

Oil paints in art: identifying and unravelling their reticulation by chemical depolymerization and ultrahigh resolution mass spectrometry

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Miniaturization for Synthesis, Analysis & Proteomics USR 3290

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“Les secrets de Modigliani”

Corpus:

- All works by Amedeo Modigliani from French public collections: 25 paintings, 2 attributed and 3 sculptures

State of the art analyses:

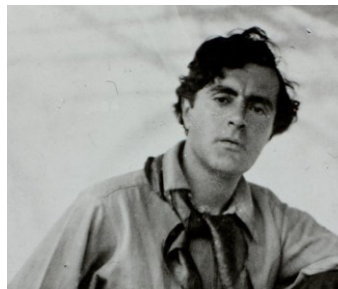
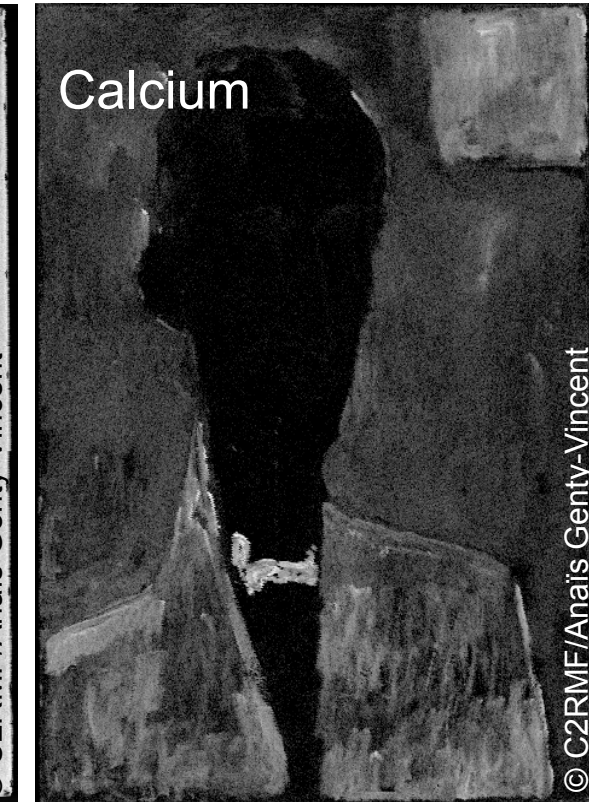
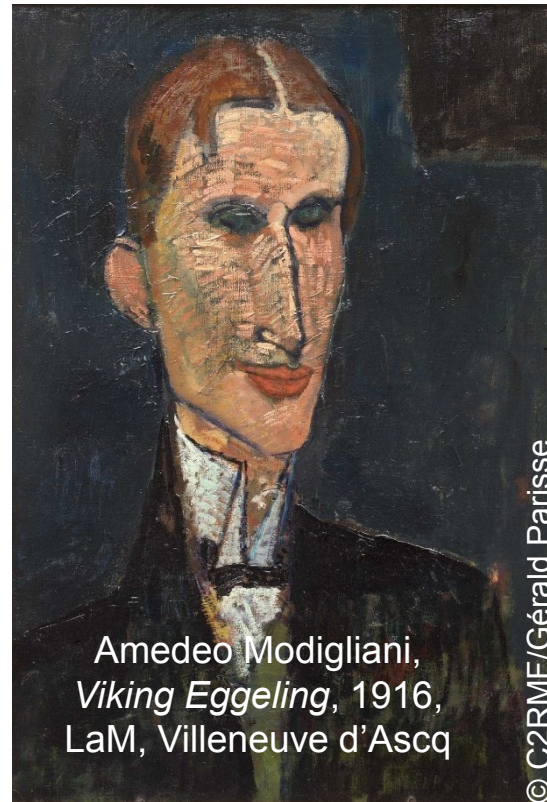
- X-ray Fluorescence: analysis of the inorganic component only

Question:

- Is the paint in Amedeo Modigliani's artworks Sennelier™ paint as according to historical sources?

Objective:

- Development of an analytical protocol for the analysis of the organic binder (siccative oil)



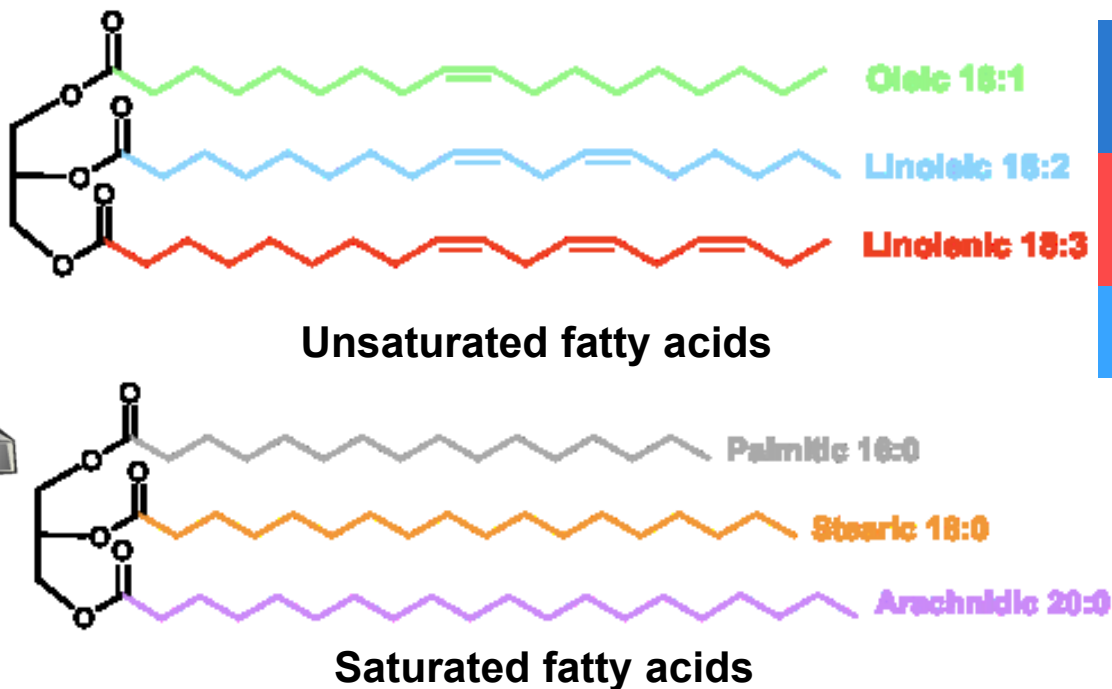
- Dr Michel Menu
- Dr Anaïs Genty
- Marie-Amélie Sénot

Oil paint

- **Siccative** vegetable oils
- Siccativity: capability of forming a **solid film** upon exposition to light and air
- Common siccative oils: **linseed**, **poppy** and **nut** oils



Triglycerides in siccative oils



Oil	Palmic	Stearic	Oleic	Linoleic	Linolenic
Linseed	7%	4%	18-22%	14-17%	52-55%
Poppy	12%	2.3%	20%	65%	0.7%

