Chapter 3

Synthetic organic pigments

3.1 Introduction

This chapter presents the study on selected synthetic organic pigments being the goal to expand the knowledge on these relatively new products and on their ageing behaviour. These researches were mainly carried out at the Getty Conservation Institute of Los Angeles, CA. First, a Py-GC/MS library was created, collecting the main pyrolysis products of 76 pigments. 45 of them have been never previously reported as being analysed by this technique. Several of the pyrolysis products were characteristic of a single pigment or of a class of pigments, thus they could be used as molecular markers and their detection may help in identifying the pigments in paint samples.

Secondly, 19 pigments were chosen for a photochemical ageing study and subjected to an artificial ageing. Several techniques were used to compare the aged and un-aged pigments: colorimetric measures, FTIR and Raman spectroscopies, Py-GC/MS, GC/MS.

Colorimetric measures assessed the change in colour after the ageing treatment, whereas FTIR and Raman techniques highlighted absorptions differences. Py-GC/MS showed different pyrolysis products in the aged pigments, with respect to the un-aged ones.

Lastly, some commercial paints, containing some of the fugitive pigments subjected to the artificial ageing, were studied and artificially aged, then analysed with the same techniques mentioned above.

3.2 Materials and methods

<u>Reference materials</u>. All the synthetic organic pigments and the commercial paint formulations analysed were collected from the Getty Conservation Institute's reference materials collection. The pigments, with the indication of the manufacturers, are listed in Appendix A, Table A1. In this Chapter only the results of the pigments never previously reported as being analysed by Py-GC/MS are presented. For the other pigments, the results were consistent with the ones of other authors [1] [2]. The commercial paints are listed in Table 3.1.

	Table 3.1 Commercial paints selected for the ageing study.							
Pigment		Medium	Manufacturer	Commercial name				
PR83	а	oil	Gamblin	Alizarin Crimson				
	b	watercolour	Liquitex	Alizarin Crimson				
PR170	а	oil	Daniel Smith	Permanent Red				
	b	watercolour	Daniel Smith	Permanent Red				
	С	acrylic	Liquitex	Naphthol Crimson				
PY3	а	water-mixable oil	Winsor&Newton	Lemon Yellow				
	b	alkyd	Winsor&Newton	Winsor Lemon				
	С	oil	Daniel Smith	Hansa Yellow Light				
	d	watercolour	Daniel Smith	Hansa Yellow Light				
	е	acrylic	Liquitex	Yellow Light Ansa				

<u>Samples preparation</u>. The amount of pigment's powder analysed with Py-GC/MS to build up the pigments' pyrolysis library was about 1 mg. We analysed the neat pigment, without any binder, avoiding any derivatisation step.

For the ageing study, each pigment, pure and in form of powder, was mixed with isopropyl alcohol (Sigma Aldrich) and the mixture spread onto a glass slide and allowed to dry for 2 weeks. Even if the majority of the pigments was not soluble in alcohol, the suspension was easily spreadable onto the glass slides, but it was not possible to achieve a completely homogeneous surface. The glass slides were placed on a specimen holder in the weather-ometer instrument. Half of each slide was covered by the holder, in order to have a colour reference of the un-aged pigment (Fig. 3.1).



Fig. 3.1 Pigments spread onto glass slides and placed in the weather-ometer instrument for the photo-chemical ageing study.

After the ageing protocol, about 1 mg of the pigment suspension was scraped off from the glass slide and analysed with Py-GC/MS and GC/MS. For the GC/MS analysis two different reagents were tested: TMTFTH (m-trifluoromethylphenyl trimethylammonium hydroxide) - also called Meth prep II[®] - (Fisher), and ethanol (Sigma Aldrich). 100 μ L of solvent were added to each sample and then the samples were heated at 60 °C for 1 hour before the analysis. For the FTIR-ATR and Raman analyses, the pigments were examined directly on the glass slides, without scraping off the material.

The commercial paints were spread both onto glass slides and onto black and white charts specifically designed for coating tests (form 2A opacity charts, Leneta, USA) with the use of a film applicator (thickness of 8 mils, corresponding to ~ 200 μ m) and allowed to dry for 3 weeks (Fig. 3.2).

About 1 mg of material was scraped off from the glass slides and analysed with Py-GC/MS. The paints on the charts, instead, were subjected directly to colorimetric measures.



Fig. 3.2 Commercial paints on b/w charts for colorimetric measures (top) and application of the same paints on glass slides with a film applicator (bottom).

<u>Apparatus.</u> Pyrolysis – Gas Chromatography/Mass Spectrometry was carried out on a 7890A gas chromatograph, coupled with a 5975C triple axis mass spectrometer (Agilent Technologies, USA), coupled with a EGA/PY 3030D multi-shot pyrolyzer (Frontier Laboratories, Japan). The mass spectrometer was operated in the electron impact (EI)

positive mode (70 eV). The pyrolysis was carried out at 550 °C for 12 s. The chromatographic separation was carried out on a DB-5ms Ultra Inert column, 40 m × 250 μ m × 0.25 μ m (Agilent J&W, USA). The helium (purity 99.9995%) flow rate was 1 mL/min. The inlet temperature of the GC was 320 °C, the MS transfer line was kept at 320 °C and the ion source at 230 °C. The GC injection program was: pulsed split mode, with an injection pulse pressure of 30 psi until 45 sec. The split ratio was 20:1, with a split flow of 20 mL/min. The GC temperature program was: initial temperature 40 °C, 2 min isothermal, 20 °C/min up to 320 °C, 14 min isothermal. The mass range of the mass spectrometer was 20-420 Da. Fragments were recognized in the pyrogram using the NIST MS library (the match factor was \geq 90%) and the AMDIS (Automated Mass spectral Deconvolution & Identification System) software (US National Institute of Standards and Technology, NIST) for mass spectra comparison.

The GC/MS analyses were carried out on a 6890N gas chromatograph coupled with a 5973C triple axis mass spectrometer (Agilent Technologies, USA), equipped with a 7673 injector, with an injection volume of 1 μ L. The mass spectrometer was operated in the electron impact (EI) positive mode (70 eV). An initial temperature of 80 °C was used, 2 min isothermal, 20 °C/min up to 200 °C, then 30 °C/min up to 320 °C. The inlet operated in splitless mode. The chromatographic separation was carried out with a DB-5ms Ultra Inert column, 30 m × 250 μ m × 0.25 μ m (Agilent J&W, USA). The MS transfer line was held at 320 °C and the ion source at 230 °C. A 7673 Injector was used and the injection volume was 1 μ L for each sample. The mass range of the mass spectrometer was 45-550 Da.

Infrared analyses were performed using a 20x ATR objective, featuring a germanium crystal, attached to a Hyperion 3000 FT-IR microscope (Bruker, USA). The aged and un-aged areas were analysed individually using a reflected infrared beam with 100 x 100 μ m aperture. The spectra were collected as a sum of 128 scans, in a spectral range of 4000-600 cm⁻¹ and at 4 cm⁻¹ resolution.

Raman analyses were carried out using a 1000 Renishaw Raman microspectrometer RL 785 HPNIR excitation laser, over the spectral range 200-100 cm⁻¹, spectra calibrated to the 520.5 cm⁻¹ line of a silicon wafer. For all the pigments analysed, the laser power was 0.5%, the time scan 30 s and the number of scans 1.

The colour measures were performed with a Cary 50 UV-Vis Spectrophotometer (Agilent Technologies, USA) with a wavelength range of 190-1100 nm.

The artificial ageing was performed with a Ci4000 Xenon weather-ometer (Atlas, USA), equipped with a 6500 W water cooled Xenon lamp. To stop far-UV light the filters employed were CIRA and Soda lime. Specimen rack rotated at 1 revolution per minute around the Xenon lamp to provide uniform exposure. The ageing conditions were adopted from the ASTM D4303-10 protocol [1]: irradiance 0.35 W/m² at 340 nm and exposure of the specimens to 100% light to reach a total radiant exposure of 510 KJ/(m² nm); uninsulated black panel temperature at 63 °C; chamber air temperature at 43 °C; relative humidity 55%; total time 410.5 hours.

3.3 Detection and identification of synthetic pigments

The creation of a library of markers of synthetic organic pigments is fundamental for their identification in unknown samples. Raman libraries already exist, while an equivalent library obtained by chromatographic techniques is lacking, mainly because authors have analysed only some classes of synthetic pigments. Moreover, the pyrolysis profiles highly depend on the instrumental parameters. The purpose of this research was to expand the knowledge on selected compounds by Py-GC/MS analysis and to integrate the work of other authors [2] [3] by assessing the characteristic pyrolysis products that can be useful in the identification.

3.3.1 Py-GC/MS library of synthetic pigments

This work presents several classes of synthetic pigments not previously reported as being analysed by Py-GC/MS: some metal complexes, β -naphthol pigment lakes, BONA pigment lakes, disazopyrazolone, triarylcarbonium, dioxazine, anthraquinone, indanthrone, isoindoline and thioindigo pigments. A number of naphthol AS, benzimidazolone, phthalocyanine and perylene pigments are also reported for the first time, together with other miscellaneous pigments, including pigments with unpublished chemical structure.

The Py-GC/MS procedure adopted for the analysis of synthetic pigments was successful in discriminating between the listed classes of synthetic pigments and in several cases, by studying the fragmentation patterns of the pigments, we were able to address characteristic pyrolysis products that can be used as specific markers.

A very useful tool for the creation of the pyrolysis products' library and for the detection of the characteristic pyrolysis products in unknown samples was the AMDIS (Automated Mass

spectral Deconvolution & Identification System) software (NIST). AMDIS was originally developed for detecting explosive residues in criminal forensics labs. It indicates the presence of target compounds in a complex matrix. First, a library of targets has to be created, and then AMDIS automatically finds any set of target compounds in a GC/MS data file. AMDIS extracts co-eluting targets, targets on the slope of another compound, as well as targets present in the baseline noise [4]. Thus, it is a very suitable tool for the analysis of complex matrices such as paint samples and commercial paints, where the pigments are present in very low amounts.

To accomplish the separation of a complex data file into distinct components, AMDIS looks not just at the TIC but at the extracted ion chromatogram (EIC), for every integer m/z value in the data acquisition range. The EICs that rise, maximize and fall together are assigned to a common component. Because every ion is examined independently, even very small components in large backgrounds can be extracted, providing the minor component has any distinct ions, or even if the ions that are common have very different relative intensities.

In the present work I created the target library by inserting all the pyrolysis products (five to ten different products for each pigments) of the 76 synthetic pigments analysed.

3.3.2 Fragmentation patterns of synthetic pigments and characteristic pyrolysis products

The pyrolysis fragmentation pattern of each class of synthetic pigment analysed is herein described and discussed. The resulting pyrolysis products can be used for the identification of the pigments in unknown paint samples.

<u>B-naphthol pigment lakes.</u> We analysed four pigments belonging to this class: lithol red PR49 (the barium PR49:1 and the calcium PR49:2 salts), PR53:1 and PO46 (both barium salts). Their structures are given in Fig. 3.3, with pyrolysis breaking points indicated by a dashed line. The results obtained by interpreting the pyrograms achieved by the analysis of these four pigments are reported in Table 3.2. The pyrogram obtained for PR49:2 is presented in Fig. 3.4 as an example.

The main products of pyrolysis for these pigments in our experimental conditions are those originated from the 2-naphthol structure. Thus, the analysed pigments have many products in common. As a consequence, their unambiguous identification is quite difficult. As an example, 2,2'-dinaphthyl ether is the only characteristic product of PR49, but it is not one of

the most abundant. This result is not in agreement with the data reported on PR49 by Stenger et al. [5]. In their work they report two specific pyrolysis products for the unambiguous identification of PR49, 2-naphthol and an unknown compound with m/z 268, 239, 134. We found, however, that 2-naphthol is a common pyrolysis product not only of the entire β -naphthol pigment lakes class, but of several other classes of synthetic pigments (see the following paragraphs), and thus cannot be used as a marker for PR49. We identified the second compound indicated by Stenger as a characteristic product of PR49 as dinaphtho[2,1b:1',2'-d]furan or dinaphtho[2,1b:1,2-d]furan, which we found also in PR52, PR53 and PR63 pyrograms. Two isobaric peaks are present in the chromatogram at 17.7 min and 18 min, which most probably correspond to the two positional isomers.

C.I. name	Substitu	uents (Fig	. 3.3)	Products of pyrolysis (main m/z)			
	X1	X2	X3	а	Others		
PR49:1	2-amino	onaphthal	ene-1-		2-naphthol		
	sulfonic	acid as d	iazo		(144, 115)		
	compor	nent					
					1-naphthalenamine		
					(143, 115)		
					dinaphtho[2,1b:1',2'-d]furan*		
					(268, 239, 119) – small peak		
PR49:2	2-amino	onaphthal	ene-1-		2-naphthol		
	sulfonic	acid as d	iazo		(144, 115)		
	compor	nent					
					1-naphthalenamine		
					(143, 115)		
					dinaphtho[2,1b:1',2'-d]furan*		
					(268, 239, 119) - most		
					abundant peak		
PR53:1	SO ₃	Cl	CH ₃	a-X ₁ -X ₂ : m-toluidine	9-chloro-5,6-		
				(106, 107, 77)	dihydronaphtho[1,2-		
					(266, 231, 202)		
				a-X ₁ : 4-chloro-3-	(200, 231, 202)		
				methylaniline			
				(141, 106, 77)			
PO46	SO ₃	Cl	C_2H_5	a-X ₁ -X ₂ : m-toluidine	9-chloro-5,6-		
				(106, 107, 77)	dihydronaphtho[1,2-		
					(266-231-202)		
					(200, 231, 202)		

Table 3.2 Pyrolysis products of β -naphthol pigment lakes.

and the positional isomer dinaphtho[2,1b:1,2-d]furan.



Fig. 3.3 General structure of β -naphthol pigment lakes with breaking points highlighted.



Fig. 3.4 Py-GC/MS chromatogram of PR49:2 (calcium salt) with fragments produced by pyrolysis. In the box on the left: structure of PR49.

<u>BONA Pigment Lakes.</u> We analysed six pigments belonging to this class: PR48 (the barium PR48:1 and the calcium PR48:2 salts), PR52 (the calcium PR52:1 and the manganese PR52:2 salts), PR57:1 and PR63:1 (both calcium salts). The fragmentation pattern undergone by these compounds during pyrolysis is shown in Fig. 3.5, and the products originated from pyrolysis are summarized in Table 3.3.

Pyrolysis causes decarboxylation on the naphthol ring and loss of X_1 substituent. Moreover, the azo bond is broken leading to the formation of 2-naphthol and X_2 and X_3 substituted benzene and benzenamine. As expected, no significant differences were observed in the pyrograms of pigments that differ only for the metal ion.



Fig. 3.5 Structure of BONA pigment lakes (top), with fragments produced by pyrolysis (bottom).

C.I. name	Substit	uents (Fig	;. 3.5)	Products (main m/z)				
	X1	X2	X3	Α	b		2-naphthol	Others
PR48:1	SO ₃	CH ₃	Cl		benzenamine,	3-	(144, 115)	2-naphthol, 1-amino
and					chloro-4-methyl			(159, 130, 103)
PR48:2					(140, 141, 106)			
								8-chloro-5,6- dihydronaphtho[1,2-c]cinnoline (266, 231, 202)
PR52:1	SO ₃	Cl	CH ₃	benzene, 1-chloro-2-	m-toluidine,	4-	(144, 115)	9-chloro-5,6-
and				methyl	chloro-			dihydronaphtho[1,2-c]cinnoline
PR52:2				(91, 126, 63)	(141, 106, 77)			(266, 231, 202)
PR57:1	SO ₃	CH ₃	Н		p-toluidine (106, 107, 77)		(144, 115)	5,6-dihydronaphtho[1,2- c]cinnoline (232, 231, 202)
PR63:1	2-amino sulfonio	onaphtha c acid	lene-1- as diazo				(144, 115)	1-naphthalenamine (143, 115)
	compoi	nent						dinaphtho[2,1b:1',2'-d]furan* (268, 239, 119)
								benzo[h]naphtho[1,2- c]cinnoline** (280, 140, 126)

 Table 3.3 Pyrolysis products of BONA pigment lakes.

* and the positional isomer dinaphtho[2,1b:1,2-d]furan.

**or benzo[f]naphtho[2,1-c]cinnoline.

<u>Naphthol AS pigments.</u> We have integrated the work of Russell et al. [1] on naphthol AS pigments by analysing PR7 and PV44. The structure and the fragmentation pattern for this class of pigments is reported in Fig. 3.6.

The results for PR7 are consistent with those described by Russell: the pigment shows two characteristic pyrolysis products (addressed to as "a" and "b" in Russell's scheme) and also o-toluidine. The pyrolysis of PV44, instead, yields aniline and 2-naphthol, which are pyrolysis products common to several classes of pigments, but we also observe other characteristic products not attributable to the fragmentation pattern indicated by Russell (see Table 3.4), for example the product "a" with the loss of X₂ substituent, or with the loss of both X₁ and X₃ substituents.



Fig. 3.6 Structure of Naphthol AS pigments with breaking points highlighted.

C.I. name	Substitu	ents (Fig.	3.6)				Products (main m/	Products (main m/z)			
	X ₁	X ₂	X ₃	R ₁	R ₂	R ₃	а	b	С	d	Others
PR7*	CH ₃	Cl	Н	CH ₃	Cl	Н	benzene, 1-	benzenamine, 4-		4-chloro-o-	
							chloro, 3-methyl	chloro, 2-methyl		tolyl	
							(91, 126, 63)	(106, 141, 140)		isocyanate	
										(167, 138,	
								b – X ₂ : o-toluidine		132)	
								(106, 107, 77)			
PV44	OCH ₃	benza	OCH ₃	Н	Н	Н	benzamide, N-(4-		aniline		benzoic acid,
		mide					amino-5-		(93, 66)		methyl ester
							methoxy-2-				(105, 77, 136)
							methylphenyl)-				
							(256, 151, 105)				naphthol AS
											(170, 273, 115,
							a – X ₂ : benzamide				152)
							(121, 105, 77)				
							$a - X_1 - X_3$:				
							benzenamide, N-				
							phenyl				
							(105, 77, 197)				

Table 3.4	Pyrolysis products of Naphthol AS pigments.	
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*A Py-GC/MS analysis of PR7 has already been published by Sonoda [2].

