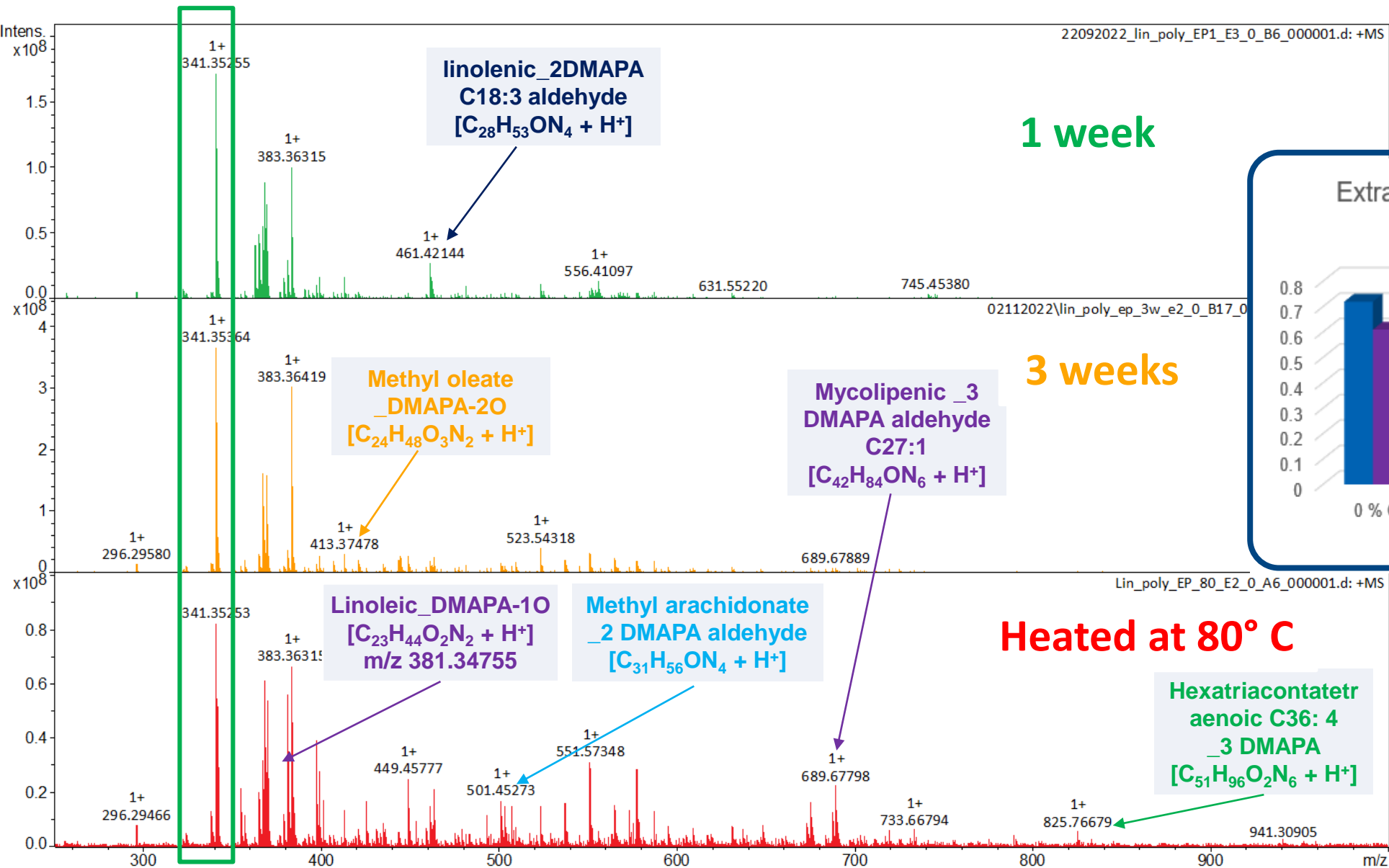


Native

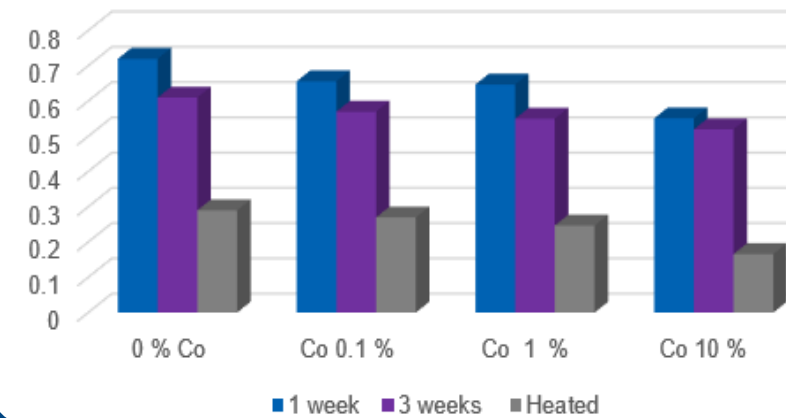
Without drier

With Co 1 %

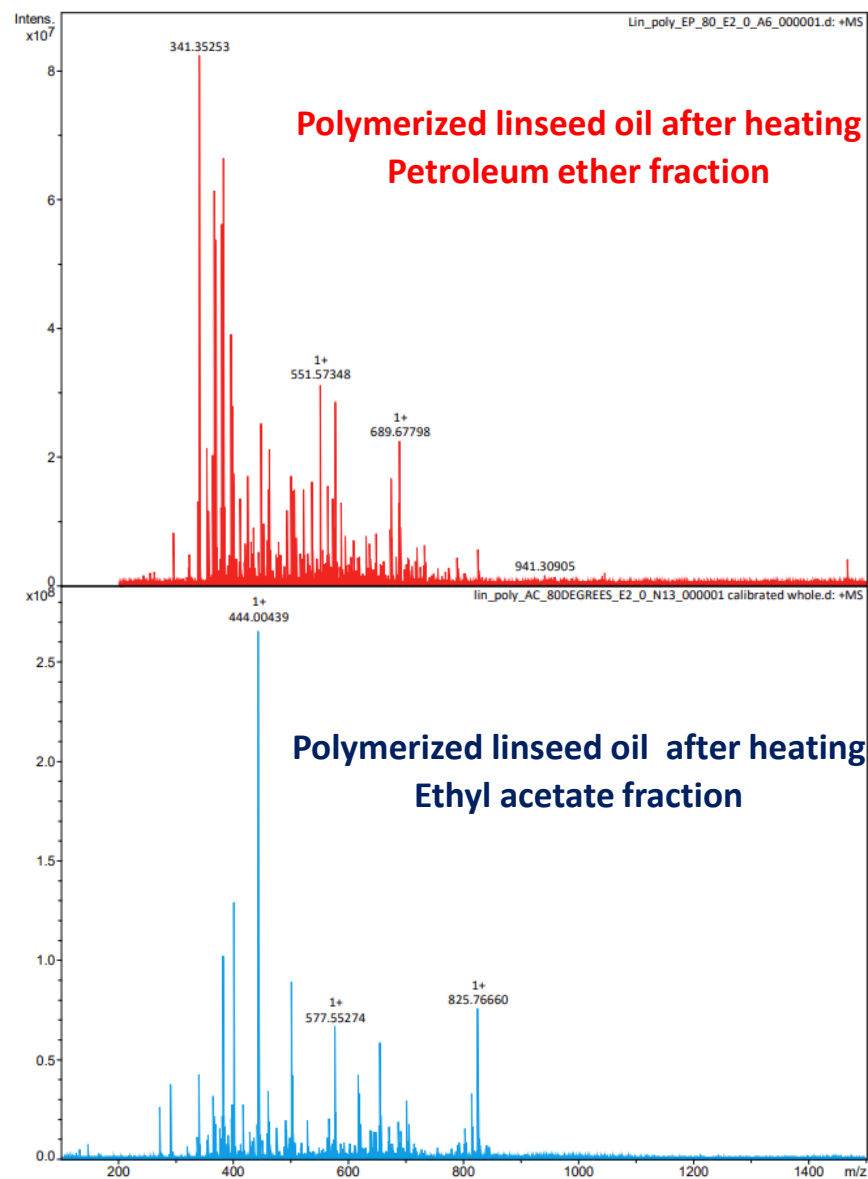
Linseed oil polymerization: influence of ageing