Oil siccative

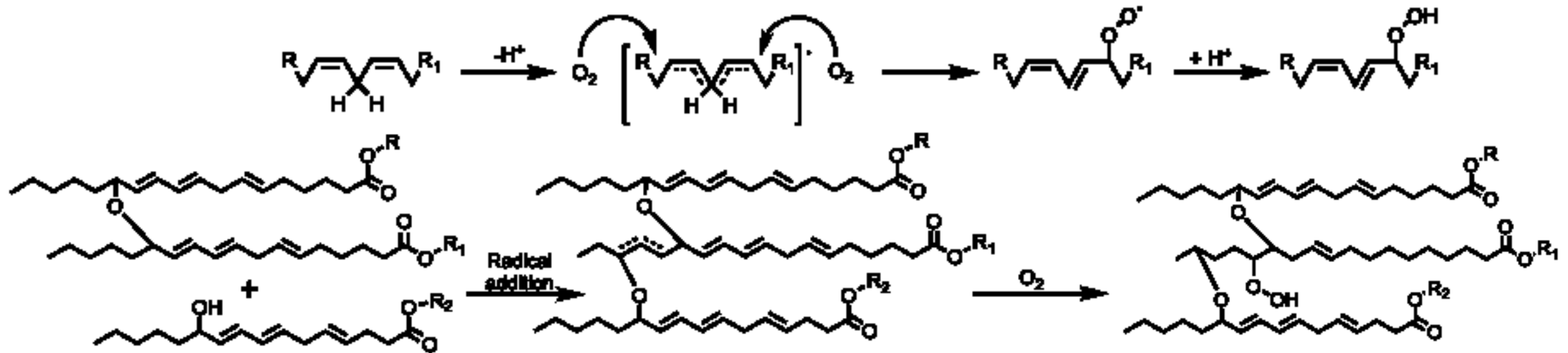
Initiation

Hydroperoxide
formation

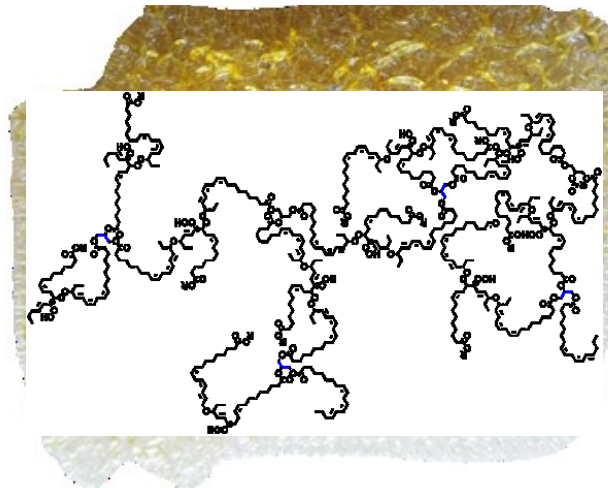
Hydroperoxide
decomposition

Polymerization and
cross-linking

Creation of a 3D
insoluble network



- Apolar environment required
- Catalyzed by added metal catalysts or pigment (Co, Cr, Fe, Mn, ... salts)

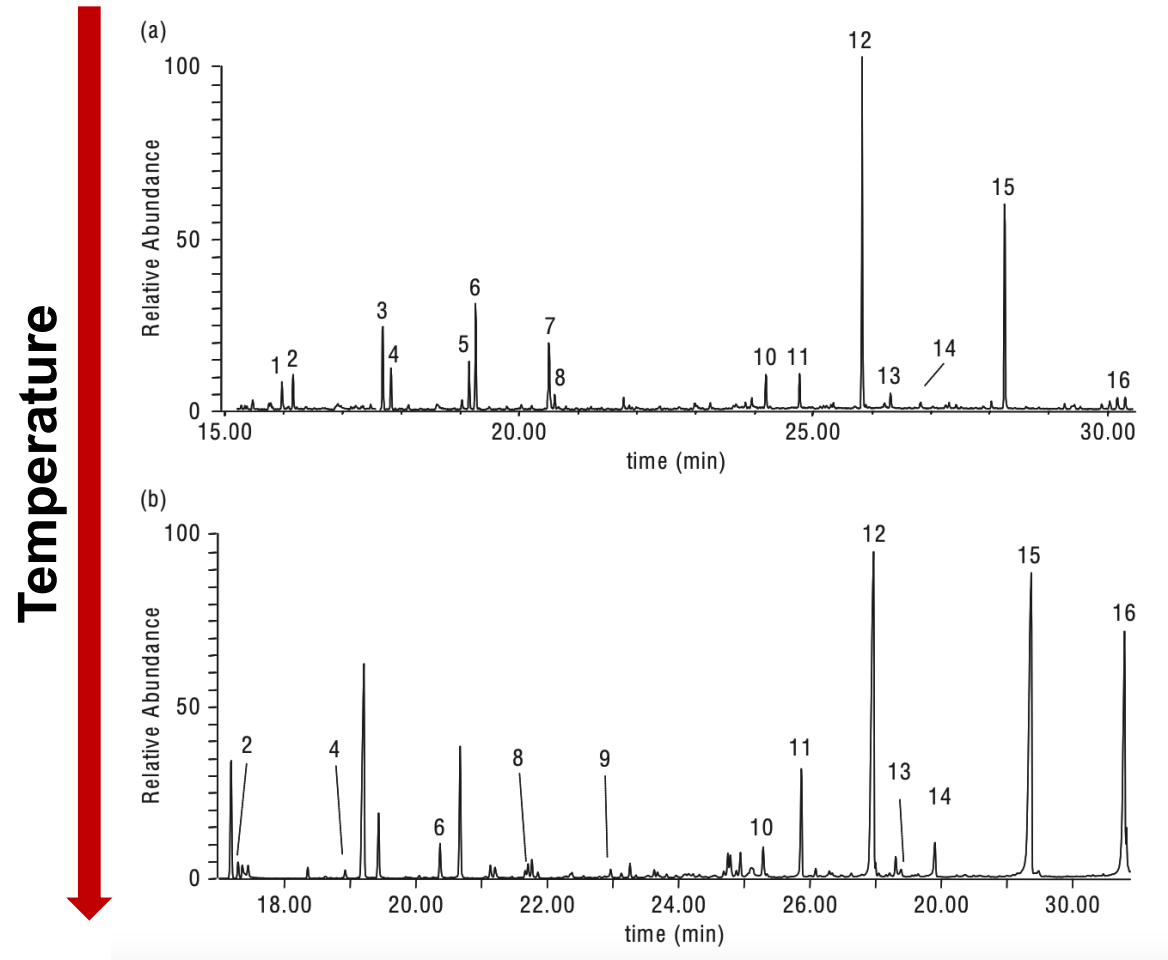


State of the art techniques for the analyses of lipid binders

Py-GCMS

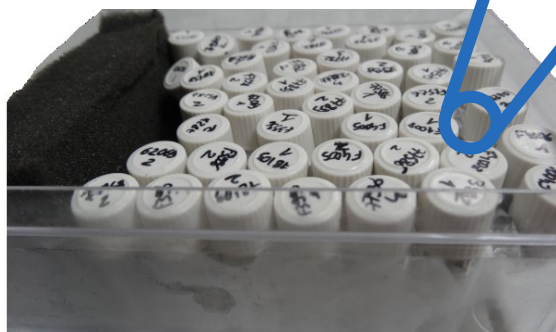
- Harsh depolymerization conditions
- No information on cross-linking structures
- Unreliable quantification
- Higher sample quantities required

Temperature determines which products are obtained and their quantities!