<u>Benzimidazolone pigments.</u> The main pyrolysis product of PV32, in Fig. 3.7, is 2-naphthol. Other characteristic products not attributable to the fragmentation pattern indicated in the literature by Russell [3] for this class of pigments are also present in the pyrogram. Their main m/z are listed in Table 3.5.

C.I. name	Substituer	nts (Fig. 3.7)		Products (main m/z)			
	X1	X2	X3	а	b	Others	
PV32	OCH ₃	SO ₂ NHCH ₃	OCH ₃	/	b-X ₂ :	unknown product	
					benzenamine,	(231, 170, 107)	
					2,5-dimethoxy		
					(138, 153, 110)	unknown product	
						(246, 231, 168,	
						202)	

 Table 3.5 Pyrolysis products of PV32, benzimidazolone violet.



Fig. 3.7 PV32 structure with breaking points highlighted.

<u>Metal complex pigments.</u> We analysed two green pigments, PGr8 and PGr10. The Py-GC/MS results are listed in Table 3.6. Interestingly, the pyrogram of PGr8 highlights the presence of the methyl ester of 11-octadecenoic acid, which could have been used during the synthesis of the pigment as in the case of PR83, whose pyrolysis profile will be discussed later on. The structure of PGr10 is shown in Fig. 3.8 as an example, with the main fragments produced by pyrolysis.

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Table 3.6 Pyrolysis products of metal complex pigments.									
C.I. name	Products (main m/z	Products (main m/z)							
	а	b	Others						
PGr8			quinoline						
			(129, 102)						
			2-naphthol						
			(144, 115)						
			11-octadecenoic acid, methyl ester						
			(264, 296, 55)						
PGr10	benzene, chloro-	p-chloroaniline	benzene, 1,3-dichloro						
	(112, 77, 114)	(127, 129, 65)	(146, 148, 111)						
			benzenamine, 2,6-dichloro – N-phenyl						
			(237, 167, 239)						



Fig. 3.8 PGr10 with fragments produced by pyrolysis.

<u>Isoindoline pigments.</u> We analysed PBr38, a methine-type isoindoline pigment. The fragmentation pattern and the pyrolysis products are shown in Fig. 3.9 and listed in Table 3.7. The 2(1H)-quinolinone is a characteristic pyrolysis product of this pigment.



Fig. 3.9 PBr38 structure (left), with fragments produced by pyrolysis: indole (top right) and 2(1H)-quinolinone (bottom right).

C.I. name	Products (main m/z)
PBr38	2(1H)-quinolinone
	(145, 117, 90)
	indole
	(117, 90, 63)
	aniline
	(93, 66)
	1H-isoindole-1,3(2H)-dione
	(147, 76, 104)

Table 3.7 Pyrolysis products of PBr38.

<u>Disazopyrazolone pigments.</u> PR41 is also known as "Pyrazolone Red". The structure is shown in Fig. 3.10, and the products of pyrolysis are listed in Table 3.8.

	Table 3.8 Pyrolysis products of PR41.										
C.I. name	Substit	tuents (Fig.	3.10)		Products (main m/	/z)					
	Х	X ₁	X ₂	а	b	Others					
PR41	OCH ₃	Н	Н	norphenazone	1,1'biphenyl,	benzene,					
				(174, 77, 91)	3,3'dimethoxy	isocyanato					
					(214, 171, 128)	(119, 91, 64)					
						aniline					
						(93, 66)					



Fig. 3.10 PR41 structure with breaking points highlighted.

<u>Phthalocyanine pigments.</u> We extended the work of Russell [3] and Sonoda [2] on phthalocyanine pigments by analysing PB15:0, PB15:1, PB15:2, PB15:3, PB15:4, PB15:6, PB16, PB17, PB76 and PGr13. The main products are shown in Fig. 3.11 and listed in Table 3.9. We confirmed that 1,2-dicyanobenzene is a characteristic pyrolysis products of the phthalocyanine pigments class. We found also that the pyrograms of the PB15 series contain the characteristic o-cyanobenzoic acid that can be considered as a marker and thus can help in the identification of this pigment.

PB15 has been already analysed by Sonoda [2]; he observed only a small peak corresponding to 1,2-dicyanobenzene, while we were able to identify other specific products, listed in Table 3.9.

As for the other phthalocyanine pigments analysed, PGr13 shows o-cyanobenzoic acid as the PB15 series, but it can be distinguished on the basis of its different colour. The pyrogram of PB76 is characterized by products originated from the chlorinated substituents.

Product (main m/z)	PB15:0*	PB15:1	PB15:2	PB15:3	PB15:4	PB15:6	PB17	PB76	PGr13
methenamine							Y		
(42, 140)							×		
tetrahydrofuran						v			
(42, 72)						^			
benzene, 1,3 dimethyl	×	v							
(91, 106)	^	^							
benzonitrile	v			×					v
(103, 76)	^			^					^
2-oxepanone					v				
(55, 42, 84)					^				
benzene, 1,2,4 trichloro	v								
(180, 182, 144)	^								
benzene, 1-(1-methylethenyl)-3-(1-methylethyl)				×					
(145, 160, 117)				^					
1,2-dicyanobenzene	v	v	v	×	v	v	v	×	v
(128, 101)	^	^	^	^	^	^	^	^	^
o-cyanobenzoic acid	v	v	v	v	v	×			v
(147, 76, 104)	^	~	~	^	~	^			^
benzene, 1,1'-(1methylethylidene)bis				×					
(181, 196, 103)				^					
oleic acid					v				
(55, 264)					^				
unknown product						×			
(160, 188, 189)						^			
naphthalene, 1,5-dichloro								×	
(196, 198, 200)								^	
naphthalene, 2,3,6-trichloro								x	
(230, 232, 234)								^	
tetrachloroisophthalonitrile								v	
(266, 264, 268)								^	

ubliched by Seneda [2] Table 2.0 Durobusis aducts of the phthale nino nia ante A Dy CC/MS alucic of DD1E by c already be



Fig. 3.11 Structure of phthalocyanine pigments (left) with fragments of the PB15 series produced by pyrolysis: 1,2-dicyanobenzene (top right) and o-cyanobenzoic acid (bottom right).

<u>Quinacridone pigments.</u> We analysed PV19 and PV42. The formulation of PV42, a mixed phase pigment, has never been published yet. The results are shown in Table 3.10.

Pyrolysis product (main m/z)	PV19	PV42
unknown product	v	
(233, 262)	^	
Biphenyl		v
(154, 153)		Λ
tetrachloroethylene		v
(166, 164, 129, 131)		^
diphenyl ether		v
(170, 141, 77)		^
unknown product		v
(195, 167, 139)		^
2-methyl-acridone		v
(209, 208, 180)		^
unknown product		v
(450, 452, 1225)		^

 Table 3.10 Pyrolysis products of quinacridone pigments.

The pyrogram of PV19 shows an unknown product, while that of PV42 contains several products, one being the characteristic 2-methyl acridone (Fig. 3.12).

Although the pyrolysis profile does not allow us to hypothesise the formulation of PV42 pigment, it might be used for its identification in unknown paint samples.



Fig. 3.12 2-methyl acridone, a characteristic pyrolysis product of PV42.

<u>Anthraquinone and indanthrone pigments.</u> PR83, alizarin crimson, is an hydroxyanthraquinone pigment and the synthetic counterpart of the natural madder lake. The identification of PR83 by Py-GC/MS is possible on the basis of its characteristic fragments (phenanthrene, anthrone; 9,10-anthracenedione; 9,10-anthracenedione, 2-hydroxy). The only other pigment with a similar fragmentation pattern is the indanthrone blue PB60, which can be easily distinguished from PR83 thanks to its blue colour. The products of pyrolysis are listed in Table 3.11 for both pigments.

Pyrolysis product (main m/z)	PR83	PB60
aniline		v
(93, 66)		^
benzene, nitro		v
(77, 123, 51)		^
2-naphthol	~	
(144, 115)	^	
phenanthrene	~	
(178)	^	
anthrone	~	v
(194, 165)	^	^
9,10-anthracenedione	~	v
(208, 180, 152)	^	^
linoleic acid	~	
(280)	^	
9,10-anthracenedione, 1-amino		v
(223, 139, 167)		^
9,10-anthracenedione, 2-hydroxy	~	
(224, 139, 196)	^	
dinaphtho[2,1b:1',2'-d]furan*	~	
(268, 239, 119)	^	

 Table 3.11 Pyrolysis products of anthraquinone and indantrone pigments.

*or dinaphtho[2,1b:1,2-d]furan.

The Py-GC/MS analysis of PR83 has an interesting feature: the pyrogram (Fig. 3.13) shows linoleic acid as the most intense peak, with the presence of other fatty acids. According to Pratt [6], the preparation of PR83 involves the precipitation of a complex made up of the dyestuff, a metal and a fatty acid source such as Turkey Red oil on an alumina hydrate base. The fatty acids peaks in the pyrogram of PR83 could be ascribed to the Turkey Red oil used for the synthesis of the pigment. Turkey red oil, also called sulphonated castor oil, is prepared by adding sulphuric acid to vegetable oils, most notably castor oil. To verify our hypothesis, we analysed PR83 with GC/MS using TMTFTH (m-trifluoromethylphenyl trimethylammonium hydroxide), commercially called Meth prep II®, as derivatising agent. A marker of castor oil, methyl ricinoleate, was detected in the GC/MS chromatogram of PR83. This result is important and must be taken into account in case of identification of the binding media in the presence of PR83. If a modified vegetable oil is added to the pigment itself, the quantitative or qualitative analysis of the fatty acids cannot be reliably applied to determine the type of oil media used.



Fig. 3.13 Py-GC/MS chromatogram of PR83 with fragments produced by pyrolysis. In the box on the left: structure of PR83. Three of the main peaks of the pyrogram are attributable to linoleic acid, derived from the oil used during the synthesis of the pigment.

<u>Triarylcarbonium pigments.</u> We analysed PV1, PV3, PV27, PV39, PB1 and PB62. The structure of this class, with breaking point highlighted, is shown in Fig. 3.14 and the results are reported in Table 3.12. In some cases the molecule did not fragment in the pyrolyzer in

the adopted conditions: the pyrograms of PV3, PV27, PV39 and PB62 all show the intact molecule peak, as shown in Fig. 3.15 for PV27 (peak #17). Unfortunately, for PV3 and PV27 the intact molecule of both pigments co-elutes with the de-methylated molecule. This makes the identification of the pigments of this class difficult but not impossible: the different relative abundances of ions in the mass spectra can be exploited to differentiate the pigments, as demonstrated in Fig. 3.16.



Fig. 3.14 Structure of triarylcarbonium pigments with breaking points highlighted.

Table 3.12 Pyrolysis products of triarylcarbonium pigments.						
C.I. name	C.I. name Substituents (Fig. 3.14)			Products (main m/z)		
	A ⁻ *	Ar	R	а	b	Others
PV1	/	/	/			1H-indole, 1,2,3-trimethyl
						(158, 159, 144)
						1H-indole, 2,3-dihydro 1,3,3-
						trimethyl-2-methylene
						(158, 173, 143)
PV3	PTM		CH ₃	benzenamine, N,N-	b1+b2: benzenamine, N,N,4-	aniline
	PM			dimethyl	trimethyl	(93, 66)
		СH ₃		(120, 121, 77)	(134, 135)	
						aniline, N-methyl
					b1: benzenamine, 4,4'-	(106, 107, 77)
		H(CH ₃)			methylenebis N,N-dimethyl	
					(254, 253, 210)	PV3 intact molecule
						(253, 373, 359, 237)
PV27	CF		CH ₃	benzenamine, N,N-	b1+b2: benzenamine, N,N,4-	aniline
				dimethyl	trimethyl	(93, 66)
		СH ₃		(120, 121, 77)	(134, 135)	
						aniline, N-methyl
						(106, 107, 77)
		H(CH ₃)				
						PV27 intact molecule
						(239, 359, 345, 253, 373)
PV39	PM		CH ₃	benzenamine, N,N-	b1+b2: benzenamine, N,N,4-	aniline
	PTM			dimethyl	trimethyl	(93, 66)
		N(CH ₃)2		(120, 121, 77)	(134, 135)	

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					b1: benzenamine, 4.4'-	aniline. N-methyl
					methylenebis N,N-dimethyl	(106, 107, 77)
					(254, 253, 210)	
						PV39 intact molecule
						(253, 373, 359, 252)
PB1	PTM		C_2H_5	N,N-diethyl aniline	b1+b2: benzenamine, N,N-	aniline
	PM			(134, 106, 149)	diethyl-4-methyl	(93, 66)
					(148, 120, 163)	
						benzenamine, N-ethyl
						(121, 106, 77)
						1-naphthalenamine, N-ethyl
						(171, 156, 129)
		NHC ₆ H ₅				
						1-naphthalenamine, N-phenyl
						(219, 218, 217)
PB62	CF		C_2H_5	N,N-diethyl aniline		aniline
				(134, 106, 149)		(93, 66)
						benzenamine, N-ethyl
						(121, 106, 77)
						1-naphthalenamine, N-ethyl
						(171, 156, 129)
		NHC ₂ H ₅				
						PB62 intact molecule
						(253, 359, 239, 373, 345)

*PM = phosphomolibdic acid; PTM = phosphotungstomolibdic acid; CF = copper ferrocyanide.



Fig. 3.15 Py-GC/MS chromatogram of PV27. 1. aniline; 2. aniline, N-methyl-; 3. benzenamine, N,N-dimethyl-; 4. benzenamine, N,4-dimethyl-; 5. benzenamine, N,N,4-trimethyl-; 6. 4-aminobenzonitrile;
7. 4-aminobenzonitrile, N-methyl; 8. 4-aminobenzonitrile, N,N-dimethyl; 9. 4,4'-methylenedianiline; 10. 4,4'-methylenedianiline, N-methyl; 11. 4,4'-methylenedianiline, N,N-dimethyl; 12. 4,4'-methylenedianiline, N,N-dimethyl; 14. 4,4'-methylenedianiline, N,N,N-trimethyl; 14. 4,4'-methylenedianiline, N,N,N,N-tetramethyl; 15. unknown products typical of PV27
(RT 16.99 min: m/z 251, 145, 221, 236; RT 17.05 min: m/z 265, 221, 159, 144; RT 17.11 min: m/z 279, 235, 158, 143); 16. 4,4'-((4-aminophenyl)methylene)bis(N,N-dimethylaniline); 17. intact molecules (4,4',4''-methanetriyltris(N,N-dimethylaniline) co-eluting with 4,4'-((4-(methylamino)phenyl)methylene)bis(N,N-dimethylaniline).





<u>Dioxazine pigments.</u> The fragmentation pattern of dioxazine pigments is shown in Fig. 3.17, and the results are listed in Table 3.13. Pyrolysis produces chlorinated benzenes deriving from the central structure of the molecule and other smaller aromatic products.



Fig. 3.17 Structure of dioxazine pigments with breaking points highlighted.

C.I. name	Product (main m/z)					
	а	b	с	Others		
PV23	benzene, 1,4-	indole	carbazole	unknown product		
	dichloro	(117, 90, 109)	(167, 166, 139)	(183, 154, 196, 211)		
	(146, 148, 111)					
				unknown product		
				(182, 195, 210, 181)		
				unknown product		
				(222, 235, 250, 153)		
PV37	benzene, 1,4-			benzonitrile		
	dichloro			(103, 76)		
	(146, 148, 111)					
				benzoic acid, ethyl		
				ester		
				(105, 77, 122, 150)		
				benzamide		
				(105, 77, 121, 51)		
				benzoxazole, 2-phenyl		
				(195, 63, 167)		
				unknown product		
				(211, 104)		

Table 3.13 P	yrolysis	products	of dioxazine	pigments
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<u>Perylene pigments.</u> We analysed PV29, which gives a single characteristic product, naphthalimide, a fragment originated from the central polycyclic structure of the pigment (Fig. 3.18). This fragmentation was not reported by Russell [4], who studied substituted perylenes only.



Fig. 3.18 Structure of PV29 (left), with naphthalimide, a fragment produced by pyrolysis (right).

<u>Thioindigo Pigments.</u> We analysed PV36. The structure of the pigment is shown in Fig. 3.19, with its pyrolysis product.



Fig. 3.19 Structure of PV36 (left) with 2,4,5-trichlorophenol, a fragment produced by pyrolysis (right).

<u>Miscellaneous pigments.</u> Of the pigments not grouped in the other two main classes, we analysed PR90. PR90, eosin lake, was used extensively to produce lake pigments (such as geranium lake), where the dyestuff was commonly precipitated with an aluminium hydroxide base or a lead (II, III) oxide [8]. The structure of the pigment is shown in Fig. 3.20 and the products of the pyrolysis are listed in Table 3.14.



Fig. 3.20 Structure of PR90 with breaking points highlighted.

C.I. name	Product (main m/z)				
	а	b	Others		
PR90	phenol	benzoic acid	1,4-dioxane		
	(94, 66)	(105, 122, 77, 51)	(88, 28, 58)		
			biphenyl		
			(154, 153)		
			unknown product		
			(135, 107)		
			unknown product		
			(135, 107, 149, 121)		
			9H-fluoren-9-one		
			(180, 152)		

Table 3.14 Pyrolysis products of PR90.

<u>Pigments with unpublished chemical structure.</u> We analysed three pigments with an unpublished chemical structure, PV51, PV52 and PV53. The results of the Py-GC/MS analysis are listed in Table 3.15. On the basis of the identified fragments, which mainly are rearrangement products, it is not possible to unambiguously hypothesise the structure of PV51, PV52 or PV53. Nonetheless, they share common fragments with the β -naphthol pigment lakes, BONA pigment lakes and naphthol AS. Thus, their structures most probably contain a 2-naphthol linked by a diazo bond to other aromatic substituents.

Table 3.15 Pyrolysis products of pigments with unpublished chemical structure.					
Pyrolysis product (main m/z)	PV51	PV52	PV53		
heptane, 3-methylene			x		
(55, 70, 41)			~		
2-propyl-1-pentanol	v		v		
(57, 41, 70, 83)	^		^		
naphthalene			v		
(128)			^		
benzenamine, 4-methoxy	v	v			
(108, 123, 80)	^	^			
phenol, 4-amino	v	v			
(109, 80)	^	^			
2-naphthol	v	v	v		
(144, 115)	^	^	^		
2-naphthalenamine			v		
(143, 115)			^		
benz[c,d]indol-2(1H)one	v				
(169, 114, 141)	^				
bis(2ethylhexyl) maleate	v	v			
(57, 117, 71, 100)	^	^			
2-butenedioic acid (E)-bis(2ethylhexyl) ester	v	v	v		
(70, 112, 57, 211)	^	^	^		
dinaphtho[2,1b:1',2'-d]furan*			x		
(268, 239, 119)			~		

*or dinaphtho[2,1b:1,2-d]furan.