Extraction yield of linseed oil in function of polymerization time and method

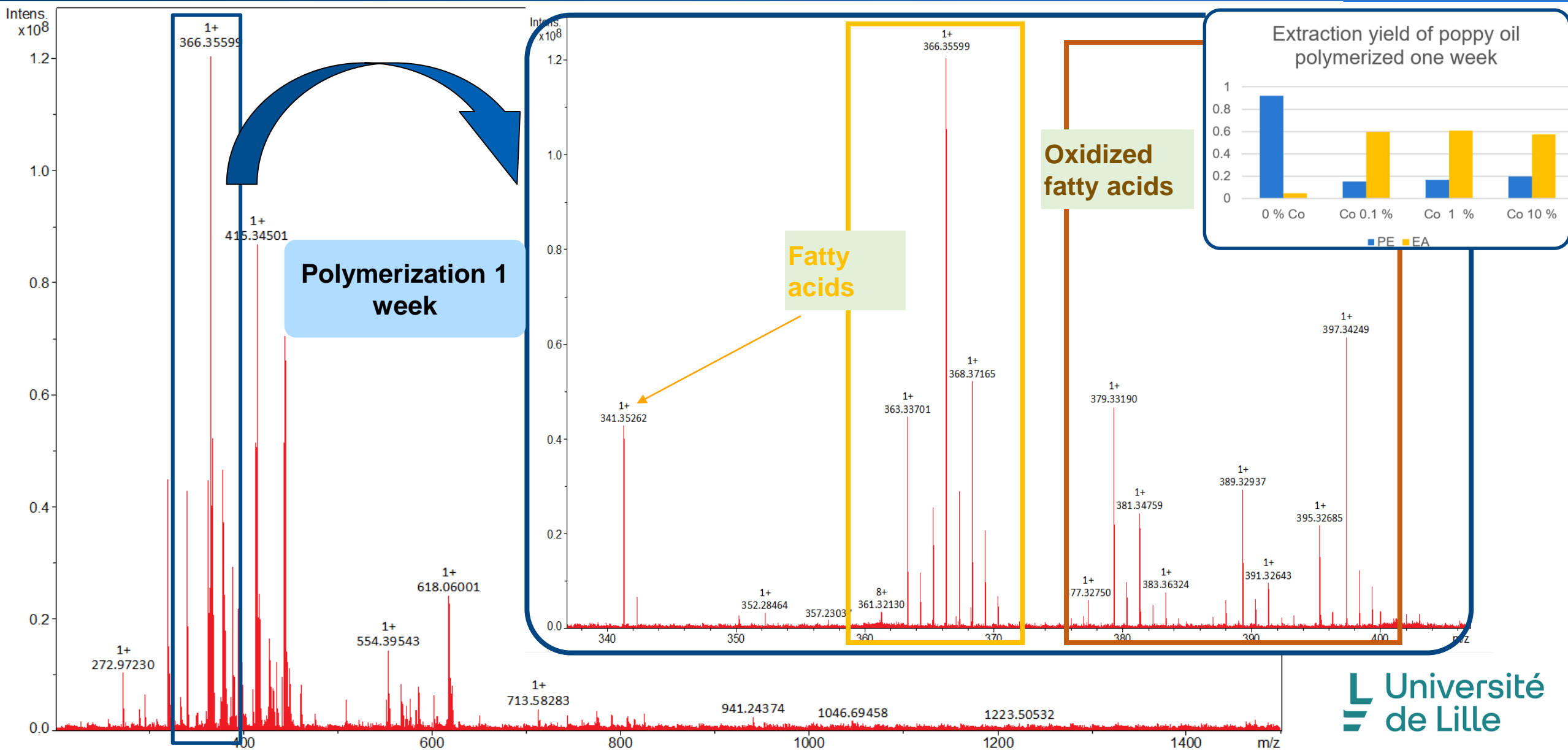


Linseed oil depolymerization: influence of solvent of extraction

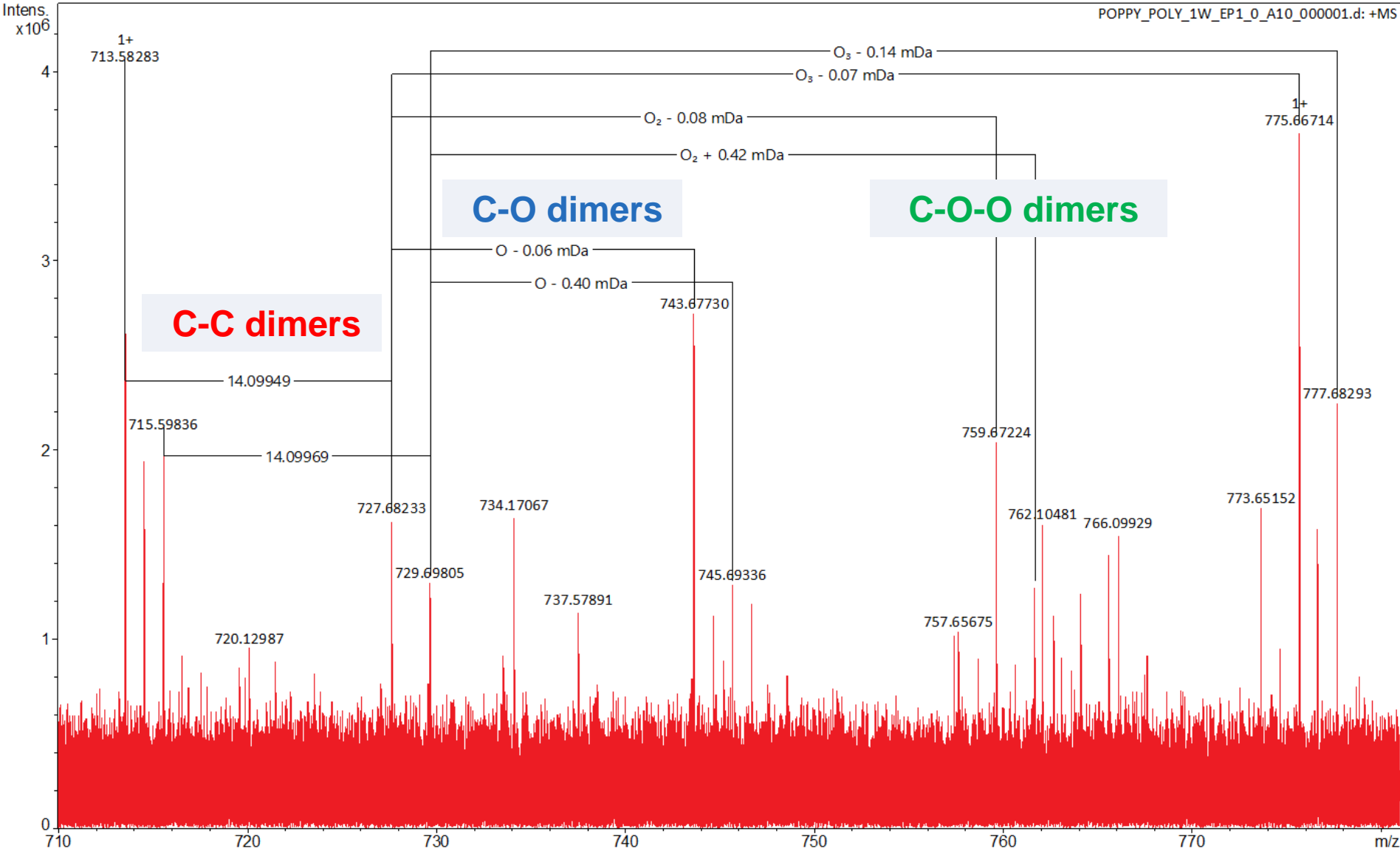


Theoretical m/z [M+H] ⁺	Formula [M+H]	Attribution	Relative intensity of polymerized + heated linseed oil at 80° C (%)	
			PE fraction	Ethyl acetate fraction
407.338053	C ₂₃ H ₄₃ N ₄ O ₂	Trideca-2,4,6-trienoic-2 DMAPA C13:3	0.55	3.02
417.368684	C ₂₃ H ₄₉ N ₂ O ₄	Stearic- 1 DMAPA- 3 O	0.99	0.62
421.353703	C ₂₄ H ₄₅ N ₄ O ₂	5,8,11-tetradecatrienoic- 2 DMAPA C14:3	1.15	0.38