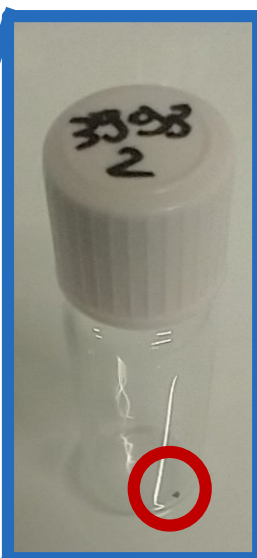


Bonaduce, I. (2009). Andreotti A. Py-GC/MS of organic paint binders. In: *Organic mass spectrometry in art and archaeology*. Colombini MP, Modugno F, editors. John Wiley, Chichester, 303-326.

Soft chemical depolymerization developed at MSAP

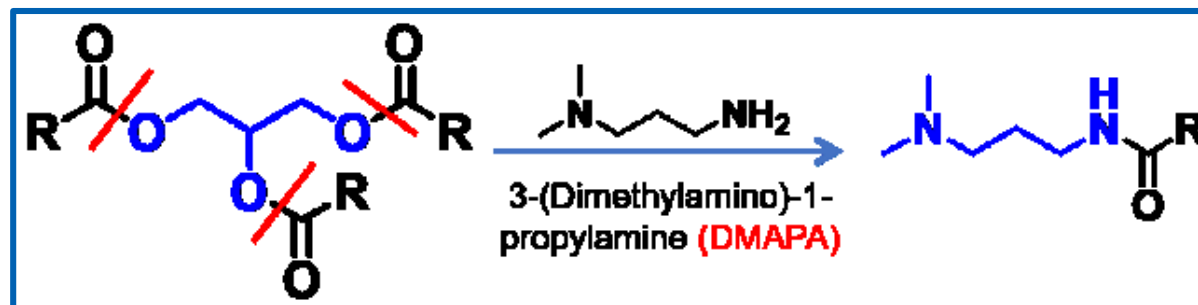


58 samples from Amedeo Modigliani's artworks



10 μ g sample

Chemical depolymerization developed at MSAP



Quenching with 10 μ L formic acid

Liquid-liquid extraction



2 mL water
2 mL petroleum ether



2 mL ethyl acetate



MS analyses

MS analyses



nanoESI source
8 Megapoints
Absorption mode

Strategies for the developement of oil paint analyses

Identification and
classification



Fresh siccatve oils



Polymerization and
reticulation



transamidation

Protocol
optimization



Painting on Sennelier™ canvas
dated between WWI and WWII



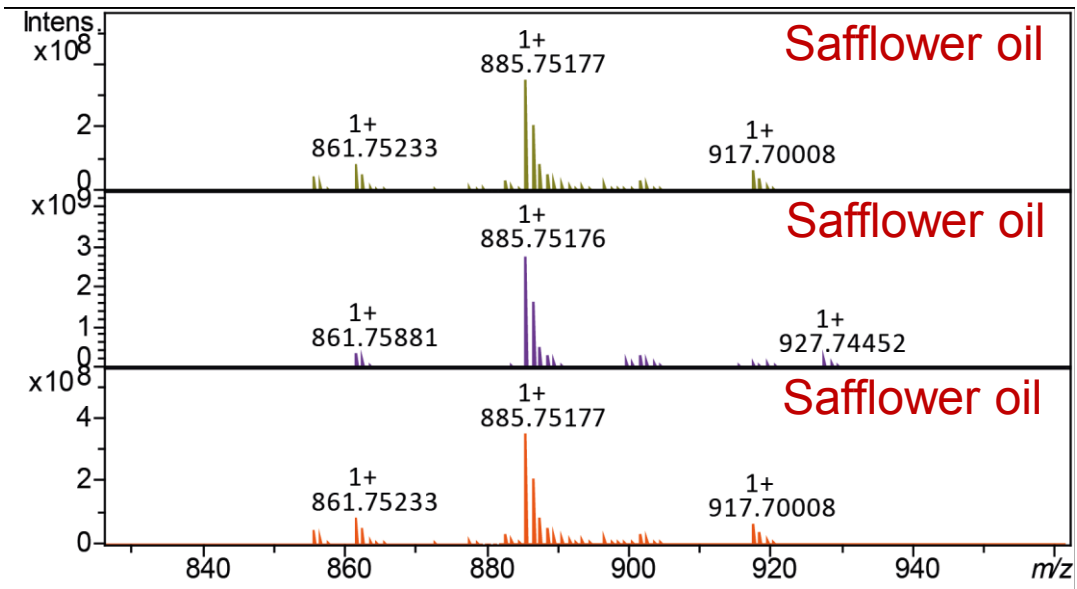
58 samples from Amedeo
Modigliani's artworks

Oil analysis on modern and historical Sennelier™ paint tubes (nanoESI FTICR MS)