3.3.3 Detection of synthetic pigments in commercial paints

We selected several commercial paint formulations containing three pigments: PR83, PR170 and PY3 (see Table 3.1 in Materials and methods). Both the commercial paints and the pure pigments in form of a powder were analysed with Py-GC/MS and compared. Our goal was to verify if the pyrolysis markers of the pigments would have still been detected in the commercial formulations, where the pigment is present in very low amounts (usually 1-5% but sometimes lower) and is mixed with the binder and with all the other compounds generally used by paint manufacturers, such as extenders. This study may help understanding if it is possible to identify a synthetic pigment through Py-GC/MS even when it's in complex matrix, such as a paint sample.

PR83 alizarin crimson. The pyrograms of both the oil paint and the watercolour paint (Fig. 3.21 and Fig. 3.22 respectively) show three characteristic PR83 pyrolysis products: phenanthrene, anthrone and 9,10-antracenedione. These three markers can thus be used for the identification of PR83. We can conclude that PR83 alizarin crimson can be identified even when it's mixed with a binding media, as lipid or polisaccharidic media.



Fig. 3.21 Comparison of the relative abundance of the py-products between the neat pigment PR83 and the pigment in the Gamblin oil paint.



Fig. 3.22 Comparison of the relative abundance of the py-products between the neat pigment PR83 and the pigment in the Liquitex watercolour paint.

<u>PR170 naphthol red</u>. The oil paint pyrogram (Fig. 3.23) shows two characteristic markers of PR170, namely the unknown product at 15.2 min (m/z 245, 244, 214) and the product identified by Russell [4] as product "d with 2-naphthol" (m/z 137, 171, 307). Other peaks (e.g. aniline) are present only in the oil paint pyrogram but not in the pigment's. The watercolour paint pyrogram (Fig. 3.24) shows a similar pattern to that of the oil paint's, while the acrylic paint pyrogram (Fig. 3.25) shows only the unknown product at 15.2 min, which, however, is a marker of PR170 and can be used for the identification of the pigment.



Fig. 3.23 Comparison of the relative abundance of the py-products between the neat pigment PR170 and the pigment in the Daniel Smith oil paint.



Fig. 3.24 Comparison of the relative abundance of the py-products between the neat pigment PR170 and the pigment in the Daniel Smith watercolour paint.



Fig. 3.25 Comparison of the relative abundance of the py-products between the neat pigment PR170 and the pigment in the Liquitex acrylic paint.

<u>PY3 hansa yellow</u>. In our Py-GC/MS library, we have analysed only three yellow pigments, one of them being PY3, so the products that are indicated as "markers" or "characteristic" of PY3 may very probably be characteristic not just of PY3, but of the PY3 class, the monoazo yellow class.

In the Winsor&Newton water-mixable oil paint pyrogram (Fig. 3.26) only one characteristic PY3 product is detectable, the benzene, 1-chloro-2-isocyanato.



Fig. 3.26 Comparison of the relative abundance of the py-products between the neat pigment PY3 and the pigment in the Winsor&Newton water-mixable oil paint.

The alkyd paint pyrogram (Fig. 3.27) contains five characteristic PY3 products, the most important being o-chloroaniline, thus this binder allows an easy identification of the pigment. The oil paint pyrogram (Fig. 3.28) shows two products of the yellow pigment, while the watercolour paint pyrogram (Fig. 3.29) does not show the o-chloroaniline, while it contains other two PY3 products, benzene,1-chloro-2-isocyanato and benzenamine,4-chloro-2-nitro. The acrylic paint pyrogram (Fig. 3.30) shows the PY3 "marker", o-chloroaniline.

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Fig. 3.27 Comparison of the relative abundance of the py-products between the neat pigment PY3. and the pigment in the Winsor&Newton alkyd paint.



Fig. 3.28 Comparison of the relative abundance of the py-products between the neat pigment PY3 and the pigment in the Daniel Smith oil paint.







Fig. 3.30 Comparison of the relative abundance of the py-products between the neat pigment PY3 and the pigment in the Liquitex acrylic paint.

Even if the characteristic pyrolysis products of the synthetic pigments are still detectable in commercial paint formulations, the relative abundances of the py-products change from the pyrogram of the pure pigment compared to that of the commercial formulations. This may be due to the very low concentration of the pigments in paint formulations (generally 1-5% or lower) and/or to the presence of several other components in the commercial paints, which may interfere with the formation or detection of the characteristic products of the pigments.

We compared our results also with already published reference pyrograms of the pure binding media, to assess if the pyrolysis products of the commercial formulations taken into consideration were originated from the pigment only and not from the binder. For watercolour paints, none of the pyrolysis products indicated in Fig. 3.22, Fig. 3.24 and Fig. 3.29 can be ascribed to gum Arabic [9], the most used binder in watercolour paints. For acrylic paints, the peaks originated from the binder are easily recognizable, being the oligomers and monomers resulting from the unzipping mechanism caused by pyrolysis [10]. Alkyd paints show a very characteristic pyrogram [10], thus the pyrolysis products originating from the pigment are readily distinguished. The pyrograms of oil-based paints, instead, are characterized by a series of fatty acids [10]. Thus, for the oil paint containing PR83 (Fig. 3.21), the fatty acids present in the pyrogram were not taken into consideration for further discussion, because they are originated not just by the pigment formulation (see Section 3.3.2), but also by the binder.

3.3.4 Results and discussion

We expanded the data available on some classes of synthetic pigments already being analysed by other authors [2] [3] – naphthol AS, benzimidazolone, phthalocyanine and perlylene classes - and the fragmentation patterns identified for our compounds are generally consistent with literature data. We also report the pyrolysis profiles of pigments never previously analysed by this technique: the metal complexes, β -naphthol pigment lakes, BONA pigment lakes, disazopyrazolone, triarylcarbonium, dioxazine, anthraquinone, indanthrone, isoindoline and thioindigo pigments. Several pyrolysis products are common to different classes of synthetic pigments, for example 2-naphthol and aniline; thus these compounds cannot be used in the identification of the pigments in paint samples. In particular, the pigments belonging to the β -naphthol and BONA pigment lakes classes cannot be easily distinguished because they share several products in common. Nonetheless, the interpretation of the profile generally allows the identification of the class. For PGr8, a metal complex pigment, and PR83, an anthraquinone pigment, we assessed the presence in the pyrograms of products derived from vegetable oils, even if the pigments analysed were not expected to contain binding media. Thus, we hypothesised that the fatty acids detected originated from an oil used in the synthesis of the pigments themselves.

With regard to the isoindoline and disazopyrazolone pigments analysed, we found characteristic products, respectively 2(1H)-quinolinone and norphenazone, that can help in the identification of these classes.

We confirmed the results of Russell [3] for the phthalocyanine pigments, but we expanded the database analysing other three phthalo pigments and the six crystal modifications of PB15. Py-GC/MS allows us to differentiate between the various PB15 crystal modifications, on tha basis of their different pyrolytic profiles.

The pyrogram of PV19, a quinacridone pigment extensively used in paint industry, shows only an unknown product, which can still be used for the identification of this pigment. The other quinacridone pigment analysed, PV42, has 2-methyl acridone as characteristic product.

The alizarin crimson PR83 is unambiguously identifiable by Py-GC/MS, and this result is important because this pigment has been widely used in artists' paints.

Another interesting result was obtained for the triarylcarbonium class: we found that the pigments belonging to this class show the intact molecule peak in the pyrograms.

As for the dioxazine pigments, the products of PV23, one of the most used pigments in paint materials, are unknown, but the m/z reported could help in the identification.

We analysed for the first time with Py-GC/MS PV36, a thioindigo pigment, obtaining a peculiar pyrogram with a single peak, the 2,4,5-trichlorophenol.

We also reported for the first time the Py-GC/MS results of three violet pigments with unpublished chemical structure, PV51, PV52 and PV53. The pyrograms obtained may be used as fingerprint for the identification of these materials in paint samples.

Moreover, PR83, PR170 and PY3 can be detected with Py-GC/MS even when they are mixed with other components inside a commercial paint formulation, because the characteristic pyrolysis products are still detectable, as long as a comprehensive library of synthetic pigments has been created. The commercial paints were not aged; for the detection of synthetic pigments in aged binding media, see Section 3.4.2.

3.4 Synthetic pigments: ageing studies

3.4.1 Ageing study of pure synthetic pigments

For the ageing study we selected 19 pigments, summed in Tables A2 and A3, Appendix A. The selection includes one blue pigment, three oranges, nine reds, three violets and three yellows. Some of them are rated by the ASTM as fugitive. It must be noted that the ASTM ratings are always referred to a specific binder. We decided instead to test the neat pigment powder, without any binder, to minimize the variables involved in the ageing pathways and to determine the lightfastness of the pure pigment. To our knowledge, this is the first time that synthetic pigments are tested without any binder to study their lightfastness properties.

3.4.1.1 Colorimetric measures

For each pigment we recorded 5 measures (both from the un-aged and from the aged layer), and calculated the CIELAB shifts on the average value.

Table 3.16 summarizes the colour changes observed for all the investigated pigments, before and after the ageing, including the shift in the values of lightness/darkness (L*), redness/greenness (a*), yellowness/blueness (b*) and total colour (E*). In the CIELAB diagram in Fig. 3.31 the differences in the a* and b* values of the un-aged and aged pigments are shown.

The differences in L* (Fig. 3.32) correspond to the brightening/darkening of the pigment due to the UV-Vis light-treatment.

Pigment	ΔL*	Δa*	Δb*	ΔΕ*
PB1	5.82	19.50	-30.22	36.43
PO5	3.99	1.74	1.12	4.50
PO16	-2.29	8.91	8.47	12.50
PO46	-2.21	6.27	24.39	25.28
PR3	0.40	-3.34	-1.52	3.69
PR48	2.54	0.55	26.06	26.19
PR49	2.58	0.36	10.80	11.11
PR53	-5.79	4.73	17.67	19.19
PR57	1.90	1.94	6.22	6.79
PR83	-7.55	2.31	4.23	8.96
PR90	-23.10	61.62	29.26	72.02
PR112	2.93	2.19	3.89	5.34
PR170	0.99	-2.20	2.90	3.78
PV1	1.90	6.09	-1.47	6.54
PV27	-3.56	6.97	0.55	6.54
РҮЗ	6.94	-2.24	5.11	8.91
PY12	9.17	-7.66	16.09	20.04
PY100	5.89	-0.33	8.59	10.42

Table 3.16 List of the ΔL^* , Δa^* , Δb^* and ΔE^* values for the pigments investigated, before and after the light-ageing study.


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Fig. 3.32 Shifts in L* values of the pigments investigated before and after the light-ageing.

<u>Blue.</u> PB1 (Fig. 3.33) has a noticeable shift in both a* and b* values: the colour of the pigment shifts from blue to yellow and from red to green. Furthermore, PB1 shows a decrease of L*, pointing out a darkening.



Fig. 3.33 PB1. Above the white dashed line: area exposed to the light-ageing, where the colour has darkened.

<u>Orange</u>. While PO5 shows a very limited shift, PO16 and PO46 (Fig. 3.34) show a decrease of b* value, but also a slightly decrease in a*. For all the three orange pigments the L* increases, indicating an increase in the brightness, corresponding to the fading of the original colour.



Fig. 3.34 PO16 (left) and PO46 (right). Above the white dashed line: areas exposed to the light-ageing, where the colour has faded.

<u>Red</u>. Apart from PR3 and PR170, which show a small increase in a*, all the reds show a decrease of the a* and b* values, meaning a decrease of the red and of the yellow components. PR90 shows the most drastic change, with the a* and b* values of the aged pigment that are almost equal to zero, indicating an extreme bleaching of the colour. These colorimetric results are confirmed by the visual appearance of the sample (Fig. 3.35): it shows a complete change in colour from an intense hue of pink to white.



Fig. 3.35 PR90. Below the red dashed line: area exposed to the light-ageing, where the colour has completely faded.

As for the L* value, three reds show a brightening of the colour: PR53, PR83 and, as expected from the a* and b* results, PR90, which, also in this case, has the most dramatic change. The other reds (PR3, PR48:1, PR49:2, PR57, PR112 and PR170) show a darkening. PR48:1 and PR49:2 are shown in Fig. 3.36 as an example.



Fig. 3.36 PR48:1 (left) and PR49:2 (right). Below the white dashed line: areas exposed to the lightageing, where the colour has darkened.

<u>Violet</u>. Both PV1 and PV27 show a decrease of a*, indicating a decrease of the red component of their violet colour. The b* value for both pigments is almost unchanged. PV1

shows a darkening, while PV27 a brightening of the colour, according to the L* value (Fig. 3.37).



Fig. 3.37 PV1 (left) and PV27 (right). Above the white dashed line: areas exposed to the light-ageing, where the colour has darkened for PV1 and faded for PV27.

<u>Yellow</u>. All three yellows (PY3, PY12 and PY100) have a noticeable shift in the b* value, pointing out a decrease of the yellow component. They also undergo a darkening, with the L* value decreasing considerably. PY12 and PY100 are shown in Fig. 3.38 as an example.



Fig. 3.38 PY12 (left) and PY100 (right). Above the white dashed line: areas exposed to the light-ageing, where the colour has darkened.

3.4.1.2 Py-GC/MS results

Out of 19 pigments, six showed noticeable differences when comparing the pyrograms of the aged and the un-aged. The main features of the pyrograms acquired for the five reference materials, showing relevant differences after artificial ageing, are described below.

<u>PR83.</u> The pyrogram of the aged sample of PR83 alizarin crimson (Fig. 3.39) contains a peak due to phthalic anhydride that was not present in the pyrogram of the un-aged pigment. This is consistent with the results of an ageing study performed on alizarin in water by Ahn and co-workers [11].

<u>PR49</u>. The pyrogram of the aged sample of PR49 (Fig. 3.40) shows a new peak at 20.2 min (m/z 298, 143, 115, 27) that has been identified as the pigment molecule without the SO_3 group.



Fig. 3.39 Comparison between the Py-GC/MS chromatograms of the un-aged PR83 (black) and the artificially aged PR83 (grey).



Fig. 3.40 Comparison between the Py-GC/MS chromatograms of the un-aged PR49 (black) and the artificially aged PR49 (grey).

<u>PR90.</u> Observing the comparison of the pyrograms of the un-aged and aged PR90 (Fig. 3.41), benzoic acid disappears in the pyrogram of the aged, while a new unidentified compound is formed, which elutes at 19.4 min (with m/z 428, 269, 239, 284).



Fig. 3.41 Comparison between the Py-GC/MS chromatograms of the un-aged PR90 (black) and the artificially aged PR90 (grey).

<u>PO16.</u> In the pyrograms of the fresh and aged PO16 the ratio between the two peaks of benzene-isocyanato and aniline is the opposite (Fig. 3.42).

<u>PV39</u>. PV39 was not treated in the weather-ometer, instead it has been exposed for five months to natural light. The result shown in Fig. 3.43 is a drastic change in the pyrogram of the aged material, where the peak corresponding to the intact molecule (m/z 253, 373, 359, 237) appears drastically decreased.



Fig. 3.42 Comparison between the Py-GC/MS chromatograms of the un-aged PO16 (black) and the artificially aged PO16 (grey).



Fig. 3.43 Comparison between the Py-GC/MS chromatograms of the un-aged PV39 (black) and the naturally aged – for five months - PV39 (grey).

3.4.1.3 GC/MS results

The reagents used were TMTFTH (m-trifluoromethylphenyl trimethylammonium hydroxide) and ethanol.

<u>PR83.</u> The only pigment that showed a significant difference between the un-aged and the aged sample, using TMTFTH as derivatising agent, is PR83, alizarin crimson (Fig. 3.44). The chromatogram of the aged PR83 shows that three peaks are decreasing in intensity: oleic acid at 12.5 min, methyl ricinoleate at 13.4 min and another fatty acid at 15.3 min indicated by an arrow in the figureⁱ. The decrease in unsaturated fatty acids may indicate that the UV-Vis light caused the cleavage of the double bonds in the lipid portion of the pigment.



Fig. 3.44 Comparison between the GC/MS chromatograms of the un-aged PR83 (black) and the artificially aged (grey).

<u>PR49.</u> Using ethanol as solvent, the chromatogram of the aged PR49 shows two "new" products, absent from the chromatogram of the un-aged PR49: phthalic anhydride and 2-naphthol, molecules formed during the light treatment (Fig. 3.45). It is interesting to note that phthalic anhydride was not detected by Py-GC/MS in this case.

ⁱ The presence of fatty acids in PR83 reference material is explained and discussed in Section 3.3.2.



Fig. 3.45 Comparison between the GC/MS chromatograms of the un-aged PR49 (black) and the artificially aged (gray).



Fig. 3.46 Comparison between the GC/MS chromatograms of the un-aged PR53 (black) and the artificially aged (gray).

<u>PR53.</u> The aged PR53 in ethanol (Fig. 3.46) shows two new products: 2-naphthalenamine-Nmethyl and 1-naphthalenamine-N,N-dimethyl, that are absent in the un-aged sample.

<u>PV27.</u> The GC/MS chromatogram of the un-aged PV27 in ethanol (Fig. 3.47) shows the peak corresponding to the intact molecule, but this peak is completely missing in the chromatogram of the aged pigment, highlighting the fact that the light-ageing treatment causes the complete breakdown of the molecule. This result is consistent with the Py-GC/MS analysis.



Fig. 3.47 Comparison between the GC/MS chromatograms of the un-aged PV27 (black) and the artificially aged (gray).

In conclusion, the GC/MS analyses showed that the light-ageing treatment causes the breaking of the chemical bonds.

3.4.1.4 FTIR-ATR results

The FTIR-ATR spectra of some of the aged pigments - PO16, PR48, PR49 and PR53, in Fig. 3.48, Fig. 3.49, Fig. 3.50, and Fig. 3.51 - show a new broad peak between 1710 and 1725 cm⁻¹. This new band in the aged samples may be attributed to formation of carbonyl groups due to oxidation. The aged PO16, PR48, and PR49 pigments also show a more pronounced absorption of the O-H stretching in the range between 3000-3500 cm⁻¹, which, combined with the formation of the band assigned to carbonyl groups, may indicate the formation of carboxylic acids.