425.373770	C ₂₅ H ₄₉ N ₂ O ₃	Eicosadienoic- 1 DMAPA- 2O C20:2	1.75	1.47
431.363205	C ₂₇ H ₄₇ N ₂ O ₂	Docosapentaenoic- 1 DMAPA- 1 O C22:5	5.26	1.47
449.337384	C ₂₆ H ₄₅ N ₂ O ₄	Heneicosapentaenoic- 1 DMAPA- 3 O C21:5	0.84	2.31
451.353034	C ₂₆ H ₄₇ N ₂ O ₄	Methyl arachidonate- 1 DMAPA- 3 O C21:4	0.80	0.60
467.347949	C ₂₆ H ₄₇ N ₂ O ₅	Methyl arachidonate- 1 DMAPA- 4 O	1.30	0.52
467.431953	C ₂₇ H ₅₅ N ₄ O ₂	Heptadecenoic- 2 DMAPA C17:1	0.67	0.46

Poppy oil polymerization

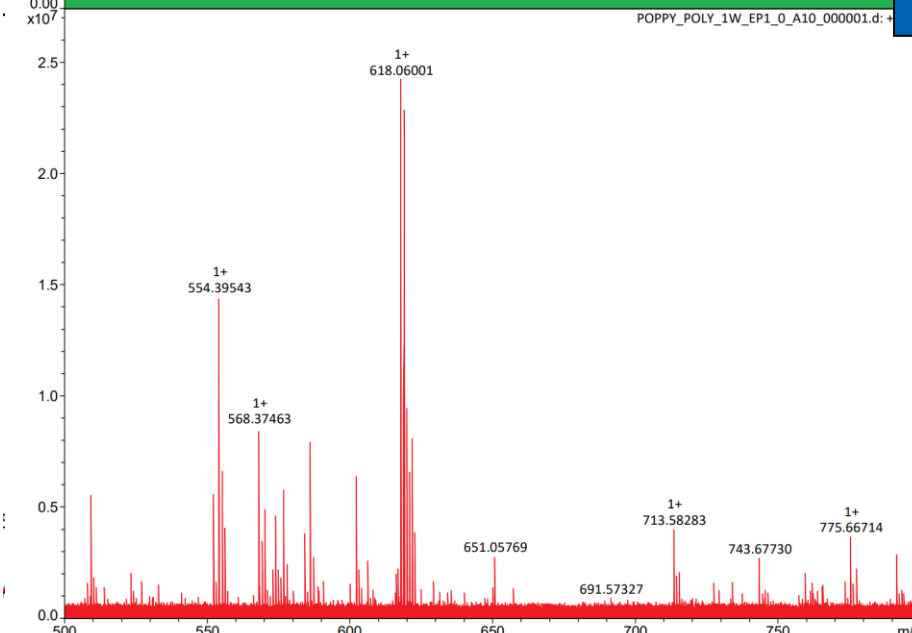
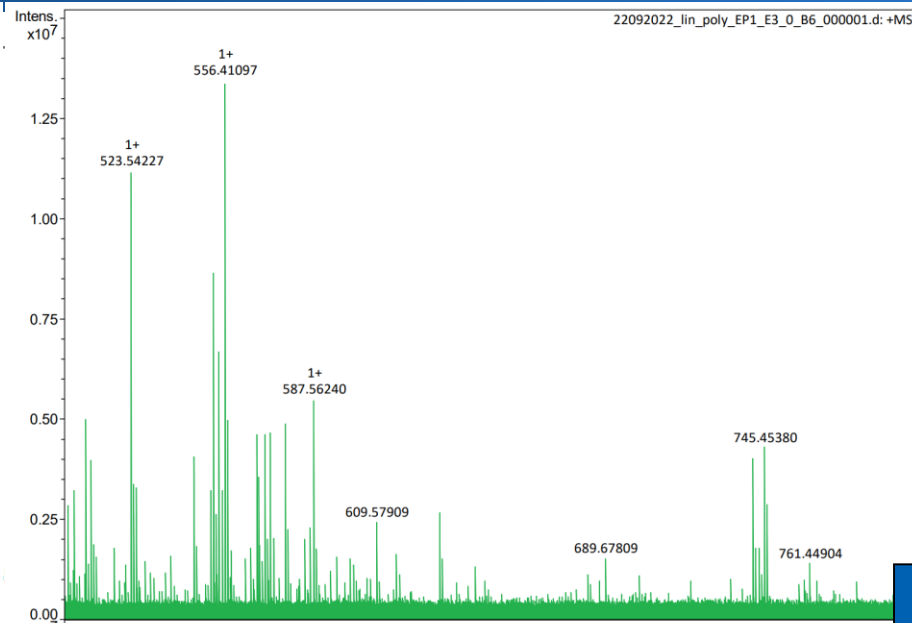
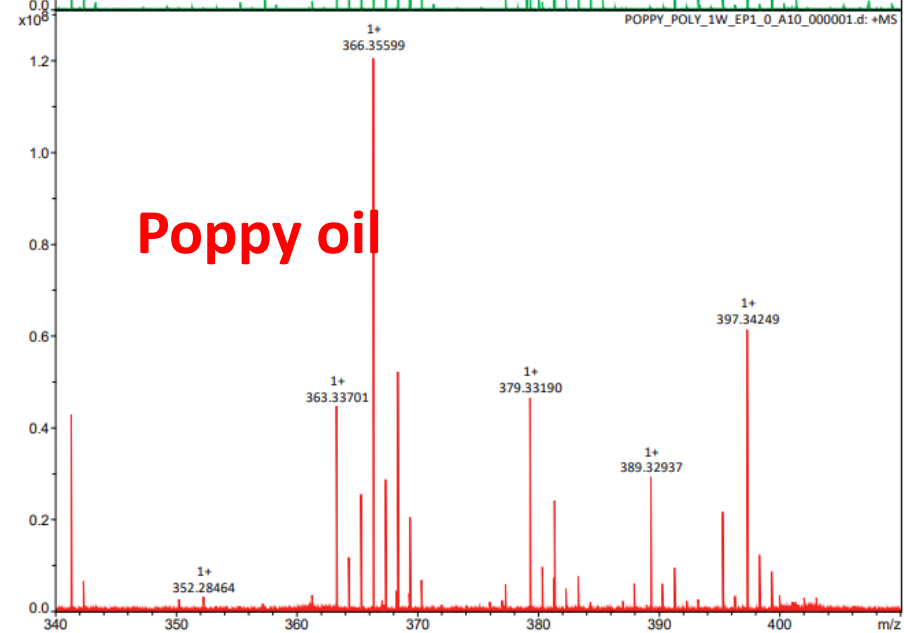
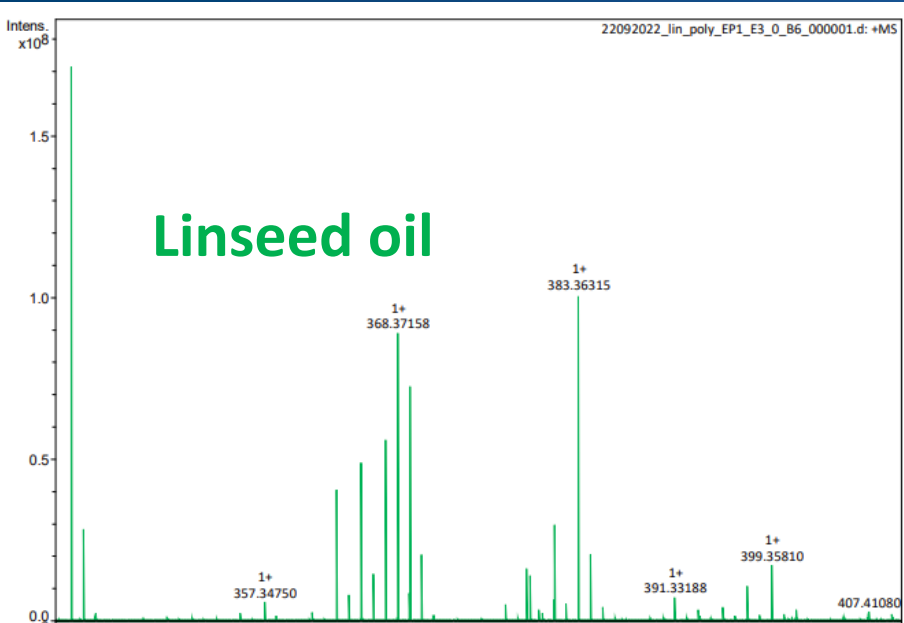