Modern Sennelier™ paint tubes



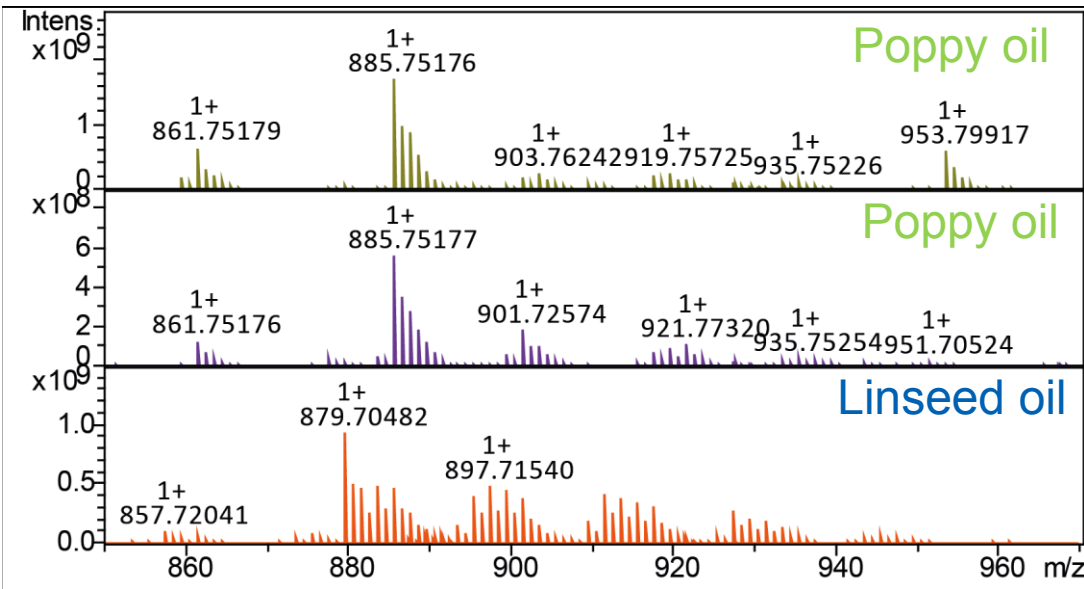
Historical Sennelier™ paint tubes



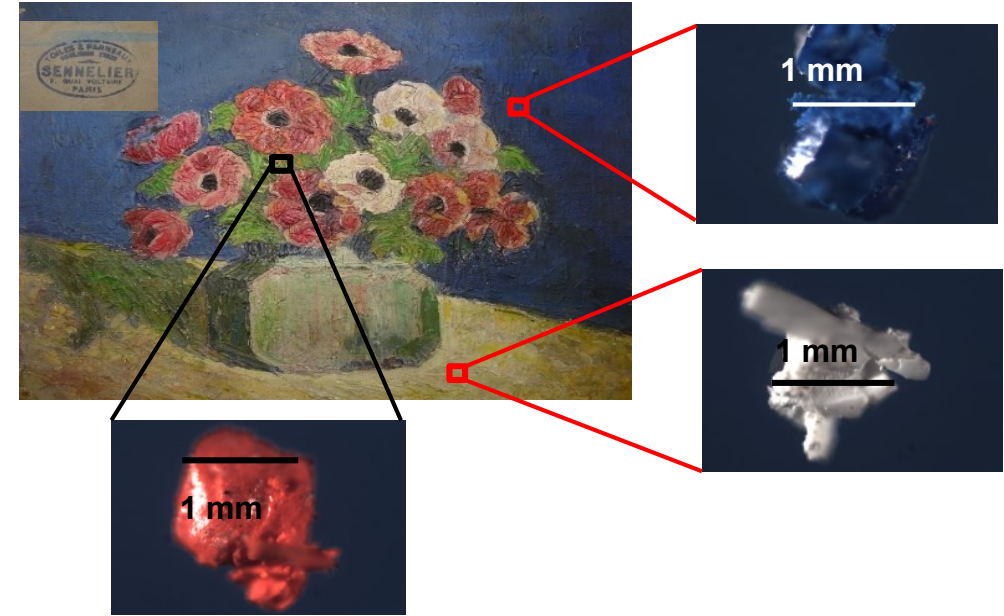
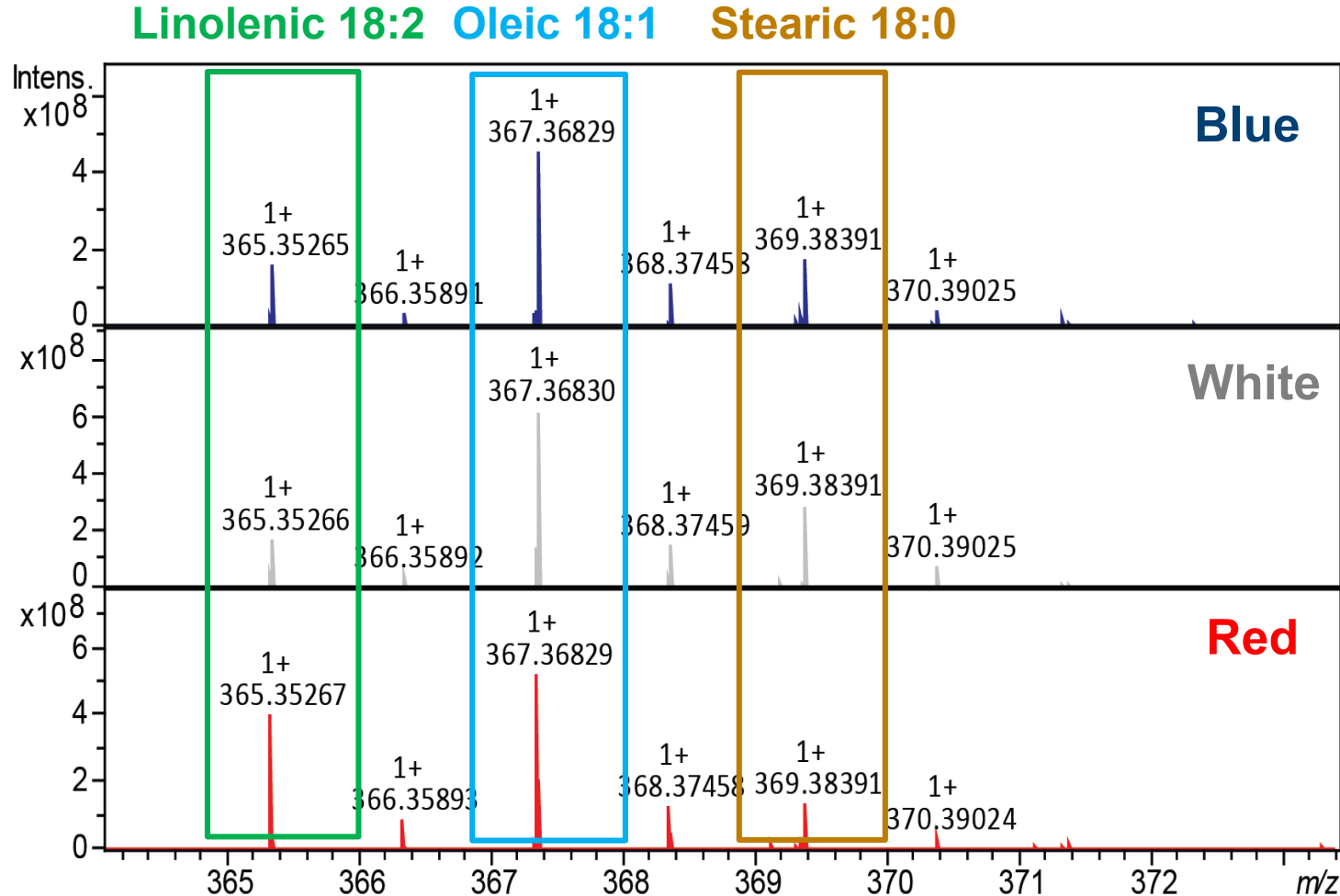
Yellow ochre