A recent paper by Stenger et al. [6] indicates the formation of sodium sulphate as the result of the photochemical reaction of the PR49 sodium salt, with the cleavage of the sulphonate group on the organic anion. Although we selected the PR49 calcium salt for our study (PR49:2), the characteristic sulphate peaks were not observed when compared with reference spectra of anhydrate and hydrate calcium sulphate.

PR90, interestingly, shows a different phenomenon (Fig. 3.52): two peaks - 1351 and 1450 cm^{-1} - that are present in the un-aged sample, are completely missing in the aged one. These absorbance peaks may be attributed to the stretching of the C-O bonds, thus we hypothesized that the UV-Vis light causes the cleavage of this chemical bonds.



Fig. 3.48 Comparison between the FTIR-ATR spectra of the un-aged (black) and aged (red) PO16.





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Fig. 3.51 Comparison between the FTIR-ATR spectra of un-aged (black) and aged (red) PR53.



Fig. 3.52 Comparison between the FTIR-ATR spectra of un-aged (black) and aged (red) PR90:1.

3.4.1.5 Raman results

14 out of 18 pigments analysed gave a Raman signal (Table 3.17), but no noticeable differences were identified in the Raman spectra between the un-aged and the aged samples.

C.I. name	C.I. number	Raman active
PB1	42595:2	no
PO5	12075	✓
PO16	21160	√
PO46	15602	~
PR3	12120	~
PR48:1	15865:1	~
PR49:2	15630:2	~
PR53:1	15585:1	✓
PR57:1	15850:1	√
PR83	58000	no
PR90:1	45380	no
PR112	12370	✓
PR170	12475	✓
PV1	45170:2	✓
PV27	42535:3	no
PY3	11710	~
PY12	21090	✓
PY100	19140:1	~

Table 3.17 List of the pigments analysed with micro-Raman.

Raman technique is thus able to identify a pigment even if it has undergone an ageing process such as that simulated in our experiments. Interestingly, the intensity of the Raman signal was higher for almost all the aged samples. This phenomenon has yet to be explained, but one hypothesis is that the Raman vibrations are stronger in the aged molecules, causing a higher signal.

3.4.2 Ageing study of pigments in commercial paint formulations

After the light-ageing study on the pure pigments we tested the system "pigment + binder". The commercial paints selected for the study are listed in Table 3.1, in Materials and methods. We studied different types of binders: oil, acrylic, alkyd, water-mixable oil, watercolour. The weather-ometer and the Py-GC/MS conditions were the same used for the pure pigments and described in Section 3.2.

3.4.2.1 Colorimetric measures

Table 3.18 summarizes the colour changes of all the investigated commercial paints, including the shift in the values of the lightness/darkness (L*), redness/greenness (a*), yellowness/blueness (b*) and total colour (E*). In the CIELAB diagram (Fig. 3.53) it is possible to see the differences in the a* and b* values of the un-aged and aged commercial paints, while in Fig. 3.54 the shifts in the L* value.

Pigment	Manufacturer and Binder	ΔL*	∆a*	∆b*	ΔΕ*
PR83	Gamblin oil	12.21	-5.18	-4.64	14.06
	Liquitex watercolor	9.02	-5.90	-4.02	11.50
PR170	Daniel Smith oil	-1.71	-4.26	-8.93	10.04
	Daniel Smith watercolor	2.15	-17.96	-28.94	34.12
	Liquitex acrylic	-1.70	0.00	1.09	2.02
РҮЗ	Winsor&Newton Artisan water-mixable oil	-9.74	5.78	-12.12	16.59
	Winsor&Newton Griffin alkyd	-8.85	3.86	-8.31	12.74
	Daniel Smith oil	-1.37	2.06	-1.90	3.12
	Daniel Smith watercolor	-10.55	14.77	-15.77	24.05
	Liquitex acrylic	1.05	0.73	1.23	1.78

Table 3.18 List of the ΔL^* , Δa^* , Δb^* and ΔE^* values for the commercial paints investigated, before and after the light-ageing study.



Fig. 3.53 CIELAB diagram of the commercial paints investigated before and after the light-ageing, showing the shifts of their a* and b* coordinates.



Fig. 3.54 Shifts in L* values of the commercial paints investigated before and after the light-ageing.

<u>PR83 alizarin crimson</u>. Both the oil and the watercolour paints show a shift from red to green in the a* value and from yellow to blue in the b* value when comparing the aged and the fresh samples. They also show an increase in the L* value, indicating a brightening/fading of the colour.

<u>PR170 naphthol red</u>. The acrylic paint does not change with respect to the a* and b* value, indicating that this formulation is not subjected to significant changes in colour. The oil and the watercolour paints, instead, show a considerable shift, with the watercolour being the most dramatic. Both a* and b* values decrease in the aged samples. All the three paints show no significant change in the L* value.

<u>PY3 hansa yellow</u>. The oil and the acrylic paints show no significant colour shifts, while the watercolour paint, the Artisan water-mixable oil and the alkyd paints show an increase of the a* value and a decrease of the b*, for the aged samples. This behaviour is echoed by the L* value: the oil and the acrylic paints have no shifts, while the other three paints show a decrease of L*, indicating a darkening of the colour.

The differences in colour and appearance are visible only for the PY3 watercolour and PR170 watercolour (Fig. 3.55). The binder of watercolour paints, most probably gum Arabic, has a very weak resistance against light, and the result is a dramatic embrittlement of the paint.



Fig. 3.55 Watercolour paint containing PY3 (left) and PR170 (right). In both samples the aged paint – indicated by the letter A at the top of the glass slide - is recognizable by the extreme brittleness of the surface. Moreover, a darkening of the yellow and red colours is also noticeable.

3.4.2.2 Py-GC/MS results

After the Py-GC/MS analysis, the products of the fresh paint were compared with those of the light-aged paint.

<u>PR83 alizarin crimson</u>. Both the aged and fresh oil paint (Fig. 3.56) show phenanthrene and anthrone, two markers of PR83. The aged oil paint shows also 9,10-anthracenedione-2-hydroxy, which is absent from the fresh paint. The main PR83 marker in the watercolour paint (both aged and fresh, Fig. 3.57) is 9,10-anthracenedione. Other four characteristic PR83 products are present, but in smaller amounts. We can conclude that PR83 can be detected and identified in the selected aged binding media.



Fig. 3.56 Comparison of the relative abundance of the py-products between the fresh and the aged Gamblin oil paint containing PR83.

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Fig. 3.57 Comparison of the relative abundance of the py-products between the fresh and the aged Liquitex watercolour paint containing PR83.

<u>PR170 naphthol red</u>. The oil paint shows (Fig. 3.58) three characteristic PR170 products that are present both in the fresh and in the aged paint: benzenamine,2-ethoxy; benzonitrile, mamino- and the unknown product at 15.2 min. Thus, PR170 can be identified in an oil paint, even if aged. In the acrylic paint in Fig. 3.59, the benzenamine,2-ethoxy product is present only in the aged sample. The identification of the PR170 pigment is more difficult, but still possible even in the aged layer, thanks to the characteristic unknown product at 15.2 min. The watercolour paint, both fresh and aged (Fig. 3.60), shows the PR170 product "d with 2naphthol" [3], in addition to the PR170 markers mentioned above, and in conclusion is the binding media which allows the easiest identification of the PR170 pigment.



Fig. 3.58 Comparison of the relative abundance of the py-products between the fresh and the aged Daniel Smith oil paint containing PR170.



Fig. 3.59 Comparison of the relative abundance of the py-products between the fresh and the aged Liquitex acrylic paint containing PR170.



Fig. 3.60 Comparison of the relative abundance of the py-products between the fresh and the aged Daniel Smith watercolour paint containing PR170.

<u>PY3 hansa yellow</u>. The Winsor&Newton water-mixable oil paint shows a contradicting results (Fig. 3.61): the marker of PY3, o-chloroaniline, is present only in the aged sample, but not in the un-aged one. The alkyd paint (Fig. 3.62), instead, allows an easy identification of the pigment, because both the un-aged and the aged paint show three characteristic products: o-chloroaniline; benzene, 1-chloro-2-isocyanato- and benzenamine, 4-chloro-2-nitro. The pyrograms of the oil paint (Fig. 3.63) contain o-chloroaniline both for the fresh and the aged paint, but they also contain benzenamine, 4-chloro-2-nitro. The pyrogram of the aged oil paint contains the peak due to p-chloroaniline, which is present in the pure pigment, but not in the fresh oil paint. The binder of the watercolour paint in Fig. 3.64 shows no significant differences between the aged and the un-aged paints and it is possible

to identify the PY3 pigment thanks to two characteristic peaks. The pyrogram of the acrylic paint (Fig. 3.65) contains the o-chloroaniline peak in both the aged and un-aged paint.



Fig. 3.61 Comparison of the relative abundance of the py-products between the fresh and the aged Winsor&Newton water-mixable oil paint containing PY3.



Fig. 3.62 Comparison of the relative abundance of the py-products between the fresh and the aged Winsor&Newton alkyd paint containing PY3.



Fig. 3.63 Comparison of the relative abundance of the py-products between the fresh and the aged Daniel Smith oil paint containing PY3.



Fig. 3.64 Comparison of the relative abundance of the py-products between the fresh and the aged Daniel Smith watercolour paint containing PY3.



Fig. 3.65 Comparison of the relative abundance of the py-products between the fresh and the aged Liquitex acrylic paint containing PY3.

3.5 Conclusions

Synthetic pigments are compounds of difficult detection and identification, particularly in complex mixtures, such as paint samples and commercial paints. Moreover, their ageing pathways are not completely understood, and until now the literature focused mainly on textile dyes, instead of pigments employed in paint formulations. Moreover, many paint manufacturers continue using pigments with poor lightfastness properties, which can lead to conservation issues for paintings.

Py-GC/MS proved to be a very reliable technique for the analysis of synthetic pigments. In the present work we created a library of pyrolysis products of 76 synthetic pigments, integrating the partial reports of other authors. We found that, in many cases, the pyrolysis products were characteristic of a single pigment or of a class of pigments, thus allowing the identification. We found also that, when present in commercial paint formulations, synthetic pigments can still be detected and identified, even if the relative abundances of the characteristic pyrolysis products are different than in the pure materials. The same can be said for aged paint formulations, where the pyrolysis products of the synthetic pigments are clearly detected in the pyrograms. For the detection of pigments in paint formulations AMDIS software proved to be a very useful tool, detecting the characteristic pyrolysis products of the pigments (the target of the library), even when in the chromatogram they were covered by the most intense peaks, corresponding to the pyrolysis products of the other components of the paint.

For the first time a survey on the lightfastness properties of the pure pigments was carried out. The ageing study of the pure pigments assessed changes in colour: in some cases a fading occurred, in others a darkening. The changes were, for some pigments, dramatic and evident, while, for others, too small to be noticeable. These results are important because some of the pigments selected for the ageing study are extensively employed in paint formulations. The Py-GC/MS, GC/MS and FTIR-ATR results all indicated that the photoageing causes changes in the pigments' molecules structure.

Interestingly, for PR83, the pure pigment showed a negative ΔL^* value, corresponding to a darkening of the colour, while the oil and the watercolour media containing PR83 showed a positive ΔL^* value, that is a fading of the colour. For PR170, the pure pigment had a slight fading, as the watercolour medium containing PR170; the opposite behaviour was observed in the oil and acrylic media, which both showed a slight darkening of their colours. The pure

PY3 showed a fading of its colour. This behaviour was found only in the acrylic medium; for all the other media the colour darkened. Thus, the changes in colour of the pigments are strongly dependent on the type of medium with which they are mixed in the commercial formulations. Summarizing, the ageing study of the commercial paint formulations highlighted a relatively higher colour change, compared to the pure pigments. This trend is valid for all the binding media, with the exception of acrylic paints, which showed very low ΔE^* and ΔL^* values, even lower than those of the pure pigments. Unfortunately, it was hard to assess if the degradation underwent by the pigments was of the same type for the pure pigments and for the pigments in commercial paints, because, during the pyrolysis step, some products due to rearrangements may be formed. Moreover, it was not possible to assess if the interaction between the binder and the pigment started specific degradation pathways.

Of the three pigments in the paint formulations, PR170 is the one with the lowest ΔL^* values, showing a high lightfastness, regardless of the type of binder. Thus, PR170 can be safely employed by paint manufacturers. PR83, on the contrary, shows relatively high ΔE^* and ΔL^* , both in oil and in watercolour binders. Thus, this pigment should not be used by paint manufacturers and should be substituted with other more light-resistant pigments. PY3, instead, proved to be stable to light-ageing when mixed with acrylic and oil binding media, while with alkyd, water-mixable oil and watercolour paints showed evident changes in colour.

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Chapter 4

Case studies

4.1 Introduction

In this chapter several case studies are presented ranging from the characterization of the pigments found in the artists' studios to the material identification of paintings dated from the 1940s to the 1980s. Samples were analysed by using different techniques, described in the previous chapters. The results obtained helped in understanding the constituent materials of the paintings and of the materials from the artists' collections. Moreover, non-original materials deriving from restorations were identified in the analysed paintings.

4.2 Ri de Pomme by Julian Schnabel

Ri de Pomme is a large scale painting by artist Julian Schnabel, dating 1988 and presently owned by the Luigi Pecci Centre for Contemporary Art of Prato (Italy). Julian Schnabel (New York, October 26, 1951) is an American artist, screenwriter and filmmaker. He was one of a number of international painters — including David Salle in the United States, Georg Baselitz and Anselm Kiefer in Germany, and Francesco Clemente in Italy — to emerge in the late 1970s, whose bold expressive style was termed Neo-Expressionist. Schnabel's art is characterized by the use of eclectic historical images to create highly personal and allusive works [1]. He was first acknowledged for canvases whose painting surface was built up of shattered crockery, called "plate paintings". He has often used unconventional supports such as black velvet, cardboards and weathered tarpaulins and his paintings frequently have massive dimensions.

The painting *Ri de Pomme* is painted on an aged tarpaulin, which is an old military equipment with evident spots of dirt. The artist did not use any kind of preparatory layer and the colour is applied directly on the tarpaulin [2]. The painting has huge dimensions, measuring 488 x 488 cm.

In 2002 the artwork underwent an extensive restoration and a re-painting that almost completely covered the original paint layer. The restorer's notes report the use of Lefranc & Bourgeois Flashe[®] polyvinyl acetate (PVAc) paints [3]. The intervention has been disputed by the owner, the Pecci Centre, being considered too invasive.

My work was in the framework of an extensive diagnostic campaign aimed at characterizing both the original and non-original paint materials and their state of conservation. In particular, we aimed at verifying the possibility to differentiate between the original paint materials and the vinyl paint employed during the restoration. This discrimination is crucial for a correct and selective removal of the repaintings, in order to bring the painting back to its original conditions. Non-invasive Fibre Optics Reflectance Spectroscopy (FORS) and Micro-Raman were employed for the identification of the pigments, while to identify the binder, both Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) and Gas Chromatography/Mass Spectrometry (GC/MS) were used.

4.2.1 Materials and methods

<u>Reference materials</u>. Three different commercial PVAc paints were analysed, namely Violet, Violet Blue and Egypt Violet from Flashe[®] (Lefranc & Bourgeois). The paints were purchased from Zecchi (Florence, Italy). Accordingly to the manufacturer, Violet paint contains the organic pigments PV23 and PR122, Violet Blue contains PV23 only, while PV23 and PB29 are the colouring materials in Egypt Violet, that also contains PW6 (titanium white). Reference paint mock-ups were prepared by casting commercial vinyl paints over glass slides. The products were left to dry for one month before testing.

<u>Sampling</u>. A micro-invasive sampling was performed for Py-GC/MS and GC/MS analyses. Four paint samples (< 0.1 mg) were collected from the edges of the painting and one sample was collected from the tarpaulin support. The samples were examined under an optical microscope prior to analysis. For three of the paint samples (S1, S2 and S3) it was not possible to separate the fibres of the tarpaulin from the paint layer. Sample S4 was in form of flakes and devoid of any fibre of the support.

<u>Reagents</u>. Pyrolysis was performed in the presence of 1,1,1,3,3,3-hexamethyldisilazane (HMDS, Sigma–Aldrich, USA) to obtain the on-line thermally assisted derivatisation of the pyrolysis products. The derivatisation agent used for the GC/MS analyses was *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% of trimethylchlorosilane (Sigma-Aldrich, USA). The fatty acids stock solution in acetone contained lauric (3.49 mg/g of Lau),

suberic (3.60 mg/g of Su), azelaic (3.47 mg/g of A), myristic (3.32 mg/g of My), sebacic (3.25 mg/g of Se), palmitic (3.70 mg/g of P), oleic (4.94 mg/g of O) and stearic (5.57 mg/g of S) acids. Tridecanoic acid solution in isooctane, 151.4 ppm, was used as derivatization internal standard. Hexadecane solution in isooctane, 200.4 ppm, was used as injection internal standard. All acids and hexadecane, purity 99%, were purchased from Sigma-Aldrich (USA). The standard solutions were used to derive calibration curves.

Apparatus. Py-GC/MS was performed with a Pyroprobe pyrolizer 5000 (CDS Analytical, USA) coupled with a 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA), interfaced with a 5973 single quadrupole mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). The pyrolysis temperature program was: initial temperature 50 °C, ramp of 20 °C/ms up to final temperature of 600 °C. The pyrolyser interface was set at 180 °C, the transfer line at 300 °C and the valve oven at 290 °C. The GC injection port was kept at 180 °C. The GC column used was an HP-5MS fused silica capillary column (5% diphenyl/95% dimethyl-polysiloxane, 30 m x 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific, Agilent Technologies, Palo Alto, CA, USA) with a deactivated silica precolumn (2 m x 0.32 mm i.d., J&W Scientific, Agilent Technologies, Palo Alto, CA, USA). The carrier gas was used in the constant flow mode (He, purity 99.995%) at 1 mL/min. Samples were injected in split mode (variable split ratio depending on the sample amount). The chromatographic oven was programmed as follows: 32 °C, isothermal for 10 min, 10 °C/min up to 280 °C, isothermal for 3 min, 15 °C/min up to 300 °C, isothermal for 30 min. Ions were generated by electronimpact (EI) ionization (electron energy 70 eV) in the ionisation chamber of the mass spectrometer and MS spectra were recorded in the range 50-800 m/z in TIC (total ion current) mode.