Dimers of poppy oil



Polymerization 1 week

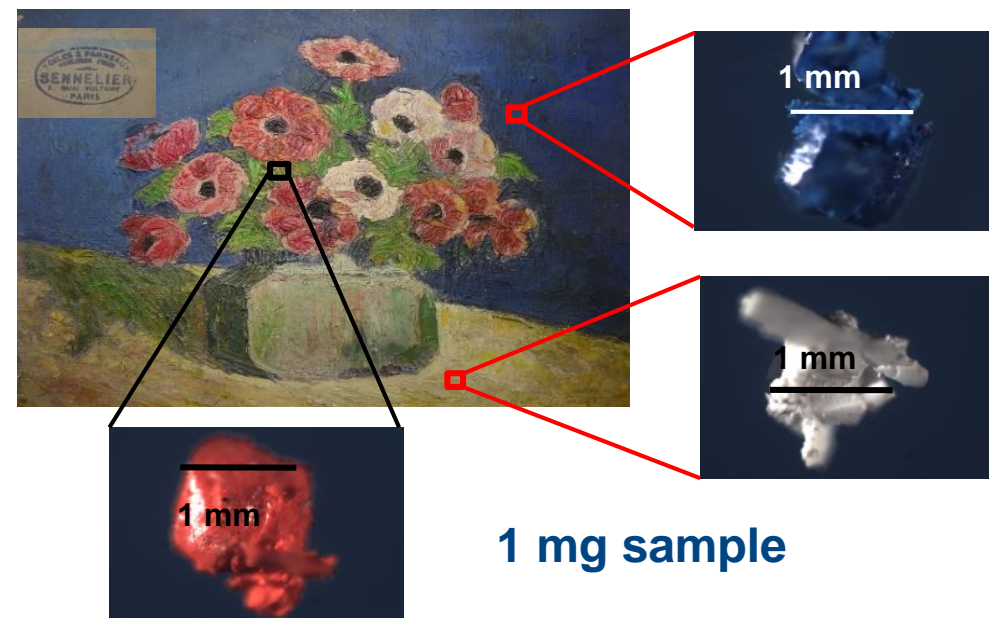
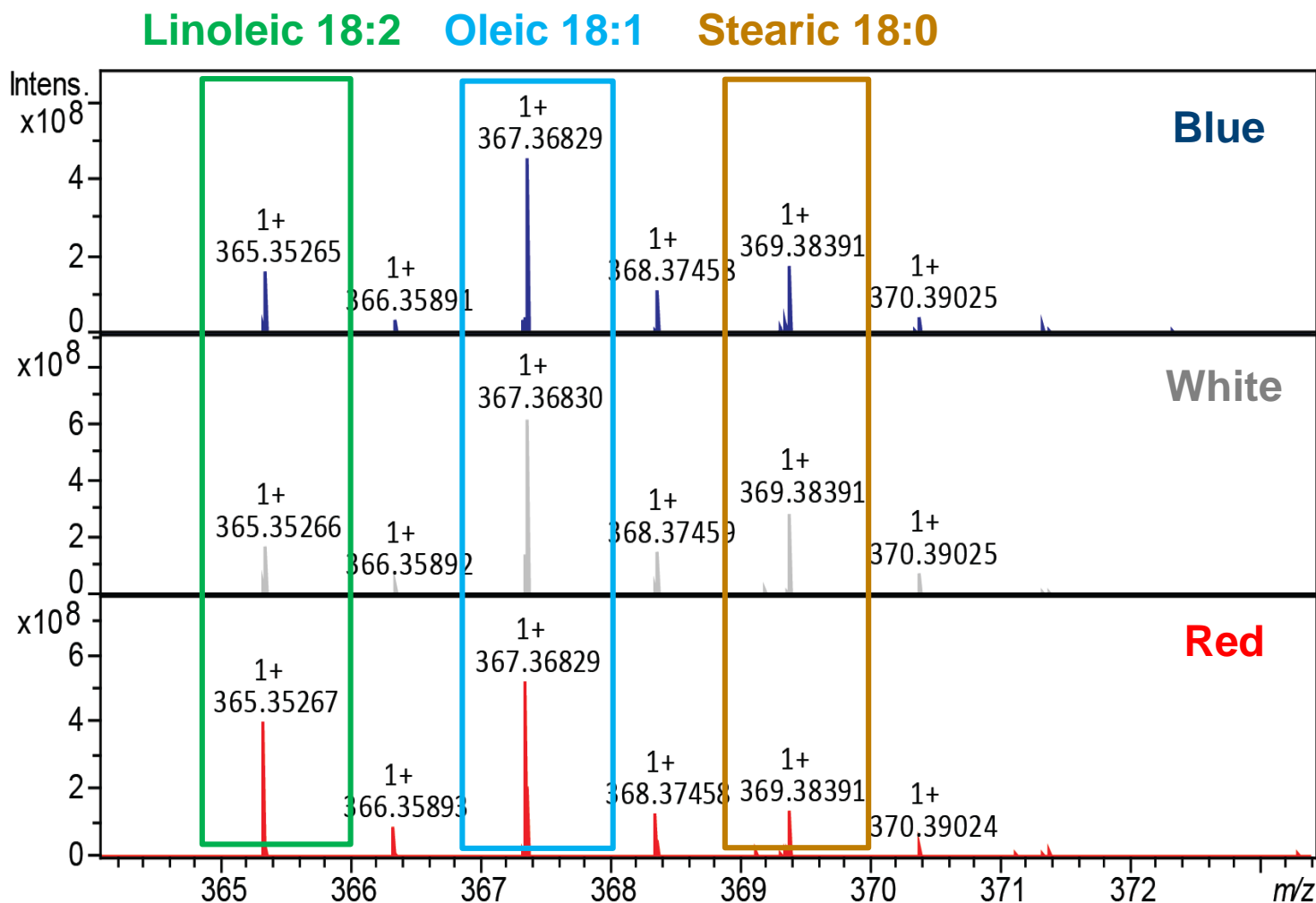
Comparison between linseed and poppy oil