Burnt Sienna

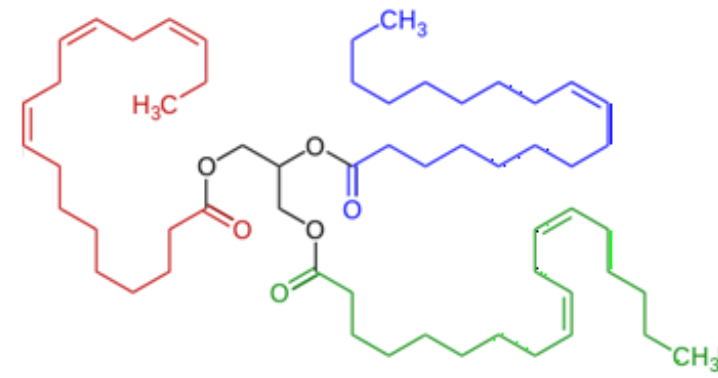
Ivory Black



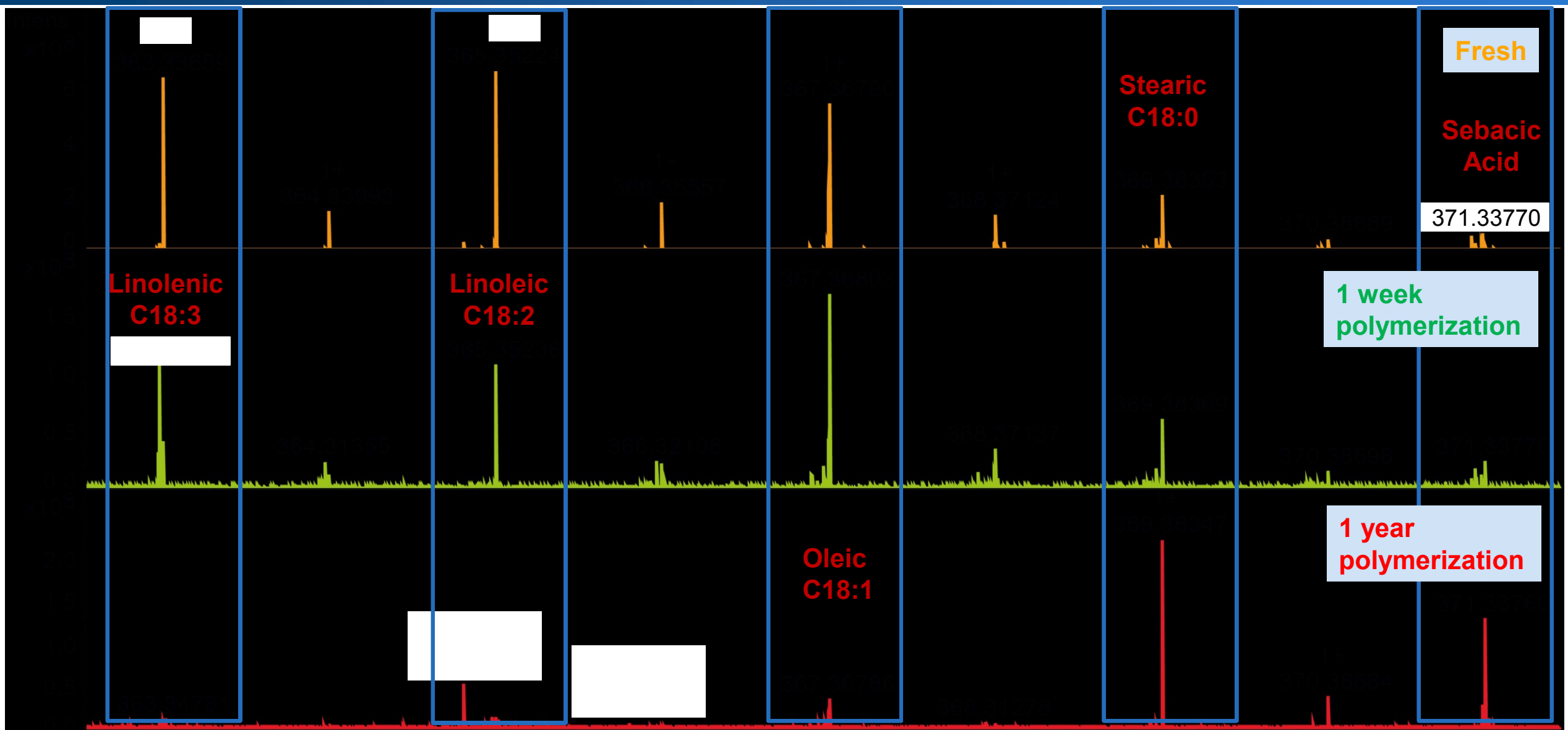
“Les secrets de Modigliani” – Polymerized organic binder analysis



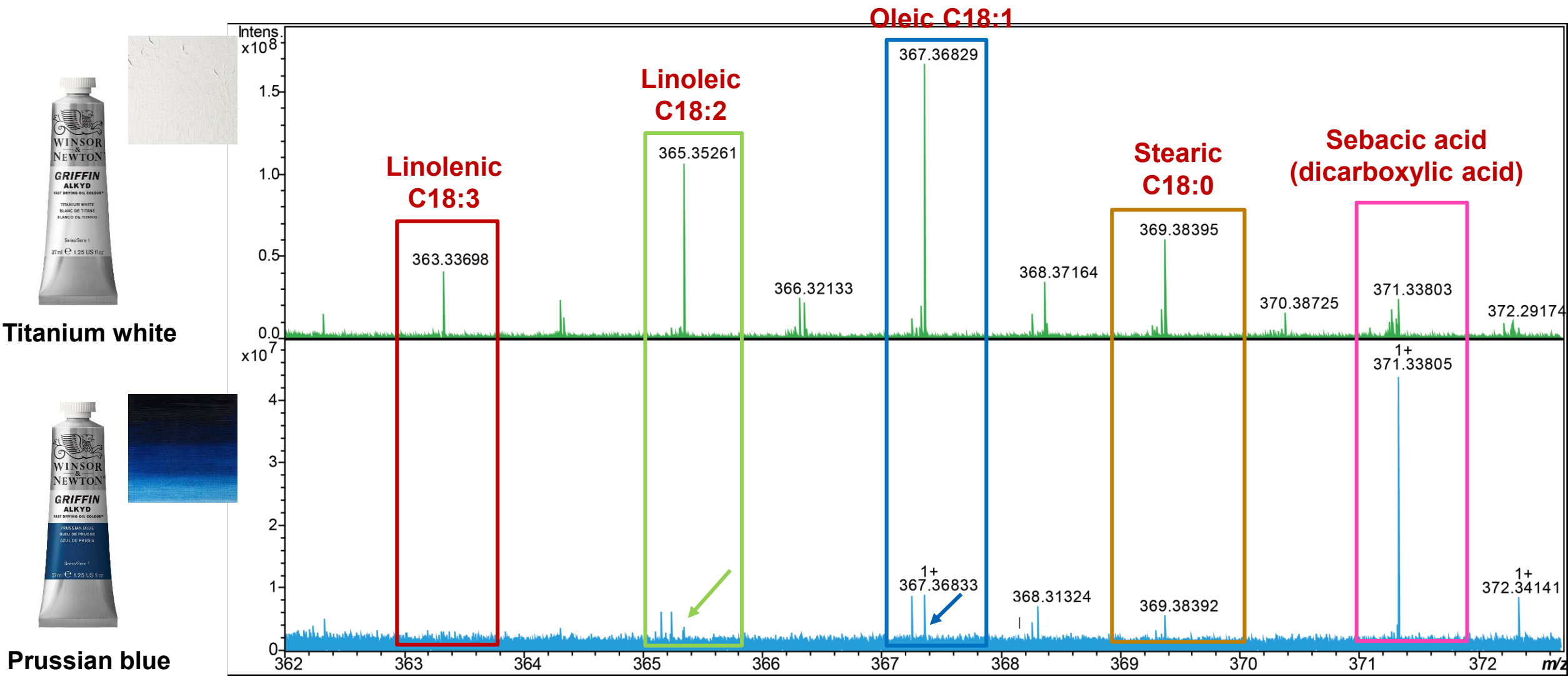
Triglyceride (TAG)
molecule formed by
one glycerol and
three fatty acids
(oleic, linoleic,
linolenic)