For the GC/MS analysis, the GC/MS apparatus, the column and the conditions used were the same as the Py-GC/MS analysis, except for the temperature programme. The GC/MS chromatographic oven was programmed as follows: initial temperature 80 °C, isothermal for 2 min, 10 °C/min up to 200 °C, isothermal for 3 min; 10 °C/min up to 280 °C, isothermal for 30 min. MS parameters: electron impact ionization (EI, 70 eV) in positive mode; ion source temperature 230°C; interface temperature 280°C. MS spectra were recorded in the range 50-800 m/z both in TIC (total ion current) and in SIM (single ion monitoring) mode. The injection volume was 2 μ L. The selected ions for the SIM acquisition were lauric acid *m/z* 117-257; suberic acid *m/z* 169-303; azelaic acid *m/z* 149-317; myristic acid *m/z* 117285; sebacic acid *m/z* 149-331; palmitic acid *m/z* 117-313; oleic acid *m/z* 117-339; stearic acid *m/z* 117-341.

The FORS measurements were performed with a high performance CCD spectrophotometer model Prime X BTC621E (B&W Tek, Newark, DE, USA) in the 200-1000 nm range, equipped with FRP optical fibres (geometry 0°/0°) and a Tungsten lamp as light source. The spectral resolution of the spectrophotometer was 10 nm/pixel. BWSpec software was used for the data acquisition.

Micro-Raman measurements were carried out using a Renishaw RM 2000 spectrophotometer, coupled with an optical Leica DLML microscope, equipped with a NPLAN objective 50x. The laser source was a Helium-Neon laser with a wavelength of $\lambda = 632.8$ nm and a laser power output at the objective of around 2 mW. The spectrometer consists of a single grating monochromator (1200 lines mm⁻¹), coupled with a CCD detector, a RenCam 578 × 400 pixels (22 µm × 22 µm) cooled by a Peltier-element. The spectral calibration of the instrument was performed on the 520.5 cm⁻¹ band of a silicon wafer.

A microwave oven model ETHOS One (High Performance Microwave Digestion System) Milestone (Sorisole, Bergamo, Italy) was used for the saponification of lipids.

GC/MS Analytical Procedure. The GC/MS analytical procedure was derived from a previously published one [4] [5], slightly modified and adapted for the analysis of the lipidresinous fraction only. About 1 mg of each sample was subjected to saponification assisted by microwaves with 300 μ L of KOH in ethanol (10% wt) at 80 °C for 60 min. After saponification, the solution was diluted in bi-distilled water, and the unsaponifiable fraction extracted in *n*-hexane (400 μ L, three times). Subsequently, the residue of the *n*-hexane extraction was acidified with HCl (6 M) and then extracted with diethyl ether (400 μ L, three times). The two extracts, containing the organic acids and the neutral fraction, were admixed and subjected to derivatization with 20 μL of N,Obis(trimethylsilyl)trifluoroacetamide (BSTFA), 50 μ L of isooctane (solvent), and 5 μ L of tridecanoic acid solution at 60 °C for 30 min. Prior to injection, 100 μL of isooctane and 5 μL of hexadecane solution were added. 2 µL of the isooctane solution of derivatized neutral and acid compounds were then analysed by GC/MS. Mass spectral assignment was based on the direct match with the spectra of NIST 1.7 and Wiley 275 libraries and a library created on purpose by the authors. Comparisons with mass spectra of reference standards, when available, were made. In the absence of reference spectra, the peak assignment was based on mass spectra interpretation.

4.2.2 FORS results

The FORS technique (see Chapter 1, Section 1.5.1.1) is generally employed for the identification of painting materials by comparison with suitable archives or reference spectra [6] [7] [8]. FORS is a non-invasive, portable, point-by-point technique and the analysis time is extremely short, thus allowing us to perform *in situ* measurements and to map the painted surface. This step was fundamental at the beginning of the diagnostic campaign, to guide a thoughtful and representative sampling. Moreover, the identification of the original paint layer is extremely important, if a removal intervention of the vinyl paint layers will be planned.

FORS measurements performed on *Ri de Pomme* entailed 18 spots on the front of the painting and 4 on the sides were examined. The map of the FORS measuring points on the front of the painting is shown in Fig. 4.1.

Two different types of violet coloured areas were identified on the painting, presenting two different FORS spectra, shown in Fig. 4.2. The lighter shade of violet corresponds to the PVAc paint used during the restoration, while the darker violet underneath can be related to the original paint, that has been almost completely covered. The FORS technique thus allowed us to differentiate between the original and non-original paint layers. Nonetheless, the identification of the original pigments was not possible, since extensive FORS libraries of synthetic organic pigments are lacking. Consequently, the results obtained by FORS were used to select the sampling areas on sides of the painting where small non-repainted areas still maintained the original colour.



Fig. 4.1 *Ri de Pomme* by Julian Schnabel (photograph by Elisa Ghelardi). The FORS measuring points are highlighted. D (drop), S (support), B (brown area), V (violet area), LV (light violet area).



Fig. 4.2 FORS spectra of the original paint (solid line) and the PVAc paint applied during the restoration (dashed line).

4.2.3 Raman results

Three paint samples from *Ri de Pomme* were analysed by Raman spectroscopy, together with the reference mock-ups prepared with the violet PVAc paints (Lefranc & Bourgeois) used during the restoration of the painting in 2002.

By comparing the Raman spectra with several libraries of pigments' spectra [9] [10] [11], it is possible to confirm that all the three Lefranc & Bourgeois violet paints contain PV23, dioxazine violet, a common synthetic organic pigment, as stated by the manufacturers. The three violet PVAc colours have the same Raman profile, thus the other pigments reported to be present in the commercial vinyl paints (PR122, PB29 and PW6) are not detectable, probably due to their very low amount. The spectrum of one of the PVAc colours ("Violet") is given in Fig 4.3 (spectrum A) as an example.

The relevant wavenumbers of the spectra and their tentative attributions are listed in Table 4.1.



Fig 4.3 Raman spectra of the PVAc paint containing PV23 (spectrum A), of sample S1 (spectrum B) and of sample S3 containing both the original paint layer and the PVAc resin layer (spectrum C). The identified bands in the three spectra are listed in Table 4.1.

Table 4.1 Raman shifts (cm ⁻¹	¹) observed in the spectra of paint samples	S1, S2 and S3 from Ri de
	Pomme, with the tentative attributions.	

Paint samples S1	Paint sample S3	Attribution
and S2		
1536 (s)	1536 (m)	phthalocyanine class
1529(sh)		
1443 (m)		linseed oil [12]
	1430 (m)	PV23
	1390 (s)	PV23
	1344 (m)	PV23
1337 (m)		phthalocyanine class
1212 (s)		green phthalo? [13]
1192 (sh)		
1080 (w)		
986 (w)	986 (w)	
886 (w)		
775 (w)	775 (w)	green phthalo? [13]
746 (m)		phthalocyanine class
680 (m)	680 (w)	green phthalo? [13]
613 (w)	613 (w)	
	589 (w)	PV23
567 (m)	566 (w)	
546 (s)	547 (m)	
	316 (w)	PV23

As expected on the basis of the preliminary survey by FORS, samples S1 and S2 did not show any of the characteristic PV23 peaks, thus these two paint samples contained the original paint and not the one used during the restoration. The spectrum of S2 is shown in Fig 4.3 (spectrum B). Unfortunately, no complete match was found in spectra libraries for the violet pigment in the original paint layer. Nonetheless, a partial match with the phthalocyanine pigments was found, based on the identification of the peaks at 1536, 1337 and 746 cm⁻¹, that are characteristic of this class of dyes. Moreover, the peaks at 1212, 775, 680 cm⁻¹ were identified as characteristic of a green phthalocyanine by Aibéo et al. [13]. Thus, we hypothesized that the violet paint used by Schnabel contained a mixture of two or more pigments, one being a phthalocyanine pigment. The peak at 1443 cm⁻¹ could be attributed to linseed oil used as a binder [12], as highlighted by the GC/MS results discussed later on. Interestingly, the Raman spectrum of the third paint sample S3 (spectrum C in Fig 4.3) shows some absorbance peaks detected in both S1 and S2, and some others characteristic of PV23. Thus, S3 contains both the original paint and the vinyl one, juxtaposed during the re-painting. The absorbance peaks of sample S3 in common with PV23 are: 1441 cm⁻¹; 1430 cm⁻¹; 1390 cm⁻¹ (most intense peak); 1344 cm⁻¹; 316 cm⁻¹. The absorbance peaks not attributable to PV23 and in common with samples S1 and S2 are: 1536 cm⁻¹; 986 cm⁻¹; 546 cm⁻¹ and 567 cm⁻¹.

Summarizing, the Raman technique confirmed the distinction made by FORS between the original and the non-original paint layers and allowed us to hypothesise the nature of the original violet pigment.

4.2.4 Py-GC/MS results

We performed Py-GC/MS to obtain information on the original binding medium. Py-GC/MS analysis showed that the binder in the paint used by Schnabel is a lipid material. As an example, the pyrogram of the paint sample S4 is shown in Fig. 4.4, and the identified compounds are listed in Table 4.2. In the pyrograms of all the paint samples, peaks corresponding to mono- and di-carboxylic fatty acids are observed [14]. The pyrolysis profile shows azelaic acid as the main peak, suggesting the use of a siccative oil.

We also analysed a sample collected from the support of the painting, constituted of a weathered tarpaulin. Saturated long-chain hydrocarbons are the most abundant peaks in the pyrogram (Fig. 4.5). Moreover, peaks related to the pyrolysis of a cellulose-derived material are observed (levoglucosan, peak #10; dehydrated glucose, peak #8; 1,2,3-trihydroxybenzene, peak #7). These features are characteristic of a fabric made of cellulosic fibres [15] and waterproofed with a paraffin wax [16] [17].



Fig. 4.4 Py(HMDS)-GC/MS chromatogram of the paint sample S4. Peak assignments are reported in Table 4.2.



Fig. 4.5 Py(HMDS)-GC/MS chromatogram of the sample S5 from the tarpaulin support of the painting. Peak assignments are reported in Table 4.2.

Number	Retention time	Compound
	(min)	
1	13,6	2-ciclopenten-1-one, 2 methyl
2	15,2	2-furancarboxaldehyde, 5 methyl
3	16,9	1,2-cyclopentanedione, 3 methyl
4	22,4	1-tetradecene
5	23,7	1-pentadecene
6	26	1-heptadecene
7	24,5	1,2,3-trihydroxybenzene, 3TMS
8	24,9	dehydrated glucose, 2TMS
9	25,1	1,2,4-trihydroxybenzene, 3TMS
10	26,4	levoglucosan, TMS
11	27,1	1-octadecene
12	28,1	1-nonadecene
13	29,2	eicosane
14	30,2	heneicosane
15	31,1	docosane
16	31,9	tricosane
17	32,8	tetracosane
18	33,5	pentacosane
19	34,3	hexacosane
20	35	heptacosane
21	35,9	octacosane
22	36,8	nonacosane
23	17,6	hexanoic acid, TMS
24	21,4	butanedioic acid (succinic acid), 2TMS
25	22	nonanoic acid (pelargonic acid), TMS
26	23,9	hexanedioic acid (adipic acid), 2TMS
27	25,1	heptanedioic acid (pimelic acid), 2TMS
28	26,2	octanedioic acid (suberic acid), 2TMS
29	27,3	nonanedioic acid (azelaic acid), 2TMS
30	28,2	decanedioic acid (sebacic acid), 2TMS
31	29,7	hexadecanoic acid (palmitic acid), TMS
32	31,3	(9Z)-octadec-9-enoic acid (oleic acid), TMS
33	31,5	octadecanoic acid (stearic acid), TMS
34	26,6	acridine 1,2,3,4,5,6,7,8 octahydro

 Table 4.2 Compounds identified in the pyrograms reported in Fig. 4.4 and Fig. 4.5.

 The TMS abbreviation stands for trimethylsilyl esters and ethers.

We also analysed with Py-GC/MS both the paint samples from *Ri de Pomme* and the reference mock-ups prepared with the PVAc paints used during the restoration of the painting. In this case, we decided to work without the HMDS derivatising reagent in order to be able to identify the PVAc monomers [18] [19]. The pyrograms obtained for the PVAc reference materials (Fig. 4.6) are characterized by the acetic acid and benzene peaks (#1 and #2, respectively), produced *via* a side group elimination reaction pathway. Moreover,

the distinctive profile of a versatate (VeoVa) plasticizer (peak #8) was detected. These results were in agreement with the literature [18] [19] [20]. None of the characteristic peaks of the PVAc resins were found in the paint samples, thus confirming that they were collected from the original layers.



Fig. 4.6 Py-GC/MS chromatogram of the "Violet" PVAc paint (Lefranc & Bourgeois). 1. acetic acid; 2. benzene; 3. methyl benzene; 4. styrene; 5. phenylpropene; 6. 1H-indene; 7. azulene; 8. VeoVa plasticizers.

4.2.5 GC/MS results

We performed GC/MS on the samples identified as the original paint layer thanks to the Raman and Py-GC/MS analyses. The chromatogram of sample S1 is reported in Fig. 4.7 as an example, and the compounds identified are listed in Table 4.3. All the paint samples show peaks due to mono- and di-carboxylic fatty acids, with azelaic acid as the most abundant [21], confirming that Schnabel used a siccative oil-based paint. The amount of fatty acids (1.20 µg) was above the LOQ of the procedure. The long chain hydrocarbons in the GC/MS chromatograms derive from the tarpaulin support.


Fig. 4.7 GC/MS chromatogram of the paint sample S1. The * indicates the peak of butyl phthalate, an ubiquitous contaminant. Peak assignments are reported in Table 4.3.

Number	Retention time	Compound
	(min)	
1	12,02	hexadecane (IS1)
2	12,65	dodecanoic acid (lauric acid), TMS
3	13,22	octanedioic acid (suberic acid), TMS
4	13,73	tridecanoic acid, TMS (IS2)
5	14,29	nonanedioic acid (azelaic acid), 2TMS
6	14,84	tetradecanoic acid (myristic acid), TMS
7	15,49	decanedioic acid (sebacic acid), 2TMS
8	17,89	hexadecanoic acid (palmitic acid), TMS
9	20,29	(9Z)-octadec-9-enoic acid (oleic acid), TMS
10	20,60	octadecanoic acid (stearic acid), TMS
11	20,01	docosane
12	21,18	tricosane
13	22,24	tetracosane
14	23,18	pentacosane
15	24,05	hexacosane
16	24,88	heptacosane
17	25,69	octacosane
18	26,6	nonacosane
19	27,70	triacontane
20	28,97	hentriacontane

Table 4.3 Compound identified in the GC/MS chromatogram reported in Fig. 4.7.The TMS abbreviation stands for trimethylsilyl ester.

To obtain more detailed information about the siccative oil used by Schnabel, the relative abundances of five mono-carboxylic (lauric, myristic, palmitic oleic, stearic) fatty acids and three dicarboxylic (suberic, azelaic, sebacic) acids were taken into consideration. The ratio between palmitic and stearic acids (P/S) is generally used to determine the botanical origin of the oil [22] [23] (see Chapter 2, Section 2.3). The sum of the dicarboxylic fatty acids (ΣD) and the ratio between azelaic and palmitic acids (A/P) are useful parameters to evaluate the degree of oxidation of the oil. The values of these characteristic parameters for the paint samples collected from *Ri de Pomme* are reported in Table 4.4. The values of P/S and the high content of di-carboxylic acids are compatible with linseed oil, or with linseed oil mixed with other siccative or semi-siccative oils used in modern oil-based paint media (P/S < 2; A/P > 1; $\Sigma D > 40$), as discussed in detail in Chapter 2 [22] [23].

Table	e 4.4 Characteristic pa	rameters of fai	tty acids calcula	ated for the <i>Ri de</i>	Pomme paint samples.
	Paint sample	P/S	A/P	ΣD (%)	μg of FA
_	S1	1,1	4,9	75	2,3
	S2	1,1	3,3	67,6	2,8
	S4	1,2	1	36	2,7

4.2.6 Discussion

The combination of non-invasive and micro-destructive spectroscopic and chromatographic techniques enabled the characterization of the paint materials used in both the original and in the restored areas. We first differentiated between the original paint used by Schnabel and the ones used during the restoration by means of non-invasive FORS survey, and confirmed our hypotheses by Micro-Raman technique. These two techniques gave us complementary information: on the one hand, FORS is a non-invasive, portable technique and the analysis time is very short, thus allowing us to map the painted surface. On the other hand, Micro-Raman is a very suitable technique for the study of synthetic organic pigments, enabling us to identify the synthetic pigment of the vinyl colours, PV23, which was not the same pigment used by the artist. This helped us confirming if our paint samples were collected from the original layers or from the restored areas. Moreover, we were able to identify the class of one of the synthetic pigments that constitute the original paint layer, the phthalocyanine class. We also performed Py-GC/MS and GC/MS to obtain information on the binder used by Schnabel. The chromatographic data revealed that the paint used by the artist contained a siccative oil as binding medium, and GC/MS quantitative analysis pointed out linseed oil as the most likely candidate, which could have been used pure, or mixed with other siccative or semi-siccative oils. Unfortunately, the amount of samples available did not allow us to perform HPLC-ESI-Q-ToF analysis of the triglyceride profile of the binding medium (see Chapter 2). Moreover, no traces of synthetic polymers were found in the samples collected from the original paint layer. The Py-GC/MS analysis gave us information on the tarpaulin support, which turned out to be composed by a cellulosic material waterproofed with a paraffin wax.

4.3 *Mural* by Jackson Pollock

Mural (247 x 605 cm), realized in 1943, is an easel painting by artist Jackson Pollock (January 28, 1912, Cody, Wyoming – August 11, 1956). The painting belongs to the University of Iowa Museum of Art and from 2012 till 2014 was at the Getty Center in Los Angeles, CA, undergoing a technical study and a conservation treatment.

Jackson Pollock was an influential American painter and a major figure in the Abstract Expressionist movement. Early on in his career, during the 1930s, he worked in the Regionalist style, being influenced by Mexican muralist painter Diego Rivera, and by much of the work in Surrealism. By the mid-1940s, the art form which Jackson Pollock was most known for was the abstract style. By 1947, he was painting with the "drip" technique. Rather than fixing his canvas to an easel, most of his canvases were either set on the floor, or laid out against a wall. From there, he used a style where he would allow the paint to drip from the paint can. Instead of using the traditional paint brush, he would add depth to his images using knives, trowels, or sticks. This form of painting, known as "action painting," had similar ties to the Surreal movement, in that it had a direct relation to the artist's emotions, expression, and mood, and showcased their feeling behind the pieces they designed. Pollock described his painting choices with these words: *"I continue to get further away from the usual painter's tools such as easel, palette, brushes, etc. I prefer sticks, trowels, knives and dripping fluid paint or a heavy impasto with sand, broken glass or other foreign matter added."* [24].