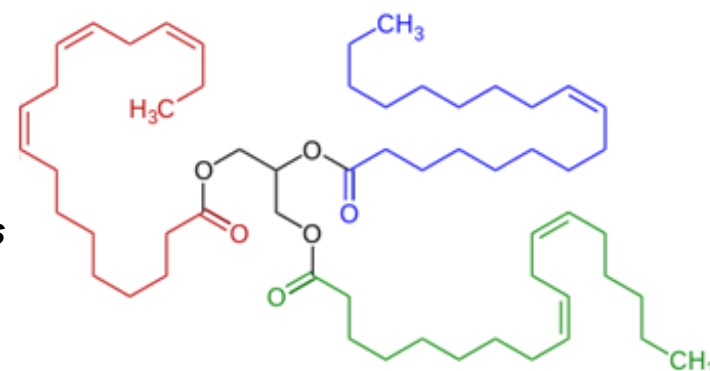
Additional FA
In poppy oil

- C13:3- 1 DMAPA- 1 O
- C13:3- 1 DMAPA- 2 O
- C20:1- 1 DMAPA
- C18:3- 2 DMAPA
- C20:0- 1 DMAPA
- Methyl linolenate- 3 DMAPA
- Linoleic- 1 DMAPA- 4 O
- Linoleic- 1 DMAPA- 5 O
- Oleic- 1 DMAPA- 4 O
- C24:4- 3 DMAPA

Historical painting on Sennelier canvas (between the 2 World War)



Triglyceride (TAG) molecule formed by one glycerol and three fatty acids (oleic, linoleic, linolenic)



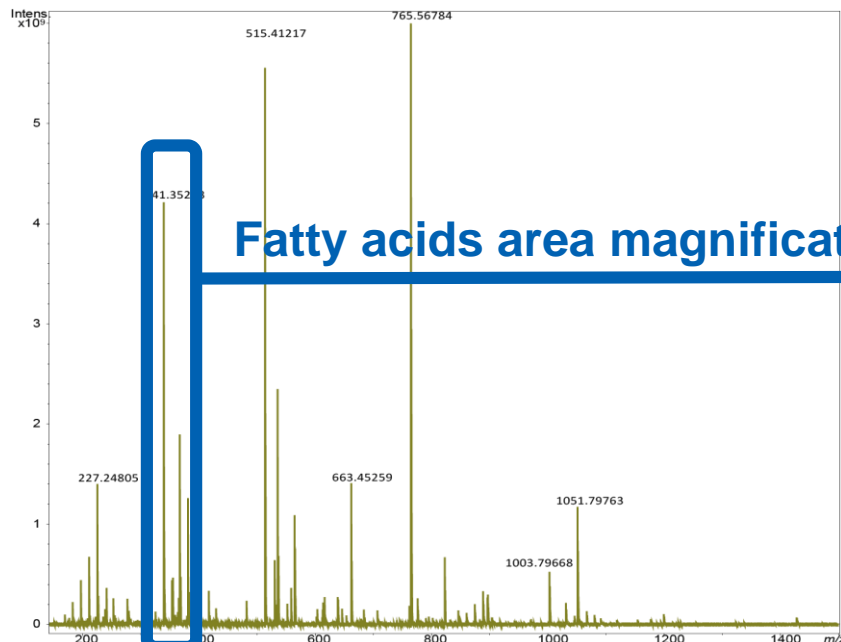
Pigments influence the relative intensities of unsaturated and saturated fatty acids, as well as polymerization and siccation