Winsor & Newton Griffin™ alkyd paint: depolymerized, derivatized fatty acids



Winsor & Newton Griffin™ alkyd paint: effect of pigments, 1 week polymerization



LTQ-Orbitrap analysis on historical canvas samples



Mass spectrometry analysis

nanoHPLC U 3000 (Thermo Scientific)

Column C18, 75 μ m, 15 cm

Pre-column C18, 300 μ m, 5 mm

Flow rate of 300 nL / min at 40 °C

Gradient duration = 65 min Injection 1 μ L

Mass spectrometry

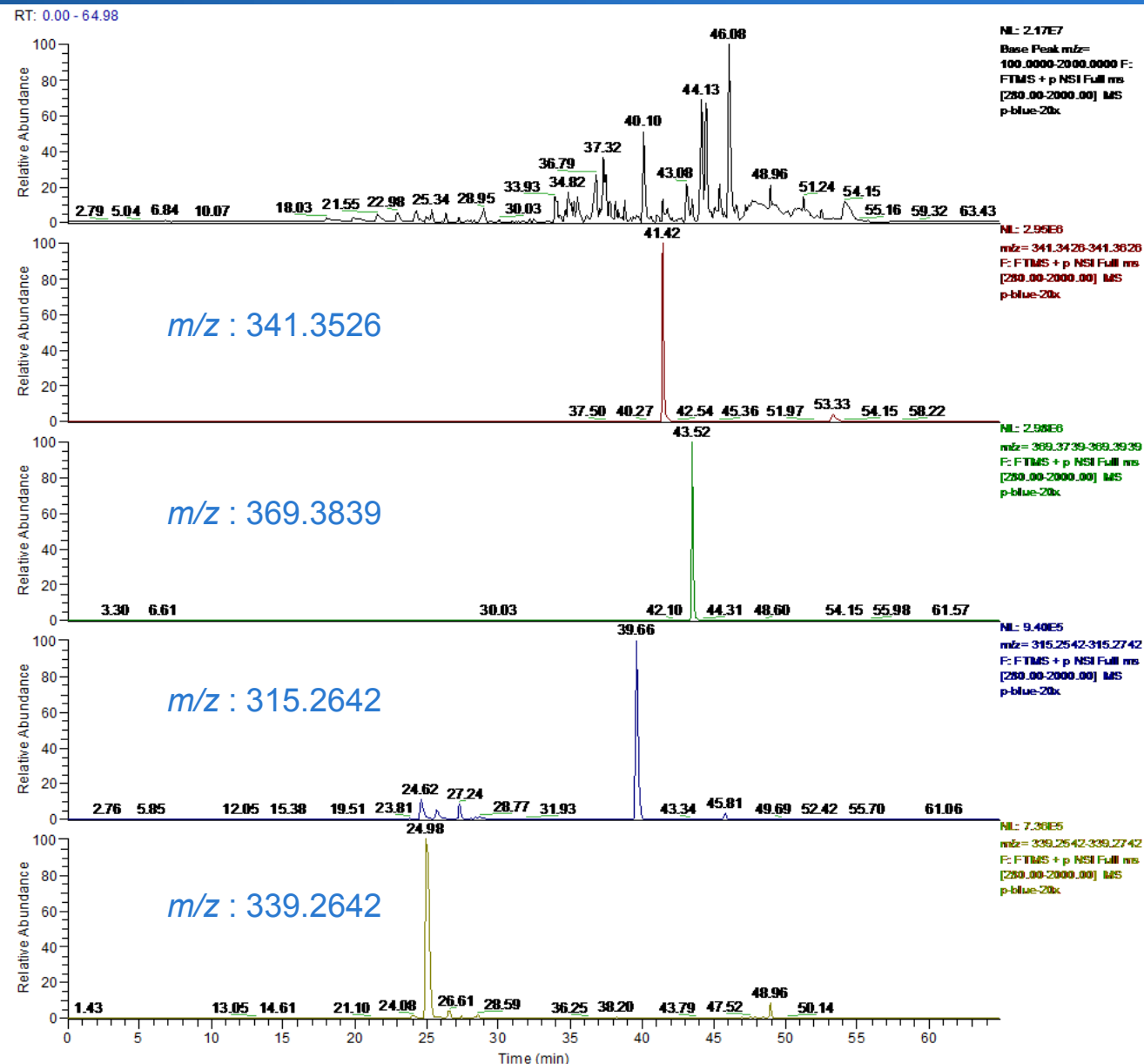
Nano électrospray

LTQ Orbitrap XL (Thermo Scientific)