Pollock explored and exploited many non-traditional materials in his paintings. The 1940s, in particular, was a period of rapid stylistic transition for Pollock, during which he developed his mature style. Technical analysis has shown that during this pivotal decade, when Pollock began to produce works rich in stylistic innovations, he simultaneously began experimenting with a range of retail trade paints in his works. Yet, contrary to the general

perception that this artist "painted with anything in reach" and chose commercial paints only because they were inexpensive, he achieved his highly radical changes in style through informed choices and a conscious selection of the materials, that, after experimentation, he decided to adopt [25].

Mural (Fig. 4.8) was commissioned to Pollock by Peggy Guggenheim in July 1943 for her new townhouse' entrance hall. The choice of the subject was to be his, and the size, immense (247 x 605 cm), was meant to cover an entire wall [26]. The painting was later given by Peggy Guggenheim to the University of Iowa Museum of Art.



Fig. 4.8 Mural (1943) by Jackson Pollock, University of Iowa Museum of Art.

The painting underwent a conservation treatment in 1959. During this treatment a brush coating of an acrylic varnish called Soluvar (by Permanent Pigments) was applied to the surface [26].

4.3.1 Materials and methods

<u>Samples</u>. Two red paint samples collected from *Mural* (Table 4.5) were analysed with Py-GC/MS. Sample #8 was collected from the end of a drip of thin, very fluid red paint. The ground was thought to be included in the sample material collected at this location. Sample #27, instead, was collected from the lower right part of the painting.



Table 4.5 Microscope photos of the two samples collected from Mural.

<u>Apparatus</u>. Pyrolysis – gas chromatography/mass spectrometry was carried out on a 7890A gas chromatograph, coupled with a 5975C triple axis detector mass spectrometer (Agilent Technologies, USA), coupled with a EGA/PY 3030D multi-shot pyrolyzer (Frontier Laboratories, Japan). The pyrolysis was carried out at 550 °C for 12 s. The chromatographic separation was carried out on a DB-5ms Ultra Inert column, 40 m × 250 µm × 0.25 µm (Agilent J&W, USA). The helium (purity 99.9995%) flow rate was 1 mL/min. The inlet temperature of the GC was 320 °C, the MS transfer line was kept at 320 °C and the ion source at 230 °C. The GC injection program was: pulsed split mode, with an injection pulse pressure of 30 psi until 45 sec. The split ratio was 20:1, with a split flow of 20 mL/min. The GC temperature program was: initial temperature 40 °C, 2 min isothermal, 20 °C/min up to 320 °C, 14 min isothermal. No derivatising agent was used for the Py-GC/MS analysis. Fragments were recognized using a library of characteristic pyrolysis products of synthetic organic pigments created by the author, together with the AMDIS software (US National Institute of Standards and Technology, NIST), as described in Chapter 3.

4.3.2 Results and discussion

AMDIS software, in combination with a target library created on purpose, proved to be a very useful tool for the identification of synthetic pigments; this software allowed the detection and identification of compounds present in very low amounts.

Sample #27 (Fig 4.9) shows all the pyrolysis products of alizarin crimson PR83, confirming that Pollock used this synthetic pigment. All the typical PR83 products are present in the

painting sample: phenanthrene; anthrone; 9,10-anthracenedione; 9,10-anthracenedione-2hydroxy; dinaphtho[1,2b:1'2''d]furan. Naphthalene and 2-naphthol, instead, are common products of many synthetic pigments. The pyrogram of this sample also shows several peaks due to fatty acids (azelaic, palmitic, stearic and linoleic), thus indicating that Pollock used an oil paint. It must be noted, however, that also commercial PR83 has linoleic acid as a pyrolysis product, because during its manufacture an oil is employed (see Chapter 2, Section 3.3.2).

The pyrogram of sample #8 (Fig. 4.10) shows a product (unknown) at 17 min (m/z 275, 246, 129) characteristic of toluidine red PR3, but other expected pyrolysis products of PR3, such as the peak corresponding to the intact molecule [27], are absent. Thus, the identification of the pigments as PR3 is only tentative.

The two paint samples analysed show also *n*-buthyl methacrylate as the most abundant peak at 7.3 min, highlighting the presence of an acrylic resin. The painting has undergone a restoration during which a varnish named Soluvar (Liquitex) has been applied. Soluvar varnishes are composed of a mixture of *n*-butyl and isobutyl methacrylate (Paraloid B-67 and F-10) resins. The presence of the restoration varnish may thus account for the detection of *n*-buthyl methacrylate in the pyrogram. The pyrograms of sample #27 and #8 are shown in Fig 4.9 and Fig. 4.10, respectively and the results are summarized in Table 4.6.



Fig 4.9 Py-GC/MS chromatogram of Jackson Pollock paint sample #27, from Mural (1943). 1. *n*-butyl methacrylate; 2. 2-naphthol; 3. diethyl phthalate; 4. azelaic acid; 5. phenanthrene; 6. palmitic acid; 7. anthrone; 8. stearic acid; 9. linoleic acid; 10. 9,10-anthracenedione,2-hydroxy.



Fig. 4.10 Py-GC/MS chromatogram of Jackson Pollock paint sample #8, from Mural (1943). 1. *n*-butyl methacrylate; 2. 2-naphthol; 3. diethyl phthalate; 4. characteristic PR3 product (unknown).

Product	Time	m/z	Marker	Sample	Sample
	(min)		of	JP #8	JP #27
naphthalene	9.2	128	generic		Х
2-Naphthol	11.5	144, 115	generic	Х	Х
phenanthrene	13.1	178	PR83		Х
anthrone	13.9	194, 165	PR83		х
9,10-anthracenedione	14.1	208, 180, 152	PR83		х
9,10-anthracenendione, 2-hydroxy	15.8	224, 139, 196	PR83		х
unknown PR3 product	17	275, 246, 128	PR3	Х	
dinaphtho[2,1b:1',2'-d]furan*	17.9	268, 239, 119	PR83		Х

Table 4.6 Results of the Py-GC/MS analysis on two paint samples from Jackson Pollock's Mural.

*or dinaphtho[2,1b:1,2-d]furan.

4.4 Clyfford Still's paintings and paint materials

Clyfford Still (November 30, 1904, Grandin, North Dakota – June 23, 1980) was an American painter, and one of the leading figures of Abstract Expressionism. Described by many as the most anti-traditional of the Abstract Expressionists, Still is credited with laying the groundwork for the movement. By the late 1930s, he began to simplify his forms as he moved from representational painting toward abstraction. Still is one of the foremost Colour Field painters: his non-figurative paintings are non-objective, and largely concerned with juxtaposing different colours and surfaces in a variety of formations and shapes. His

indented fields of colour give the impression that one layer has been torn off the painting, revealing the colours underneath.

We analysed by Py-GC/MS ten paint samples from six different paintings and several pigments form the artist' studio collection. In his studio Still had a big collection of pigments that he used to prepare the paints. The paints were prepared by pouring dry pigments onto a palette in a mound and creating a well at the top, where Still poured boiled linseed oil as well as a small amount of turps and driers. He then mixed the ingredients with a palette knife [28].

4.4.1 Materials and methods

<u>Apparatus</u>. The apparatus was the same of the Jackson Pollock case study (see Section 4.3.1 - Materials and methods).

<u>Samples</u>. Ten samples from six different paintings and seven samples from the pigments found in the artist's studio were analysed with Py-GC/MS. The samples from Still's paintings are listed in Table 4.7 and included: two samples from "Untitled", dating 1951-1952, one sample from "Untitled" (1954), and two samples from "Untitled" (1974), all owned by the San Francisco Museum of Modern Art; one sample from "Untitled-322" (b) (1948); one sample from "Untitled" (1960), owned by the Hirshhorn Museum of Washington and three samples from "Untitled", dating 1948 (private collection).

	Table 4.7 List of the paint samples analysed from Still's paintings.					
Title	Date	Owner	Painting	Paint samples		
				n°		
Untitled (a)	1948	Private	1 C F A C	339_8		
		collection	1. Martin and a state	339_11		
				339_12		
Untitled (b)	1948	Private collection		322_11		
Untitled	1951-1952	San Francisco		968 1		
Childred	1551 1552	Museum of Modern Art		968_2		
Untitled	1954	San Francisco Museum of Modern Art		969_2		
Untitled	1960	Hirshhorn Museum, Washington D.C.		693_4		
Untitled	1974	San Francisco Museum of Modern Art		920_1 920_2		

4.4.2 Results and discussion

In this case, as for the Pollock paint samples, the creation of a library of characteristic pyrolysis products of synthetic pigments proved to be fundamental for the subsequent identification of synthetic pigments in unknown samples. We were able to identify the class of the pigment used in five of the ten paint samples analysed, namely the red azo pigment lakes class. The pyrograms of the most significant paint samples are shown in Fig. 4.11, Fig. 4.12, Fig. 4.13, Fig. 4.14. In two paint samples we identified PR83, anthraquinone red. The pyrograms of the two paint samples from "Untitled", 1948 are reported in Fig. 4.15 and Fig. 4.16. For the pigments in the artist's studio, we identified four pigments as PR49, belonging to the red azo pigment lakes class (Fig. 4.17, Fig. 4.18, Fig. 4.19).



Fig. 4.11 Py-GC/MS chromatogram of Clyfford Still paint sample #968_1, from Untitled (1951-52). 1. toluene; 2. cyclohexanone; 3. benzene, 1-methylethyl; 4. alpha-methylstirene; 5. benzene, tert-butyl-; 6. octanoic acid; 7. naphthalene; 8. 2-naphthol; 9. naphthalene, 1-isocyanato-; 10. azelaic acid; 11. palmitic acid; 12. stearic acid; 13. linoleic acid; 14. naphthalene, 1-(2-naphthalenyloxy)-; * unknown product characteristic of red pigments.



Fig. 4.12 Py-GC/MS chromatogram of Clyfford Still paint sample #969_2, from Untitled, 1954. 1. toluene; 2. ethylbenzene; 3. styrene; 4. benzene, 1-methylethyl; 5. alpha-methylstyrene; 6. benzene, tert-butyl; 7. benzene, 2-methyl-1-propenyl; 8. octanoic acid; 9. naphthalene; 10. naphthalene, 2-methyl-; 11. octanedioic acid; 12. 2-naphthol; 13. 2-naphthalenamine; 14 azelaic acid; * unknown product characteristic of red pigments; 15. palmitic acid; 16. stearic acid; 17. linoleic acid; 18. naphthalene, 1-(2-naphthalenyloxy)-.



Fig. 4.13 Py-GC/MS chromatogram of Clyfford Still paint sample #693_4, from Untitled, 1960. 1. toluene; 2. cyclopentanone; 3. ethylbenzene; 4. cyclohexanone; 5. benzene, 1-methylethyl; 6. alpha-methylstyrene; 7. cycloheptanone; 8. p-aminotoluene; 9. octanoic acid; 10. naphthalene; 11. benzenamine, 3-chloro-4-methyl-; 12. 2-naphthol; 13. 2-naphthalenamine; 14. azelaic acid; 15. palmitic acid; 16. stearic acid; 17. linoleic acid; 18. naphthalene, 1-(2-naphthalenyloxy)-.



Fig. 4.14 Py-GC/MS chromatogram of Clyfford Still paint sample #322_11, from Untitled, 1948 (b). 1. aniline; 2. 2,naphthol; 3. naphthalene, 1-isocyanato-; 4. p-nitroaniline; * unknown product characteristic of red pigments (m/z 183, 154, 114); 5. 2-naphthol, 1-amino; 6. 4-hydroxy-3methylbeta-phenylcinnamonitrile? (m/z 235); ** unknown product (m/z 263, 207, 92, 107, 281).



Fig. 4.15 Py-GC/MS chromatogram of Clyfford Still paint sample #339_11, from Untitled (1948). 1. naphthalene; 2. 2-naphthol; 3. 1-naphthalenamine; 4. 2-naphthalenamine; 5. cyclododecane; 6. 1-hexadecanol; 7. cyclotetradecane; 8. 1,13-tetradecadiene; 9. 2,2'-dinaphthyl ether; 10. naphthalene, 1-(2-naphthalenyloxy)-; 11. dinaphtho[2,1b:1'2'-d]furan; 12. benzo[f]naphtho[2,1-c]cinnoline.



Fig. 4.16 Py-GC/MS chromatogram of Clyfford Still paint sample #339_12, from Untitled (1948). 1, caprylic acid; 2, azelaic acid; 3, phenanthrene; 4, palmitic acid; 5, anthrone; 6, 9-10-anthracenedione, 2-hydroxy; 7, stearic acid.



Fig. 4.17 Py-GC/MS chromatogram of a pigment found in Clyfford Still' studio (sample #18). 1. naphthalene; 2. 2-naphthol; 3. 2-naphthalenamine; 4. 1-propene 1,2,3-tricarboxylic acid, tributyl ester; 5. 2,2'-dinaphthyl ether; 6. naphthalene, 1-(2-naphthalenyloxy)-; 7. dinaphtho[2,1b:1'2'-d]furan; 8. benzo[f]naphtho[2,1-c]cinnoline.



Fig. 4.18 Py-GC/MS chromatogram of a pigment found in Clyfford Still' studio (sample #38). 1. naphthalene; 2. 2-naphthol; 3. 1-naphthalenamine; 4. 2-naphthalenamine; 5. cyclododecane; 6. 1-hexadecanol; 7. cyclotetradecane; 8. 1,13-tetradecadiene; 9. 2,2'-dinaphthyl ether; 10. naphthalene, 1-(2-naphthalenyloxy)-; 11. dinaphtho[2,1b:1'2'-d]furan; 12. benzo[f]naphtho[2,1-c]cinnoline.



Fig. 4.19 Py-GC/MS chromatogram of a pigment found in Clyfford Still' studio (sample #40a). 1. naphthalene; 2. phthalic anhydride; 3. 2-naphthol; 4. 2-naphthalenamine; 5. 2-naphthol, 1-amino; 6. 2Hphenantro[9,10b]pyran; 7. 2,2'-dinaphthyl ether; 8. naphthalene, 1-(2-naphthalenyloxy)-; 9. dinaphtho[2,1b:1'2'-d]furan; 10. benzo[f]naphtho[2,1-c]cinnoline.

Туре	Painting	Sample n°	Py-GC/MS results
paint sample	Untitled, 1948 (a)	339_8	/
		339_11	PR83
		339_12	PR83
	Untitled, 1948 (b)	322_11	Red azo pigment lakes class
	Untitled, 1951-1952	968_1	Red azo pigment lakes class
		968_2	Red azo pigment lakes class
	Untitled, 1954	969_2	Red azo pigment lakes class
	Untitled, 1960	693_4	Red azo pigment lakes class
	Untitled, 1974	920_1	/
		920_2	/
pigment from		18	PR49
the artist' studio		21	PR49
		31	/
		35	/
		38	PR49 or PR63
		39	/
		40a	PR49

 Table 4.8 Py-GC/MS results of the Clyfford Still's paint samples and pigments.

Three paint samples and three pigments form the artist's studio showed products common to several classes of pigments, or too few pyrolysis products to allow an identification.

The Py-GC/MS analyses of the paint samples also showed the fatty acids products characteristic of a vegetable oil [29] [30] [31], confirming that Clyfford Still used this binding medium. Palmitic, stearic and azelaic acids are the main peaks in all the pyrograms. The results are summarized in Table 4.8.

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Concluding remarks

The present research aimed at chemically characterizing the paint materials commonly employed in Contemporary Art, and at studying and understanding their ageing processes. My focus was on two classes of compounds scarcely investigated until now: synthetic organic pigments and oils used in modern paint formulations. Moreover, several case studies were analysed and discussed.

This thesis highlighted the peculiarities and the importance of the study of modern paint materials that constitute contemporary artworks. A multi-analytical approach was set for the study of modern paint products.

In detail, we selected six different oils used in modern paint formulations: linseed, sunflower, safflower, soybean, castor and tung oils. The literature protocol with GC/MS for the study of lipids was performed. The fatty acids profiles obtained for the oils analysed were in agreement with the literature. The characteristic fatty acids ratios and relative abundances commonly used to obtain detailed information on the oil binders were implemented by calculating the P/S, A/P, O/S and Σ dic of sunflower, safflower, soybean, tung and castor oils, fresh and naturally aged. We found that these characteristic parameters need a thoughtful revision, which must contemplate also the oils used in modern paint media. The palmitic over stearic ratio, for example, proved to be an unreliable parameter for the identification of the raw source of modern oils, thus it should be used with caution when a quantitative analysis is performed on a paint sample collected from a modern painting. In order to overcome this deficiency in the current approaches, an innovative HPLC-mass spectrometric method to perform analyses on lipids was developed and optimized. HPLC-ESI-Q-ToF proved to be a very suitable technique for the analysis of the oils used in modern paint formulations. The possibility of acquiring high resolution mass spectra enabled the separation of about 40 triglycerides, along with DAGs and possible oxidation products, and the HPLC-MS² analyses enabled their identification.

I also performed a natural and an artificial ageing experiment on the oils, applied as paint layers on glass slides. The GC/MS results highlighted the problems in differentiating the various types of oils mentioned above, when aged: with the exception of castor oil, they all showed the same profile of di-acids and hydroxy-acids. With HPLC-ESI-Q-ToF, the disappearance of TAGs containing unsaturated fatty acids, together with the appearance of oxidised TAGs were observed in the more aged oils. Moreover, by performing a semiquantitative analysis, some intermediate oxidation TAGs, which increased and then decreased until disappearing, were detected. The results obtained from this survey gave an insight on the ageing processes underwent by the oils.

I analysed for the first time with Py-GC/MS several synthetic pigments. By studying their pyrolysis patterns I found that in many cases the pyrolysis products were characteristic of a single pigment or at least of a class of pigments. I created a library of pyrolysis products, which helped in the identification of several pigments in the case studies analysed. The library was particularly efficient for the red pigments.