Historical painting early XIXth century

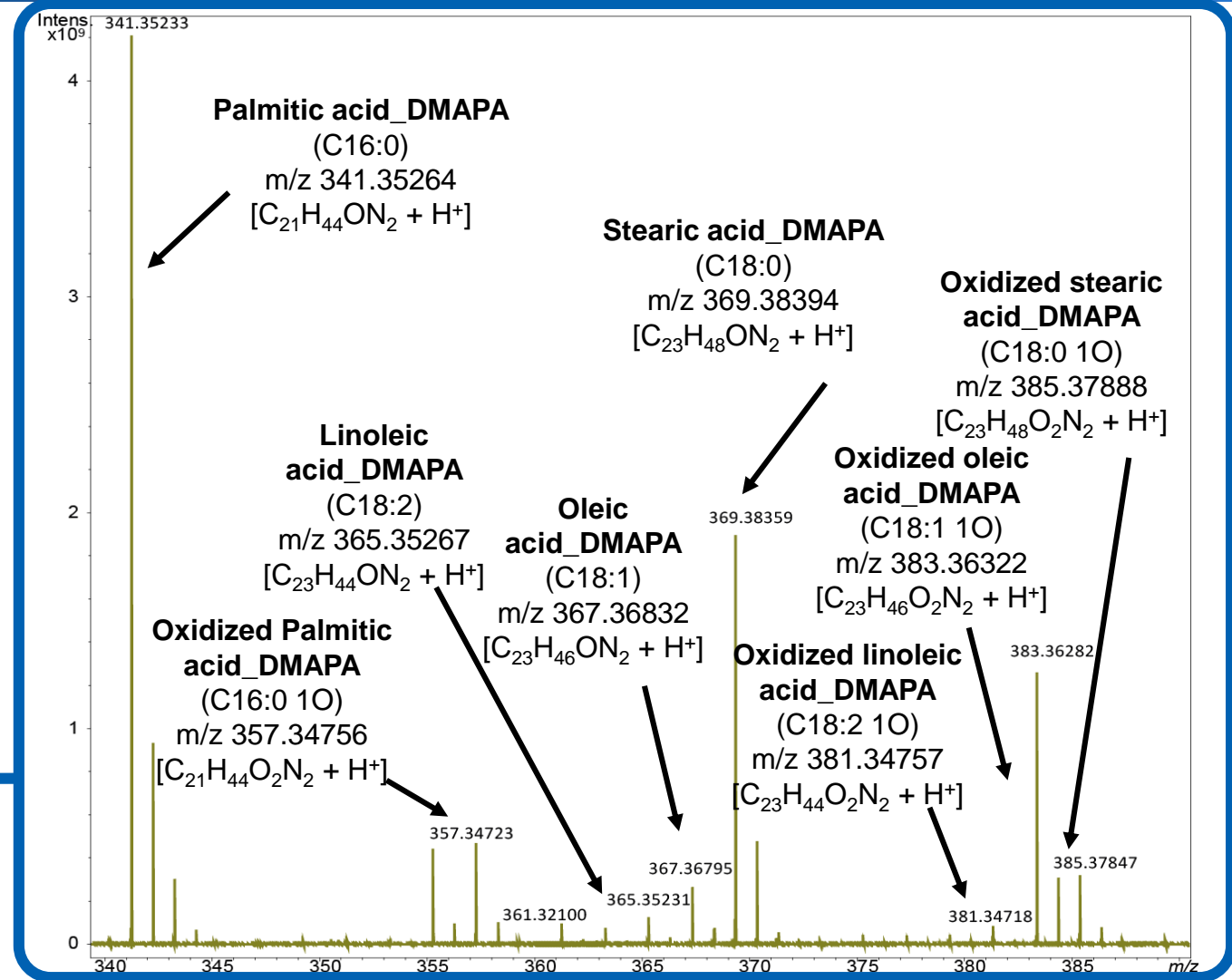


~ 10 µg
Museum scale
(white)

Full spectrum



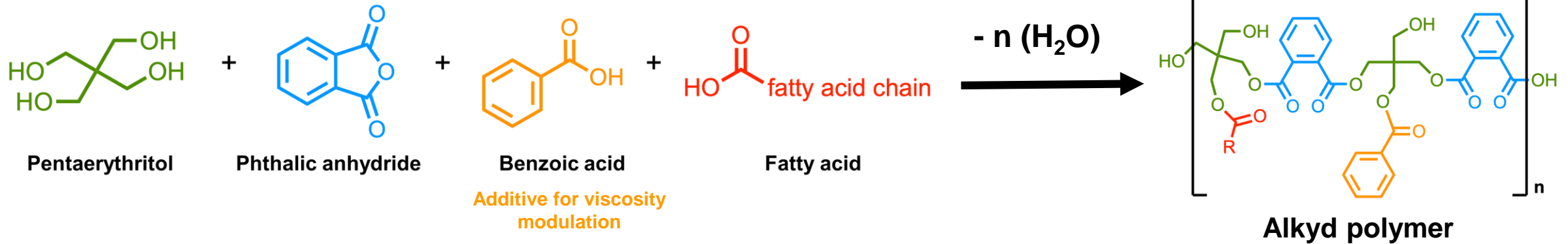
Fatty acids area magnification



Alkyd paints

Alkyds are organic polyesters synthesized for the first time in 1927 by R. H. Kienle