Analyzer : FTMS

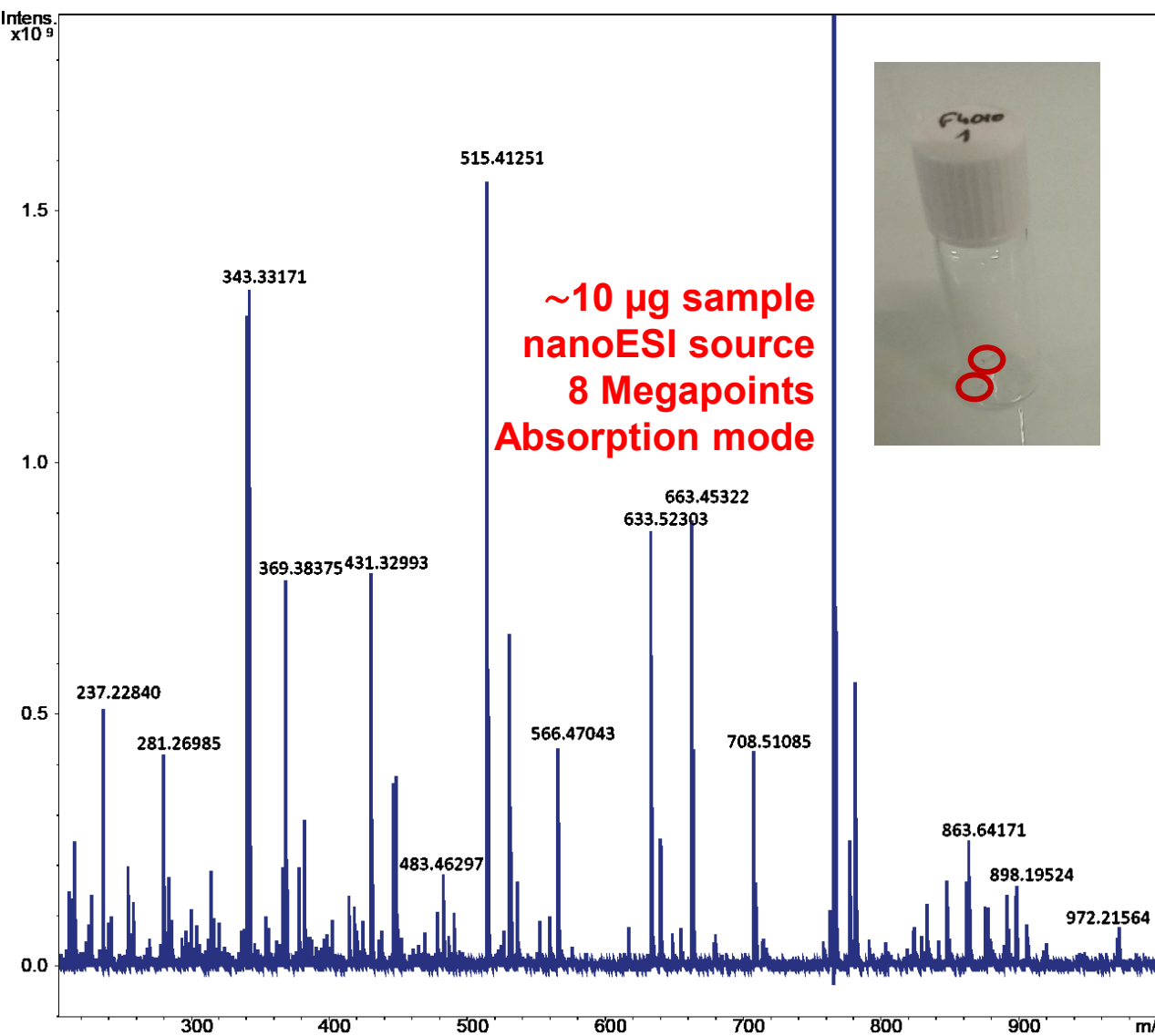
MS résolution 60 000

Scan ranges : 280-2000

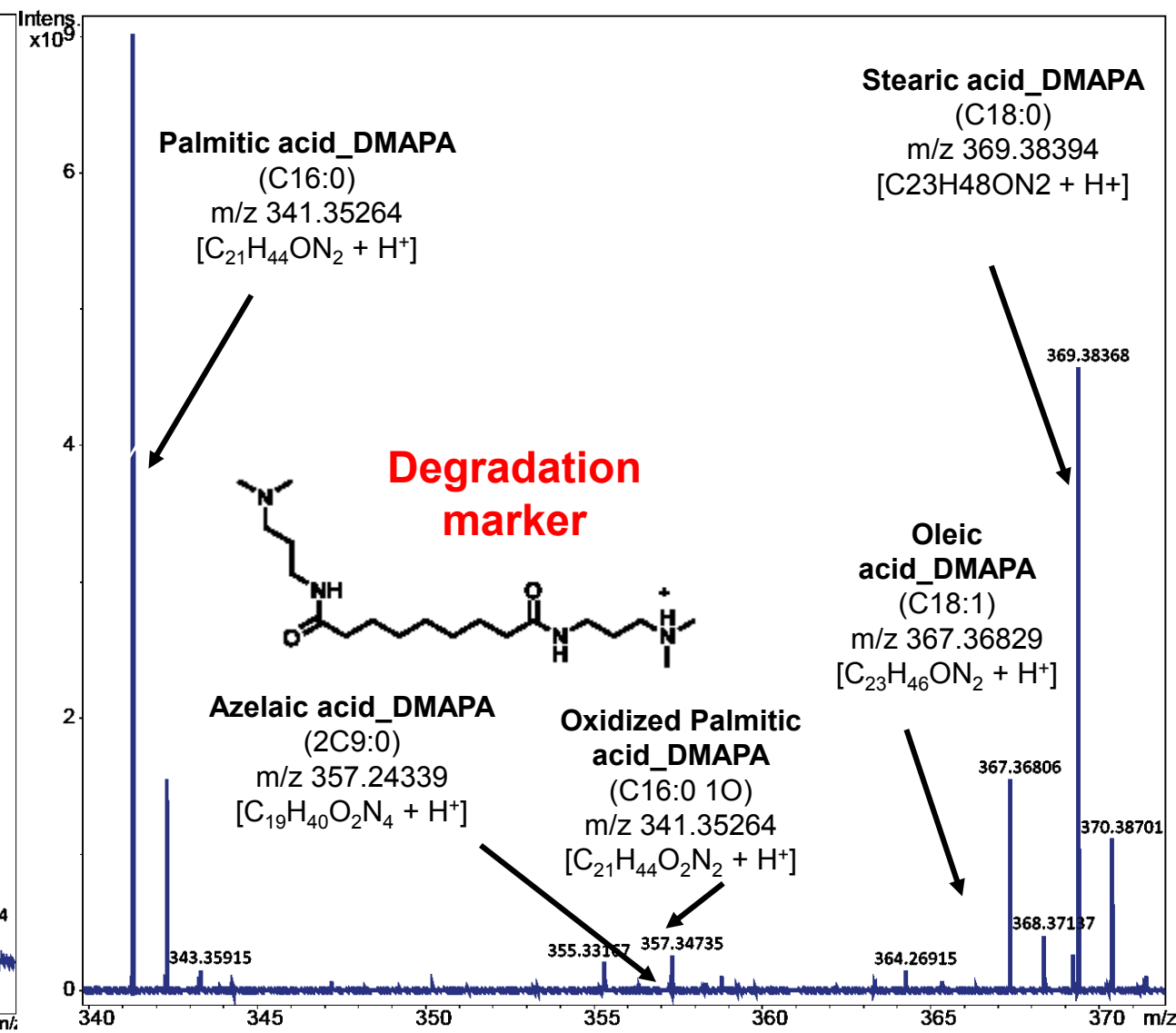


Modigliani F4010 (2)