Moreover, several commercial paint formulations were analysed. Even if the characteristic pyrolysis products of the synthetic pigments were still detectable in commercial paint formulations, the relative abundances of the products changed from the pyrogram of the pure pigment compared to that of the commercial formulations. This may be due to the very low concentration of the pigments in paint formulations and/or to the presence of several other components in the commercial paints, which may interfere with the formation or detection of the characteristic markers.

Also in (artificially) aged paint formulations the pyrolysis products of the synthetic pigments were still present in the pyrograms.

It is important to notice that AMDIS software (NIST) proved to be a very sensible tool for the detection of the characteristic pyrolysis products of the synthetic pigments, even when in the TICs they were covered by the most intense peaks corresponding to the pyrolysis products of the other components of the paint.

A survey on the ageing of synthetic pigments was also performed: for the first time the synthetic pigments were tested pure, without any binder. The ageing study of the pure pigments highlighted significant changes in colour: in some cases a fading occurred, in others a darkening. The changes were, for some pigments, dramatic and evident, while, for others, too small to be noticeable. These results are important because some of the pigments selected for the ageing study are still extensively employed in paint formulations, e.g. PR83. The Py-GC/MS, GC/MS and FTIR-ATR techniques used to compare the "fresh" and the aged pigments all indicated that the photo-ageing causes changes in the pigments' molecules structure.

The ageing study of the commercial paint formulations containing pigments with poor lightfastness highlighted a relatively higher colour change, compared to the pure pigments. This trend is valid for all the binding media, with the exception of acrylic paints, which showed very low ΔE and ΔL values, even lower than those of the pure pigments.

In conclusion, the adopted multi-analytical approach entailing the study of reference materials and paint model systems allowed the complete characterisation of the materials under study. Important features of the modern oils and synthetic pigments were highlighted, with special regard to the degradation pathways underwent by these materials. The optimized procedures were also applied to several case studies, and often proved efficient in identifying the artists' materials, thus allowing a better comprehension of the painting techniques, and, most importantly, providing important insights for the preventive conservation of works of art.

Synthetic organic pigments analysed with Py-GC/MS and chemical structure of the pigments selected for the ageing study

C.I. name	Cl number	Common name	Class	Manufacturer or Supplier	Year
PR1	12070	β-naphthol	β-naphthol	Clariant	nd
PR3	12120	Hansa Scarlet RNC	β-naphthol	Clariant	2002
PR4	12085	Hansa Red R	β-naphthol	Clariant	2002
PR5	12490	Monolite Red CB	Naphthol AS	ICI (Avecia)	2002
PR6	12090	Pigment Red 6	β-naphthol	Kremer	nd
PR7*	12420	Monolite Red 4RH	Naphthol AS	ICI	1996
PR8	12335	3149 Fast Red F4R-Y	Naphthol AS	HY pigments	2002
PR12	12385	Monolite Rubine 2R	Naphthol AS	Avecia	2002
PR14	12380	Permanent Bordeaux FGR	Naphthol AS	Clariant	2002
PR17	12390	Sunbrite Red 17	Naphthol AS	Clariant	nd
PR23	12355	1523 Naphthol Red 23	Naphthol AS	Lansco	2002
PR31	12360	Symuler Fast Red 4085	Naphthol AS	Dainippon	2002
PR41*	21200	Suimei Dianisidine Red R	Disazopyrazolone	Sansui	2003
PR48:1*	15865:1	Cortone Scarlet 2BBT	BONA, Ba	EC pigments	nd
PR48:2*	15865:2	Rubine Toner 2BO	BONA, Ca	Avecia	2002
PR48:2*	15865:2	Eljon Rubine 2BRC	BONA, Ca	EC pigments	2002
PR49:1*	15630:1	Sunbrite Red 49:1	β-naphthol, Ba	Sun	2002
PR49:2*	15630:2	Sunbrite Red 49:2	β-naphthol, Ca	Sun	2002
PR52:1*	15860:1	Sunbrite Red 52:1	BONA, Ca	Sun	2002
PR52:2*	15860:2	BR-522 Bon Maroon	BONA, Mn	Lansco	2002
PR53:1*	15585:1	1320 Red Lake C	β-naphthol, Ba	Lansco	2002
PR57*	15850	Irgalite Rubine 4BP	BONA	Ciba	2002
PR57:1*	15850:1	Cortone Rubine 4BCT	BONA, Ca	EC pigments	2002
PR63:1*	15880:1	Sunbrite Red 63:1	BONA, Ca	Sun	2002
PR83*	58000:1	Alizarin Crimson	Anthraquinone, Ca	W&N	nd
PR90:1*	45380	Cogilor Almandine 90110	Eosine	Anstead	nd
PR112	12370	Naphthol Red Light	Naphthol AS	Golden	1996
PR144	20735	Cromopthal Red BRN	Disazo condensation	Ciba	2002

PR166	20730	Cromophtal Red RN	Disazo condensation	Ciba	2002
PR170	12475	Napathol Red Medium	Naphthol AS	W&N	1996
PR175	12513	Novoperm Red HFT	Benzimidazolone	Clariant	2002
PR176	12515	Pigment Red 176	Benzimidazolone	Royal Talens	2002
PR185	12516	Novoperm Carmine HF4C	Benzimidazolone	Sun	nd
PO5	12075	Pigment Orange 5	β-naphthol	W&N	1996
PO16	21160	Spectra Pac E Orange 16	Diarylide yellow	Sun	2002
PO46	15602	Sunbrite Orange 46	β-naphthol, Ba	Sun	2002
PY3	11710	Hansa Yellow Light	Monoazo yellow	Golden	1996
PY12	21090	Sunbrite Yellow 12	Diarylide yellow	Sun	2002
PY100	19140:1	Tartrazine yellow	Monoazopyrazolone, Al	H. Kohnstamm & Co., Inc. 83-	nd
				93 Park Place, NY, NY	
				Tartrazine 640 F.D&C Yellow	
				Certified	
PGr7	74260	Pigment Green 7	Cu-Phthalogreen	W&N	1996
PGr8*	10006	Bricofor Green L5837	Metal complex	Albion / Hays	2002
PGr10*	12775	Nickel Azo Yellow	Metal complex		nd
PGr13*	74200	Phthalochrome Green	Cu-Phthalogreen	Avecia	nd
PGr36	74265	Monastral Green 6Y-C	Cu-Phthalogreen	Avecia	2002
PB15:0*	74160	5561 Cu Phthalocyanine Blue	Cu Phthaloblue	Lansco	2002
PB15:1*	74160	Monastral Blue LBX	Cu Phthaloblue	Avecia / Zeneca	2002
PB15:2*	74160	Monastral Blue FBN	Cu Phthaloblue	Avecia / Zeneca	2002
PB15:3*	74160	Monastral Blue BG	Cu Phthaloblue	Avecia	nd
PB15:4*	74160	Monastral Blue FGX	Cu Phthaloblue	Avecia	2002
PB15:6*	74160	Heliogen Blue	Cu Phthaloblue	Kremer	2002
PB16*	74100	Heliogen Blau D7490	Phthaloblue metal free	BASF	2002
PB17*	74180	4230 Fast Sky Blue Lake	Cu Phthaloblue	HY pigs	2002
PB60*	69800	Monolite Blue 3R	Indanthrone	Avecia / Zeneca	2002
PB62*	44084	Eljon Blue FR	Triarylcarbonium	EC pigments	2002
PB63	73015:x	Indigo Carmine Aluminium	Indigo, sulphonic acid,	ККК	2003

		Lake	Al		
PB76*	-	Fastogen Blue 10GN	Cu Phthaloblue	Dianippon	2002
PV1*	45170:2	Rhodamine B PTMA	Triarylcarbonium	Magruder	2002
PV3*	42535:2	1903 PTM Violet	Triarylcarbonium	Lansco	2002
PV5	58055	Alizarine Violet	Anthraquinone	Kremer	2002
PV19*	73900	Monolite Violet 4R	Quinacridone	Avecia	2002
PV23*	51319	Monolite Violet RN	Dioxazin	Avecia	2002
PV27*	42535:3	Eljon Violet CMW	Triarylcarbonium	EC pigments	2002
PV29*	71129	CI Pigment Violet 29	Perylene	Bayer	2002
PV32*	12517	Novoperm Bordeaux HF3R	Benzimidazolone	Clariant	2002
PV36*	73385	Thio Violet	Thioindigo		nd
PV37*	51345	Cromophtal Violet B	Dioxazine	Ciba	2002
PV39*	42555:2	Crystal Violet	Triarylcarbonium	Sigma Aldrich	nd
PV42*	-	Quinacridone Violet	Quinacridone		nd
PV44*	-	Symuler Fast Violet 4142	Naphthol AS	Dianippon	2002
PV51*	-	1120 Rightfit Violet	Monoazo	Engelhard	2003
PV52*	-	1118 Rightfit Pink	Monoazo	Engelhard	2003
PV53*	-	1117 Engeltone Red 4B		Engelhard	2003
PBr23	20060	Cromophtal Brown 5R	Disazo condensation	Ciba	nd
PBr25	12510	Hostaperm Brown HFR 01	Benzimidazolone	Clariant	2002
PBr38*	561660	Pigment Brown 38	Isoindoline		nd
PBr41	-	Translucent Brown	Disazo condensation		nd
PBr42	-	Azo Golden Brown	Disazo condensation		nd

		Table A2	Pigments selected for the lig	nt-ageing study.	
C.I. name	C.I. number	Common name	Manufacturer	Pigment class	ASTM lightfastness* (referred to a binder)
PB1	42595:2	Victoria blue	EC pigments	Triarylcarbonium	V (gouache)
PO5	12075	Hansa orange RN	Winsor & Newton	β naphthol	II (oil)
PO16	21160	Benzidine orange	Sun	Diarylide yellow	V (gouache)
PO46	15602	Pigment orange 46	Sun	β naphthol , Ba	/
PR3	12120	Toluidine red	Clariant	βnaphthol	IV (oil)
PR48:1	15865:1	Permanent red BB	EC Pigments	BONA, Ba	/
PR49:2	15630:2	Calcium lithol red	Sun	β naphthol, Ca	/
PR53:1	15585:1	Pigment lake red C	Lansco	β naphthol , Ba	V (oil)
PR57:1	15850:1	Lithol rubine	EC Pigments	BONA, Ca	V (gouache)
PR83	58000	Alizarin crimson	Winsor & Newton	Anthraquinone, Ca	III (oil)
PR90:1	45380	Geranium lake	Anstead	Precipitated on aluminium hydroxide	/
PR112	12370	Naphthol red AS-D	Golden	Naphthol AS	II (oil)
PR170	12475	Naphthol red	Winsor & Newton	Naphthol AS	II (oil)
PV1	45170:2	Rhodamine violet	Magruder	Triarylcarbonium	V (gouache)
PV27	42535:3	Permanent violet	EC Pigments	Triarylcarbonium	/
PV39*	42555:2	Crystal violet	Sigma Aldrich	Triarylcarbonium	IV (gouache)
PY3	11710	Hansa yellow 10G	Golden	Monoazo Yellow	II (oil)
PY12	21090	Benzidine yellow G	Sun	Diarylide Yellow	/
PY100	19140:1	Tartrazine lake	H. Kohnstamm & Co	Monoazopyrazolone, Al	V (watercolor)

* ASTM lightfastness categories: I excellent; II good; III fair; IV poor; V very poor.

The / symbol indicates pigments that have not been tested by ASTM yet.









Appendix B

Experimental data –

Triacylglycerols detected with HPLC-ESI-Q-ToF in the oils

analysed

Table B1 TAGs detected in the oils analysed with HPLC-ESI-Q-Tol	, with the indication of the integrated
areas.	