Example of reaction synthesis of alkyd paints



Alkyd polymer

Applications



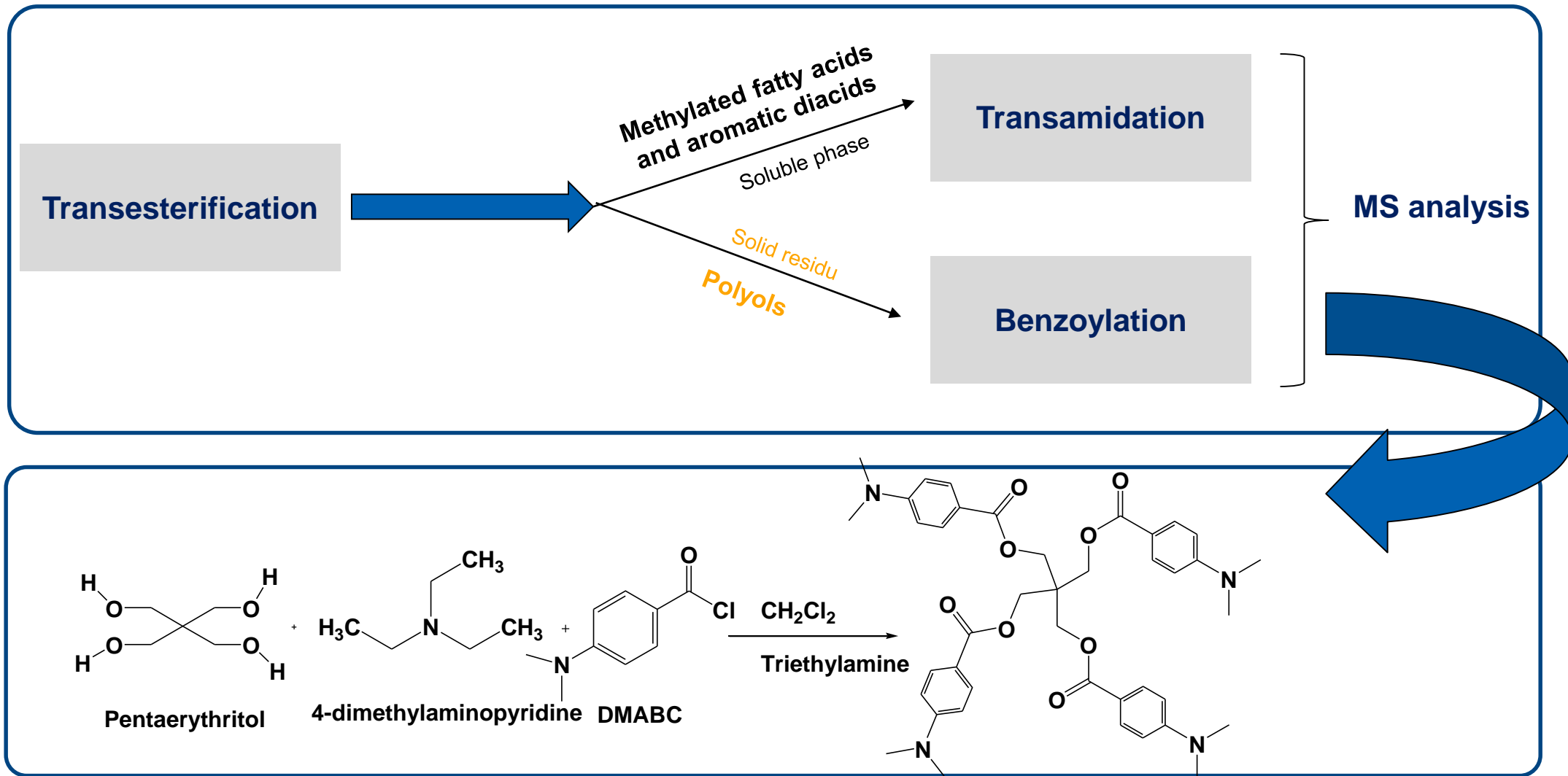
+ Pigment

Alkyd paints

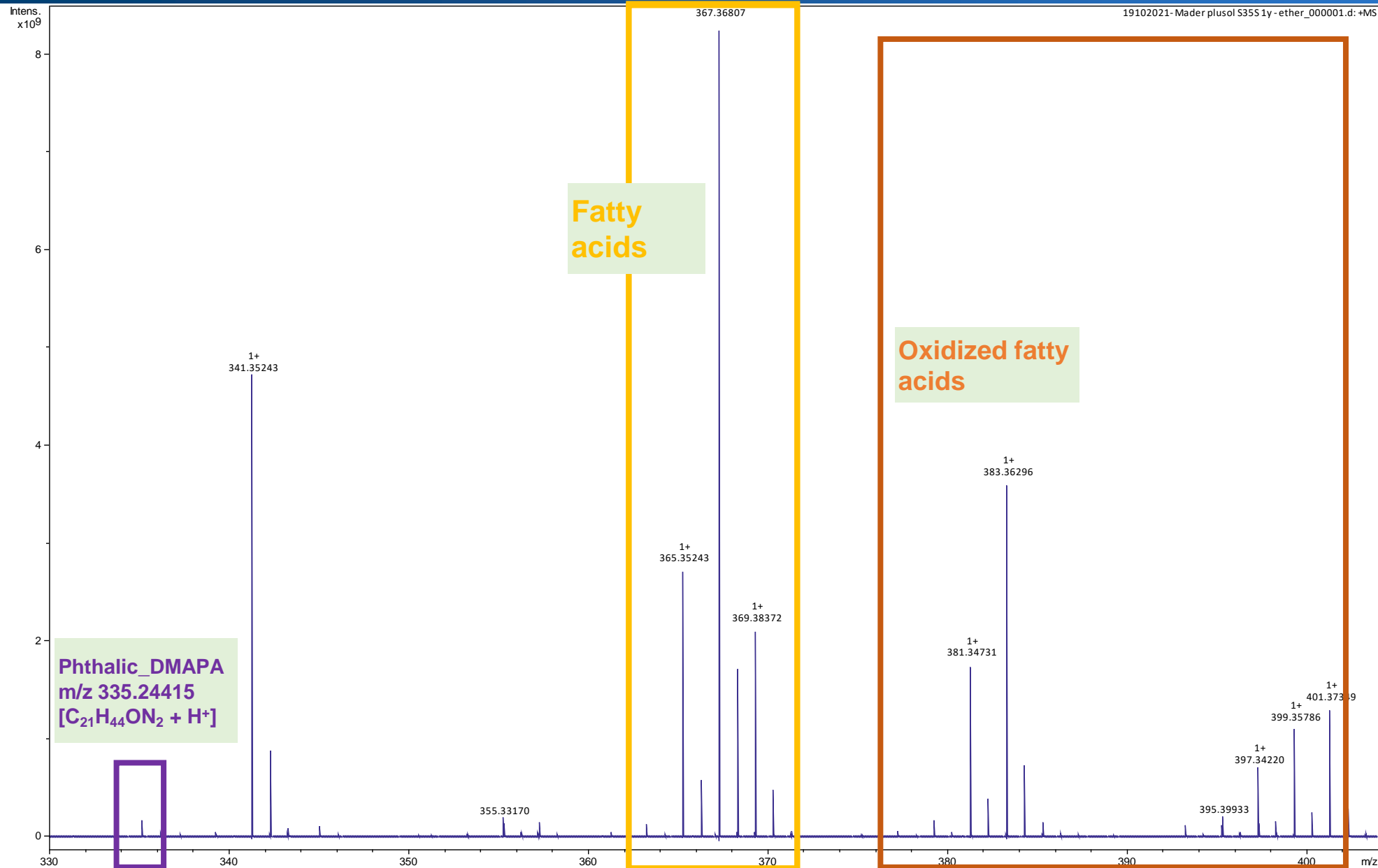


Same autoxidation process as oil paints

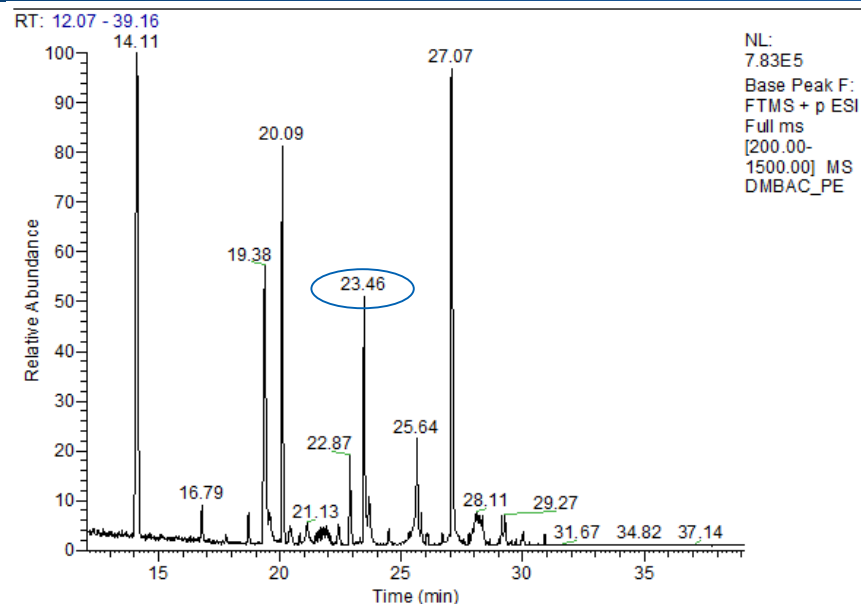
Analytical method adaptation for alkyd paints analysis



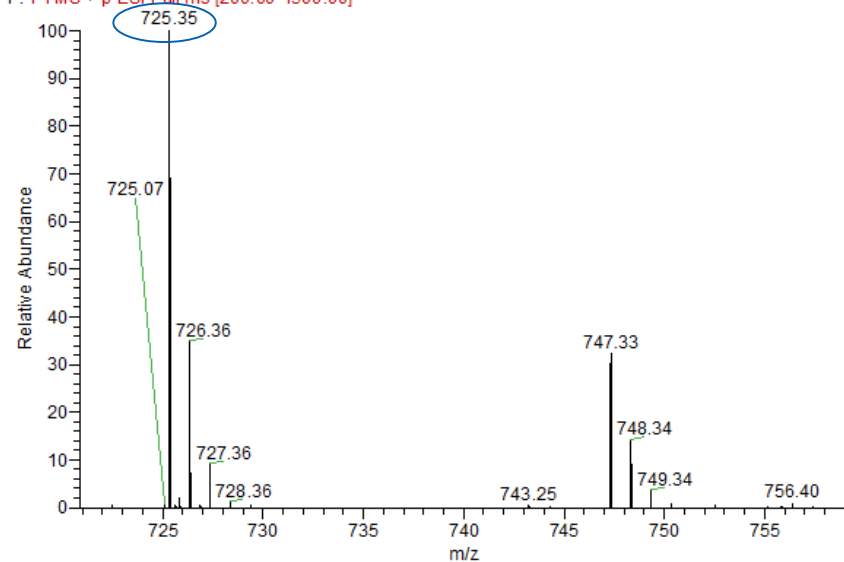
Industrial alkyd paint analysis 'Plusol' by MALDI FTICR MS_ transamidation