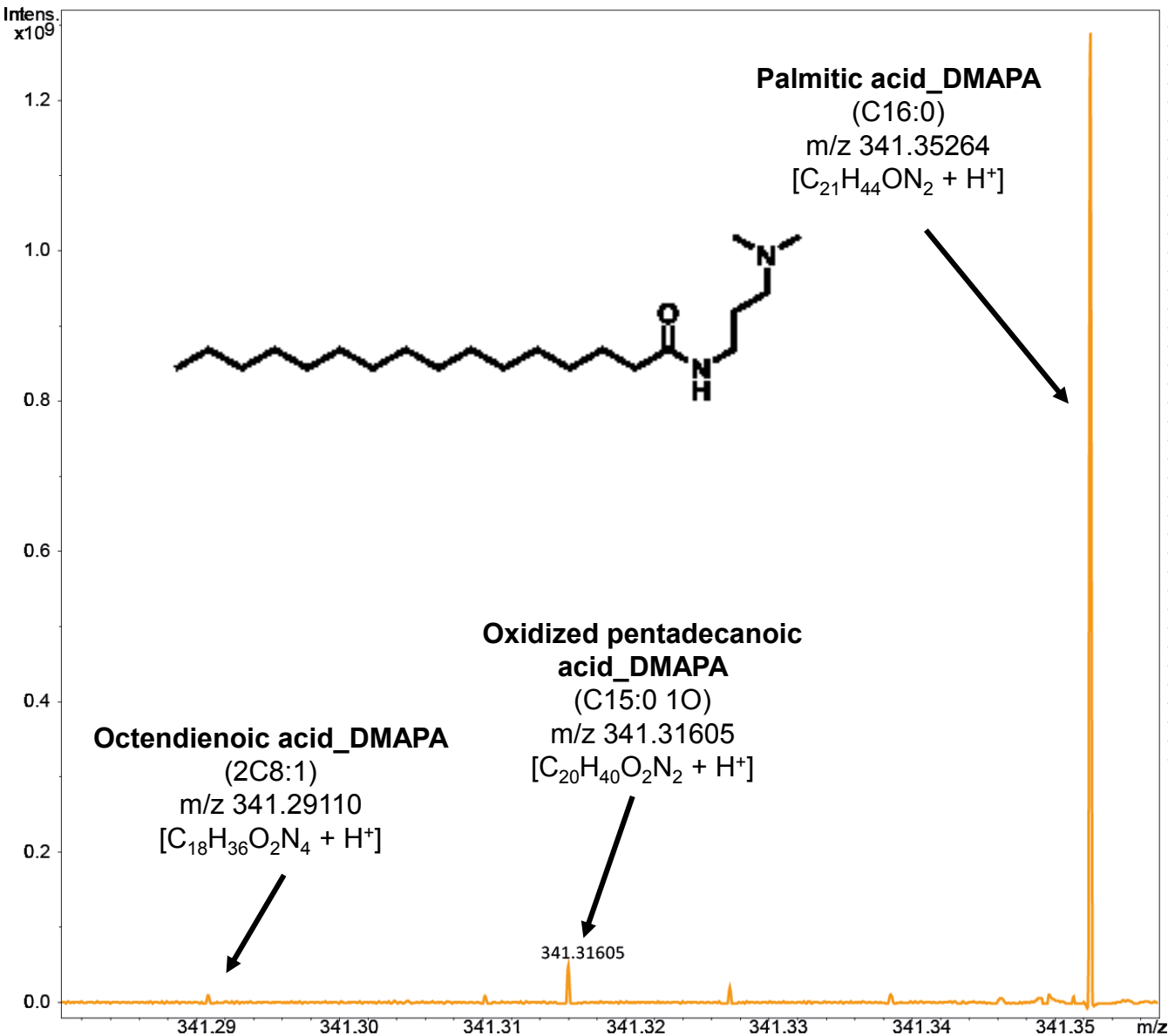
Full spectrum



Fatty acids area close up



Modigliani F4010 (2)



1	CN_5_u2_d1	183,149189	183,1492	0,00316632	3293324		0,25528346	
2	CN_5_u1_d1	185,164839	185,1648	0,10488001	20821508		1,61398839	
3	CN_5_s_d1	187,180489	187,1805	0,0565225	24385598		1,8902604	
4	CN_6_u2_d1	197,164839	197,1649	0,05366022	5360630		0,4155316	
5	CN_5_u2_o1_d1	199,144104	199,1441	0,12262523	5208972		0,40377577	
6	CN_6_u1_d1	199,180489	199,1805	0,04729425	50660708		3,92698716	
7	CN_5_u1_o1_d1	201,159754	201,1597	0,07168477	8291460		0,64271619	
8	CN_6_s_d1	201,196139	201,1961	0,09652318	252658672		19,5849486	
9	CN_5_s_o1_d1	203,175404	203,1754	0,02175505	145668864		11,2915864	
10	CN_6_u2_o1_d1	213,159754	213,1598	0,02617712	3047901		0,23625939	
11	CN_7_u1_d1	213,196139	213,1962	0,04962524	13824952		1,07164726	
12	CN_6_u1_o1_d1	215,175404	215,1754	0,0205418	17759258		1,37661673	
13	CN_7_s_d1	215,211789	215,2118	0,04327176	134156488		10,3991994	
14	CN_6_s_o1_d1	217,116	### CN_8_u1_d2	341,291102	341,2911	0,00709099	9295240	0,72052464
15	CN_5_s_o2_d1	219,117	### CN_15_u1_o1_d1	341,316254	341,3162	0,10084516	48373216	3,74967121
16	CN_8_u2_d1	225,118	### CN_16_s_d1	341,352639	341,3526	0,0861868	1,29E+09	100
17	CN_8_u1_d1	227,118						
18	CN_7_u1_o1_d1	229,91054	229,1911	0,01928562	7835772		0,60739333	
19	CN_8_s_d1	229,227439	229,2275	0,04615464	140700064		10,9064276	
20	CN_6_u1_o2_d1	231,170319	231,1703	0,04074957	5903505		0,4576128	
21	CN_7_s_o1_d1	231,206704	231,2067	0,01911749	11850531		0,91859915	
22	CN_6_s_o2_d1	233,185969	233,186	0,08328156	14118310		1,09438704	
23	CN_9_u3_d1	237,196139	237,1962	0,08676325	12963331		1,00485833	
24	CN_9_u2_d1	239,211789	239,2118	0,08603217	14872433		1,15284321	
25	CN_9_u1_d1	241,227439	241,2274	0,08050532	28365904		2,19879558	
26	CN_8_u1_o1_d1	243,206704	243,2067	0,0592915	9806233		0,76013448	
27	CN_9_s_d1	243,243089	243,2431	0,04349521	97747200		7,57691739	
28	CN_445	### CN_32_u1_o2_d1	595,577219	595,5774	0,3032015	3475102		0,26937407
29	CN_446	### CN_23_u2_o3_d2	597,494947	597,4948	0,1797841	3547695		0,27500115
30	CN_447	### CN_30_u2_o4_d1	597,520099	597,52	0,09944451	4295855		0,3329951
31	CN_448	### CN_31_u6_o4_d1	603,473149	603,4726	0,97671303	4486591		0,34778008
32	CN_449	### CN_26_u4_o1_d2	603,520767	603,521	0,35223296	4254299		0,32977387
33	CN_450	### CN_25_u1_o2_d2	611,546982	611,5471	0,24132227	4607625		0,35716209
34	CN_451	### CN_26_u3_o2_d2	621,531332	621,5315	0,25353494	4171607		0,32336396
35	CN_452	### CN_34_u2_o2_d1	621,592869	621,5929	0,08137144	9092748		0,70482838
36	453	### CN_26_u2_o2_d2	623,546982	623,5471	0,18856624	4617715		0,35794422
37	454	### CN_32_u2_o4_d1	625,551399	625,5514	0,04888473	3704033		0,28711975
38	455	### CN_26_u1_o2_d2	625,562632	625,5627	0,17197304	6784496		0,5259032
39	456	### CN_25_u4_o4_d2	637,489862	637,4902	0,5766051	4522301		0,35054816
40	457	### CN_27_u2_o2_d2	637,562632	637,5628	0,18442095	11351006		0,87987825
41	458	### CN_25_u3_o4_d2	639,505512	639,5057	0,21513483	7046968		0,54624884
42	459	### CN_36_u2_o2_d1	649,624169	649,6242	0,02989435	5741940		0,44508902
43	460	### CN_34_u2_o4_d1	653,582699	653,5827	0,01441301	3516498		0,2725829
44	461	### CN_27_u1_o3_d2	655,573197	655,5734	0,2632504	6147173		0,47650083
45	462	### CN_29_u2_o3_d2	681,588847	681,589	0,16517276	4136560		0,32064728

$\Delta m/z = 0.02\text{ Da}$

More than 400 identified peaks

$\Delta m/z = 0.02 Da$

More than 400 identified peaks

Acknowledgements

"Les secrets de Modigliani" at LAM (Lille Métropole Musée d'art moderne, d'art contemporain et d'art brut) 19.02.21 > 20.02.22



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MSAP, séminaire d'Unité, juillet 2020

MSAP

§ Dr. Christian Rolando § Ziad Mahmoud
§ Dr. Fabrice Bray § Nathan Roy

And all the MSAP staff!