Industrial alkyd paint analysis 'Plusol' by LC-MS_ benzoylation

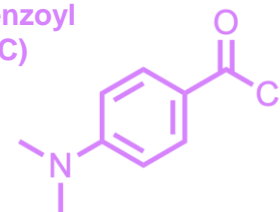


DMBAC_PE #1124 RT: 23.46 AV: 1 NL: 1.87E5
F: FTMS + p ESI Full ms [200.00-1500.00]

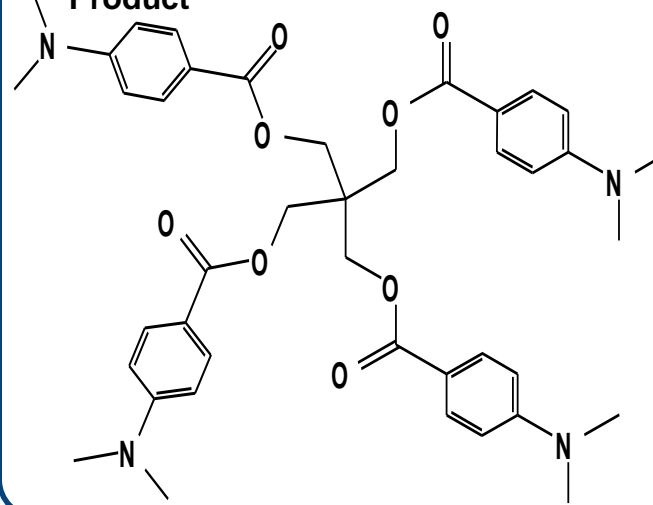


Benzoylation agent

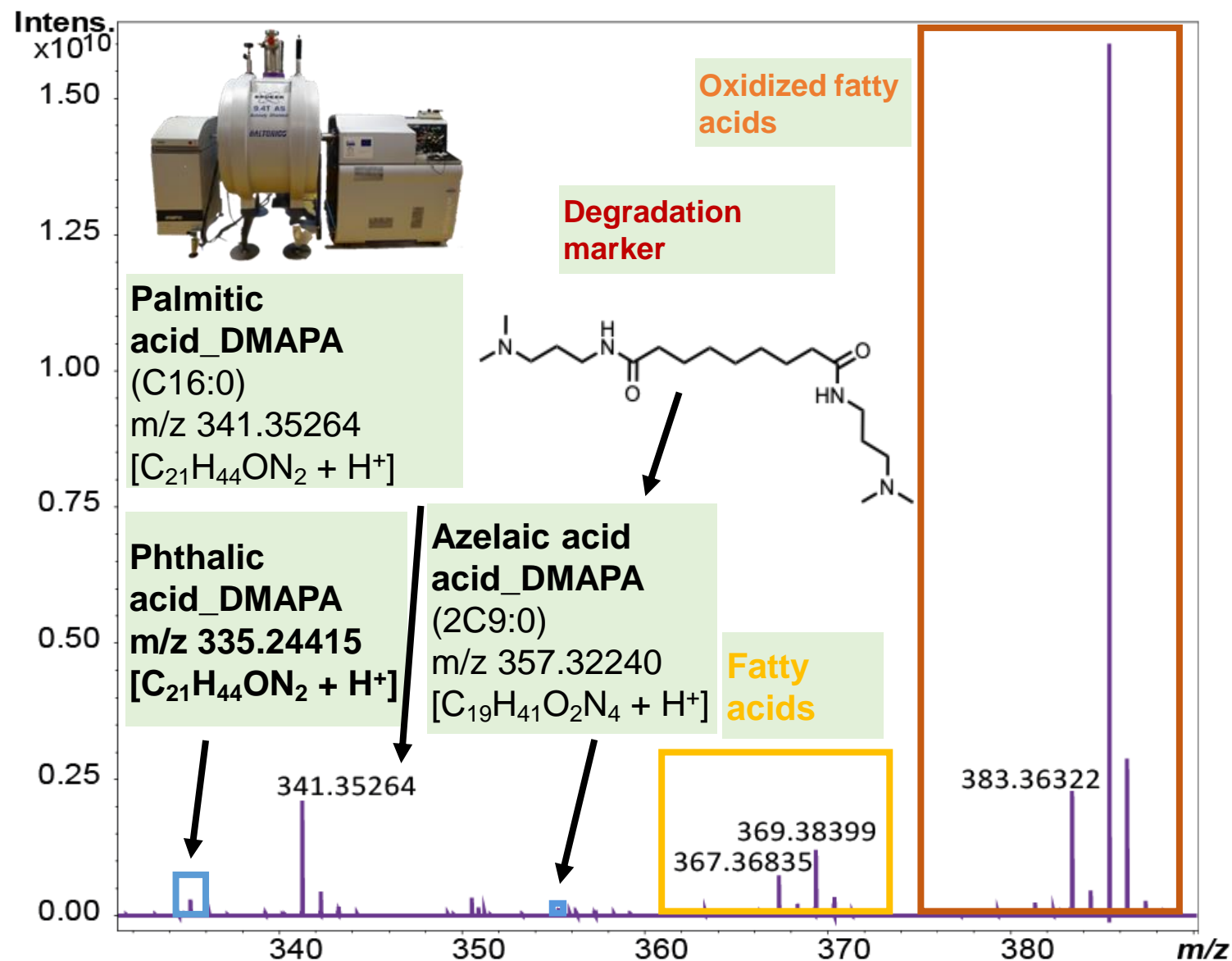
4-Dimethylaminobenzoyl
chloride (DMABC)



Product



FT-ICR MS analyses on museum-size alkyd paint samples



~10 μ g, museum scale sample (red)

Michael Dayon, "Fritz the artist", 2011
9" \times 12"

Alkyd (oil) on paper,
San Diego, CA

Protocol optimization for museum-size samples

Detection of the main components of alkyd paints

Detection of polymerization-related products

Conclusions and perspectives

Conclusions

- A new, original and sensitive method for the depolymerization of oil-based paints was developed.
- For alkyd paints: fatty acids and polyols were separated, derivatized with distinct methods and detected using high resolution MS.

Perspectives

- Scale down optimization will be pursued for the derivatization of museum-size, paintings samples.
- The role of pigments and driers and their effect on the paint film formation and composition in fatty acids will be studied with other industrial pigments.
- Depolymerization of other polyesters for example PET and PET microplastics will be studied.

Acknowledgements



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Thank you for your kind attention !