Linseed oil 1 0 0		TAG	formula	area	area (%)	area/weight
OC181.0.mC 182.0.H CS7H10208 4522573 4.78 4610.17 C18.1.0.MC 182.0.HS CS7H10407 2861911 3.03 2917.34 C18.1.0.MC 12.2.0.HS CS5H10207 229346 2.36 2272.52 C18.1.0.MO CS5H10207 1815971 8.63 8313.94 C182.0.MO CS7H10407 7815999 8.27 7972.48 C182.0.MO CS5H10207 2740135 2.90 2273.21 C181.0.MS CS5H10207 617652 0.65 629.62 POP CS5H10206 1780591 13.57 13077.59 OOO CS7H10406 8765055 9.26 892610 OSF CS5H10206 876505 9.26 892610 OSS CS7H10406 8765055 9.26 892610 OSF CS5H10206 876420 9.35 9007.58 SOS CS7H10406 8764238 5.06 4876.90 Linseed oilt C C 282.04 242.16 643.34	Linseed oil t _o	C _{18:2,OH} C _{18:1,OH} P	C55H100O8	4250608	4.50	4332.93
Insert of Classon/Class		OC _{18:1,OH} C _{18:2,OH}	C57H102O8	4522573	4.78	4610.17
Linseed oil t C182.0mQP C5SH10207 2229346 2.36 2272.52 C182.0mQO CS7H10407 8155971 8.63 8313.94 C182.0mQP CS5H10007 11420807 12.08 11642.01 C182.0mQP CS5H10207 2740135 2.90 2793.21 C182.0mSS CS7H10807 617662 0.65 629.62 POP CS5H10206 12829119 13.57 1307.759 OOO CS7H10406 7003368 7.41 7139.01 OSP CS5H10206 12829119 13.57 13077.59 OOO CS7H10406 876505 9.26 8926.10 OSF CS5H10206 128248 5.06 4876.90 OSO CS7H10806 4784238 5.06 4876.90 C18.10mC188.0mF CS5H10028 3251339 9.71 2289.34 C18.10mC188.0mF CS5H10208 321834 2.16 643.34 C18.10mC188.0mF CS5H10207 250279 0.75 223.07		C _{18:1,OH} C _{18:2,OH} S	C57H104O8	2861911	3.03	2917.34
Linseed oil t C182.0040 C57H10407 8155971 8.63 8313.94 C182.0040 C55H10007 11420807 12.08 11642.01 SC181.0040 C57H10607 7820999 8.27 7972.321 C182.0045P C55H10207 2740135 2.90 2733.21 C181.0045S C57H10807 617662 0.65 629.62 POP C53H10006 7696066 8.14 7845.12 OOP C55H10206 12829119 13.57 13077.59 OOO C57H10406 8756505 9.26 8926.10 OS C55H10206 8756505 9.26 8926.10 OOS C57H10406 8756505 9.26 8926.10 OOS C57H10406 8756505 9.26 8926.10 OS C55H10206 8236440 9.35 9007.58 SOS C57H10406 8734238 5.06 4876.90 C181.004C181.00P C55H10207 220.77 1544.43 C181.004C181.00P <th></th> <th>С_{18:1,ОН}ОР</th> <th>C55H102O7</th> <th>2229346</th> <th>2.36</th> <th>2272.52</th>		С _{18:1,ОН} ОР	C55H102O7	2229346	2.36	2272.52
Lise.on/OP CS5H10007 11420807 12.08 11642.01 Sciss.on/O CS7H10607 7820999 8.27 7972.48 Ciss.on/SP CS5H10207 2740135 2.90 2793.21 Ciss.on/SS CS7H10807 617662 0.65 629.62 POP CS3H10006 7696066 8.14 7845.12 OOP CS5H10206 12829119 13.57 13077.59 OOO CS7H10406 705505 9.26 8926.10 OSP CS5H10206 4784238 5.06 4876.90 OSS CS7H10806 4784238 5.06 4876.90 OSS CS7H10408 503460 1.18.4 4429.35 SOS CS7H10408 503460 1.18.4 4429.35 C181.0n/C181.0n/P CS5H10207 250279 0.75 223.07 C181.0n/C181.0n/P CS5H10207 250279 0.75 223.07 C181.0n/C181.0n/P CS5H10207 250279 0.75 223.07 C181.0n/		C _{18:1,OH} OO	C57H104O7	8155971	8.63	8313.94
SC181.0HO CS7H10607 7820999 8.27 7972.48 C182.0HSP CS5H10207 2740135 2.90 2793.21 C181.0HSS CS7H10807 617662 0.65 629.62 POP CS5H10206 12829119 13.57 13077.59 OOP CS5H10206 7896056 8.14 784512 OOP CS5H10406 703368 7.41 7139.01 OSP CS5H10406 8756505 9.26 8926.10 OOS CS7H10806 4784238 5.06 4876.90 SOS CS7H10808 4969726 14.84 4429.35 C181.0HC182.0HS CS5H10008 4969726 14.84 4429.35 C181.0HC182.0HS CS5H10007 250279 0.75 223.07 C181.0HC182.0HS CS5H10207 250279 0.75 223.07 C181.0HC182.0HP CS5H10207 250279 0.75 223.07 C181.0HC182.0HP CS5H10207 251421 7.15 244.43 SC181.		С _{18:2,ОН} ОР	C55H100O7	11420807	12.08	11642.01
Linseed oil t C182.0n/SP C55H10207 2740135 2.90 2793.21 C182.0n/SS C57H10807 617662 0.65 629.62 POP C53H10006 769606 8.14 77845.12 OOP C55H10206 12829119 13.57 13077.59 OOO C57H10406 8756505 9.26 8926.10 OSP C55H10006 8786404 9.35 9007.58 SOS C57H10406 876605 9.26 8926.10 OOS C57H10406 878640 9.35 9007.58 SOS C57H10406 878428 5.06 4876.90 VEX C181.0n/C181.0n/P C55H10208 3251939 9.71 2898.34 PC18.0n/C181.0n/P C55H10207 250279 0.75 223.07 C181.0n/C181.0n/P C55H10407 5338339 1.594 4757.88 C181.0n/D C55H10407 5338339 1.594 4757.88 C181.0n/P C55H10207 2541421 7.59 226		SC _{18:1,OH} O	C57H106O7	7820999	8.27	7972.48
Linseed oil t C181.0H/SS C57H10807 617662 0.65 629.62 POP C53H10006 7696066 8.14 7845.12 OOP C55H10206 12829119 13.57 13077.59 OOO C57H10406 8756505 9.26 8926.10 OOS C57H10406 8756505 9.26 8926.10 OOS C57H10806 4784238 5.06 4876.90 SOS C57H10806 4784238 5.06 4876.90 C181.0HC181.0HP C55H10208 2325139 9.71 2898.34 PC18.0HC181.0HP C55H10208 3251939 9.71 2898.34 PC18.0HC181.0HP C55H10207 250279 0.75 223.07 C181.0HC181.0HP C55H10207 250279 0.75 223.07 C181.0HC18.10HP C55H10207 250279 0.75 223.07 C181.0HC18.0H C55H10207 2541421 7.59 226.07 C181.0HC18.0H C55H10207 254421 7.59 2265.08 <th></th> <th>C_{18:2,OH}SP</th> <th>C55H102O7</th> <th>2740135</th> <th>2.90</th> <th>2793.21</th>		C _{18:2,OH} SP	C55H102O7	2740135	2.90	2793.21
POP C53H10006 7696066 8.14 7845.12 OOP C55H10206 12829119 13.57 13077.59 OOO C57H10406 7003368 7.41 7139.01 OSP C55H10206 8836440 9.35 9007.58 SOS C57H10806 4784238 5.06 4876.90 V C55H10008 <th></th> <th>C_{18:1,OH}SS</th> <th>C57H108O7</th> <th>617662</th> <th>0.65</th> <th>629.62</th>		C _{18:1,OH} SS	C57H108O7	617662	0.65	629.62
OOP CS5H10206 12829119 13.57 13077.59 OOO C57H10406 7003368 7.41 7139.01 OSP C55H10406 8756505 9.26 8926.10 OOS C57H10606 8836440 9.35 9007.58 SOS C57H10806 4784238 5.06 4876.90 Linseed oil t ₁ C182.0HC181.0HP C55H10008 4969726 14.84 4429.35 C181.0HC182.0HS C57H10408 503460 1.50 448.72 C183.0HC183.0HP C55H10208 3251939 9.71 2898.34 PC18.0HC183.0HP C55H10207 250279 0.75 223.07 C183.0HC183.0HP C55H10207 250279 0.75 223.07 C183.0HC183.0HP C55H10207 250279 0.75 223.07 C183.0HC C57H10608 1732852 5.17 1544.43 SC181.0HP C55H10207 2541421 7.59 2265.08 C183.0HC C57H10807 4367796 13.04 38		РОР	C53H100O6	7696066	8.14	7845.12
OOO C57H10406 7003368 7.41 7139.01 OSP C5SH10406 8756505 9.26 8926.10 OOS C57H10606 8836440 9.35 9007.58 SOS C57H10806 478238 5.05 4876.90 SOS C57H10086 4969726 14.84 4429.35 C181.0n/C182.0n/S C57H10408 503460 1.50 448.72 C181.0n/C182.0n/S C57H10408 503460 1.50 448.72 C181.0n/C181.0n/P C55H10207 250279 0.75 223.07 C181.0n/D181.0n/S C57H10608 1732852 5.17 1544.43 SC181.0n/P C55H10007 1686333 5.04 1502.99 S181.0n/P C55H10007 1333724 1.00 297.44 C182.0n/OP C55H10027 2541421 7.59 2265.08 C182.0n/D C55H10026 797538 2.33 694.78 OOP C55H10026 797538 2.33 694.78 OOP <th></th> <th>OOP</th> <th>C55H102O6</th> <th>12829119</th> <th>13.57</th> <th>13077.59</th>		OOP	C55H102O6	12829119	13.57	13077.59
OSP C55H10406 8756505 9.26 8926.10 OOS C57H10606 8836440 9.35 9007.58 SOS C57H10806 4784238 5.06 4876.90 Uinseed oil 1 C1 _{82,0} µC1 _{81,0} µP C55H10008 4969726 14.84 4429.35 C1 _{81,0} µC1 _{82,0} µS C57H10408 503460 1.50 448.72 C1 _{81,0} µC1 _{82,0} µS C57H10208 3251939 9.71 2898.34 C1 _{81,0} µC1 _{81,0} µP C55H10207 250279 0.75 223.07 C1 _{81,0} µC1 _{81,0} µP C55H10207 250279 0.75 223.07 C1 _{81,0} µP C55H10007 1586353 5.04 1502.99 SC1 _{81,0} µP C55H10007 1686353 5.04 1502.99 SC1 _{81,0} µP C55H10007 133724 1.00 297.44 C1 _{82,0} µSP C55H10207 241421 7.59 2265.08 C1 _{81,0} µSS C57H10807 4367766 13.04 3892.87 POP C55H10207 241421 7		000	C57H104O6	7003368	7.41	7139.01
OOS CS7H10606 8836440 9.35 9007.58 SOS CS7H10806 4784238 5.06 4876.90 Unseed oil t, C181.0HC181.0HP C55H10008 4969726 14.84 4429.35 C181.0HC181.0HP C55H10208 503460 1.50 448.72 C181.0HC181.0HP C55H10208 3251339 9.71 2898.34 PC18.0HC181.0HP C55H10207 250279 0.75 223.07 C181.0HC181.0HP C55H10207 250279 0.75 223.07 C181.0HC181.0HS C57H10608 1732852 5.17 1544.43 SC181.0HC C55H10207 250279 0.75 223.07 C181.0HC181.0HS C57H10608 1732852 5.17 1544.43 SC181.0HC C55H10207 2541421 7.59 2265.08 C181.0HS C57H10607 333724 1.00 297.44 C182.0HS C57H10206 158120 4.74 1414.55 OOP C55H10207 2541421 7.59 2265.08 <th></th> <th>OSP</th> <th>C55H104O6</th> <th>8756505</th> <th>9.26</th> <th>8926.10</th>		OSP	C55H104O6	8756505	9.26	8926.10
SOS C57H10806 4784238 5.06 4876.90 Linseed oil t1 C182.0HC18:1.0HP C55H10008 4969726 14.84 4429.35 C181.0HC182.0HS C57H10408 503460 1.50 448.72 C181.0HC182.0HS C55H10208 3251939 9.71 2898.34 PC18.0HC18.0H C55H10207 250279 0.75 223.07 C181.0HC18.1.0HP C55H10207 250279 0.75 223.07 C181.0HC18.1.0HS C55H10207 250279 0.75 223.07 C181.0HC18.1.0HS C55H10207 250279 0.75 223.07 C181.0HC18.1.0HS C55H10207 2541421 7.59 2265.08 S18.1.0HP C55H10207 2541421 7.59 2265.08 S18.1.0HS C57H10606 1587120 4.74 1414.55 0OP C55H10206 779538 2.33 694.78 0OO C57H10406 318156 0.95 283.56 0SP C55H10206 771938 1.41		OOS	C57H106O6	8836440	9.35	9007.58
Linseed oil t1 C182,0HC18:1,0HP C55H10008 4969726 14.84 4429.35 C18:1,0HC18:2,0HS C57H10408 503460 1.50 448.72 C18:1,0HC18:2,0HS C55H10208 3251939 9.71 2898.34 PC18,0HC18:0H C55H10207 250279 0.75 223.07 C18:1,0HP C55H10207 250279 0.75 223.07 C18:1,0HP C55H10207 250279 0.75 223.07 C18:1,0HP C55H10207 2533339 15.94 4757.88 C18:1,0HP C55H10007 1338339 15.94 4757.88 C18:2,0HO C55H10207 2541421 7.59 2265.08 C18:1,0HS C57H10607 333724 1.00 297.44 C18:2,0HS C55H10207 2541421 7.59 2265.08 C18:1,0HS C57H10606 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10606 471893 1.41		SOS	C57H108O6	4784238	5.06	4876.90
Linseed oilt 1 C182.0HC18:1.0HP C55H10008 4969726 14.84 4429.35 C181.0HC18:2.0HS C57H10408 503460 1.50 448.72 C181.0HC18:2.0HP C55H10208 3251339 9.71 2898.34 PC18.0HC18.0H C55H10207 250279 0.75 223.07 C181.0HC18:1.0HP C55H10207 250279 0.75 223.07 C181.0HC18:1.0HP C55H10407 5338339 15.94 4757.88 C181.0HC18:1.0HP C55H10407 5338339 15.94 4757.88 C182.0HP C55H10007 1686353 5.04 1502.99 SC18:1.0HP C55H10207 2541421 7.59 2265.08 C18:2.0HSP C55H10207 2541421 7.59 2265.08 C18:1.0HSS C55H10206 179538 2.33 694.78 OOP C55H10206 179538 2.33 694.78 OOS C57H10806 1466773 4.38 1307.28 OOS C57H10406 318156 0.95<						
Lineed oil C181.0H	Linseed oil t_1	C _{18:2,OH} C _{18:1,OH} P	C55H100O8	4969726	14.84	4429.35
Linseed oil t C18:1,0HC18:1,0HP C55H10208 3251939 9.71 2898.34 PC18,0HC18,0H C55H10608 721824 2.16 643.34 C18:1,0HOP C55H10207 250279 0.75 223.07 C18:1,0HC18:1,0HS C57H10608 1732852 5.17 1544.43 SC18:1,0HP C55H10407 5338339 15.94 4757.88 C18:2,0HOP C55H10007 1686353 5.04 1502.99 SC18:1,0HO C57H10607 333724 1.00 297.44 C18:2,0HSP C55H10207 2541421 7.59 2265.08 C18:1,0HS C57H10807 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10206 779538 2.33 694.78 OOS C57H10406 318156 0.95 283.56		C _{18:1,OH} C _{18:2,OH} S	C57H104O8	503460	1.50	448.72
PC18,0HC18,0H C55H10608 721824 2.16 643.34 C18:1,0HOP C55H10207 250279 0.75 223.07 C18:1,0HC18:1,0HS C57H10608 1732852 5.17 1544.43 SC18:1,0HP C55H10407 5338339 15.94 4757.88 C18:2,0HOP C55H10007 1686353 5.04 1502.99 SC18:1,0HO C57H10607 333724 1.00 297.44 C18:2,0HSP C55H10207 2541421 7.59 2265.08 C18:1,0HSS C57H10807 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10206 771940 15.09 3788.97 C181,0HC182,0HS		C _{18:1,OH} C _{18:1,OH} P	C55H102O8	3251939	9.71	2898.34
Linseed oil t2 C181.0HOP C55H10207 250279 0.75 223.07 C181.0HC181.0HS C57H10608 1732852 5.17 1544.43 SC181.0HP C55H10407 5338339 15.94 4757.88 C182.0HOP C55H10007 1686353 5.04 1502.99 SC181.0HO C57H10607 333724 1.00 297.44 C182.0HSP C55H10207 2541421 7.59 2265.08 C181.0HSS C57H10807 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10406 2346684 7.01 2091.52 OOS SC57H10406 1466773 4.38 1307.28 SOS <th></th> <th>PC_{18,OH}C_{18,OH}</th> <th>C55H106O8</th> <th>721824</th> <th>2.16</th> <th>643.34</th>		PC _{18,OH} C _{18,OH}	C55H106O8	721824	2.16	643.34
Linseed oil t2 C18:1,0HC C55H10407 5338339 15.94 4757.88 C18:1,0HP C55H10407 5338339 15.94 4757.88 C18:2,0HOP C55H10007 1686353 5.04 1502.99 SC18:1,0HQ C57H10607 333724 1.00 297.44 C18:2,0HSP C55H10207 2541421 7.59 2265.08 C18:1,0HSS C57H10807 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10406 2346684 7.01 2091.52 OOS C57H10806 1466773 4.38 1307.28 SOS C57H10807 11611921 24.10 6051.03 C18:1,0HP<		С _{18:1,ОН} ОР	C55H102O7	250279	0.75	223.07
SC18:1,OHP C55H10407 5338339 15.94 4757.88 C18:2,OHOP C55H10007 1686353 5.04 1502.99 SC18:1,OHO C57H10607 333724 1.00 297.44 C18:2,OHSP C55H10207 2541421 7.59 2265.08 C18:2,OHSP C57H10807 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10206 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Linseed oil tz C182,OHC18:1,OHP C55H10007 271040 15.09 3788.97 C18:1,OH C18:2,OHC18:1,OH C55H10007 2739991 5.69 1427.82		C _{18:1,OH} C _{18:1,OH} S	C57H106O8	1732852	5.17	1544.43
C18:2,0HOP C55H10007 1686353 5.04 1502.99 SC18:1,0HO C57H10607 333724 1.00 297.44 C18:2,0HSP C55H10207 2541421 7.59 2265.08 C18:1,0HSS C57H10807 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10406 2346684 7.01 2091.52 OOS C57H10806 1466773 4.38 1307.28 SOS C57H10806 1466773 4.38 1307.28 Linseed oil t2 C18:2,0HC18:1,0HP C55H10008 7271040 15.09 3788.97 C18:1,0HP C55H10407 11611921 24.10 6051.03 C18:2,0HG S1:1,0H C55H10007 273991 5.69 1427.82 SC18:1,0H C55H10007 273991 5.69 1427.82<		SC _{18:1,OH} P	C55H104O7	5338339	15.94	4757.88
SC _{18:1,OH} O CS7H10607 333724 1.00 297.44 C _{18:2,OH} SP C55H10207 2541421 7.59 2265.08 C _{18:1,OH} SS C57H10807 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10206 471893 1.41 420.58 SOS C57H10806 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Linseed oil t2 C _{18:2,OH} C _{18:1,OH} P C55H10008 7271040 15.09 3788.97 C _{18:1,OH} C _{18:2,OH} S C57H10408 5063206 10.51 2638.46 SC _{18:1,OH} P C55H10007 2739991 5.69 1427.82 SC _{18:1,OH} O C57H10607 361686 0.75 188.48 C _{18:2,OH} SP C55H10207 6926453 <td< th=""><th></th><th>C_{18:2,OH}OP</th><th>C55H100O7</th><th>1686353</th><th>5.04</th><th>1502.99</th></td<>		C _{18:2,OH} OP	C55H100O7	1686353	5.04	1502.99
Linseed oil t2 C18:2,OH C18:1,OH C18:1,OH OP C55H102O7 2541421 7.59 2265.08 C18:1,OH OP C57H108O7 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10406 2346684 7.01 2091.52 OOS C57H10606 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Linseed oil t2 C18:2,OH C18:1,OH C18:1,OH C18:1,OH C18:1,OH C18:1,OH C18:1,OH C18:1,OH C18:2,OH SC18:1,OH C55H10008 7271040 15.09 3788.97 C18:2,OH C18:2,OH SC18:1,OH C55H10407 11611921 24.10 6051.03 C18:2,OH C18:2,OH SC18:1,OH C55H10207 6926453 14.38 3609.41 C18:2,OH SC18:1,OH SC18:1,OH SC18:1,OH SC53H10006 3727982 7.74 1942.67 OOP C55H10206 1930461 4.01 1005.97 </th <th></th> <th>SC_{18:1,OH}O</th> <th>C57H106O7</th> <th>333724</th> <th>1.00</th> <th>297.44</th>		SC _{18:1,OH} O	C57H106O7	333724	1.00	297.44
C18:1,0HSS C57H10807 4367796 13.04 3892.87 POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10406 2346684 7.01 2091.52 OOS C57H10606 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Linseed oil t2 C18:2,0HC18:1,0HP C55H10008 7271040 15.09 3788.97 C18:1,0HP C55H10008 7271040 15.09 3788.97 C18:2,0HC18:1,0HP C55H10007 2739991 5.69 1427.82 SC18:1,0HP C55H10007 2739991 5.69 1427.82 SC18:1,0HO C57H10607 361686 0.75 188.48 C18:2,0HSP C55H10207 6926453 14.38 3609.41 C18:1,0HSS C57H10807 1242562 2.58 647.50		C _{18:2,OH} SP	C55H102O7	2541421	7.59	2265.08
POP C53H10006 1587120 4.74 1414.55 OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10406 2346684 7.01 2091.52 OOS C57H10606 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Inseed oil t2 C _{182,OH} C _{18:1,OH} P C55H10008 7271040 15.09 3788.97 C _{18:1,OH} C _{18:2,OH} S C57H10408 5063206 10.51 2638.46 SC _{18:1,OH} P C55H10007 11611921 24.10 6051.03 C _{18:2,OH} OP C55H10007 273991 5.69 1427.82 SC _{18:1,OH} O C57H10607 361686 0.75 188.48 C _{18:2,OH} SP C55H10207 6926453 14.38 3609.41 C _{18:1,OH} SS C57H10807 1242562 2.58 647.50 POP C53H10206 3727982 7.74 1942.67		C _{18:1,OH} SS	C57H108O7	4367796	13.04	3892.87
OOP C55H10206 779538 2.33 694.78 OOO C57H10406 318156 0.95 283.56 OSP C55H10406 2346684 7.01 2091.52 OOS C57H10606 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Linseed oil t ₂ C _{18:2,OH} C _{18:1,OH} P C55H10008 7271040 15.09 3788.97 C _{18:1,OH} C _{18:2,OH} S C57H10408 5063206 10.51 2638.46 SC _{18:1,OH} P C55H10007 273991 5.69 1427.82 SC _{18:1,OH} O C57H10607 361686 0.75 188.48 C _{18:2,OH} SP C55H10207 6926453 14.38 3609.41 C _{18:1,OH} SS C57H10807 1242562 2.58 647.50 POP C53H10006 3727982 7.74 1942.67 OOP C55H10206 1930461 4.01 1005.97		РОР	C53H100O6	1587120	4.74	1414.55
OOO C57H10406 318156 0.95 283.56 OSP C55H10406 2346684 7.01 2091.52 OOS C57H10606 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Linseed oil t ₂ C _{18:2,OH} C _{18:1,OH} P C55H10008 7271040 15.09 3788.97 C _{18:1,OH} C _{18:2,OH} S C57H10408 5063206 10.51 2638.46 SC _{18:1,OH} P C55H10007 2739991 2.69 1427.82 SC _{18:1,OH} O C57H10607 361686 0.75 188.48 C _{18:2,OH} SP C55H10207 6926453 14.38 3609.41 C _{18:1,OH} SS C57H10807 1242562 2.58 647.50 POP C53H10006 3727982 7.74 1942.67 OOP C55H10206 1930461 4.01 1005.97		OOP	C55H102O6	779538	2.33	694.78
OSP C55H10406 2346684 7.01 2091.52 OOS C57H10606 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Linseed oil t2 C18:2,0HC18:1,0HP C55H10008 7271040 15.09 3788.97 C18:1,0HC18:2,0HS C57H10408 5063206 10.51 2638.46 SC18:1,0HP C55H10407 11611921 24.10 6051.03 C18:2,0HOP C55H10007 2739991 5.69 1427.82 SC18:1,0HO C57H10607 361686 0.75 188.48 C18:2,0HSP C55H10207 6926453 14.38 3609.41 C18:1,0HSS C57H10807 1242562 2.58 647.50 POP C53H10006 3727982 7.74 1942.67 OOP C55H10206 1930461 4.01 1005.97		000	C57H104O6	318156	0.95	283.56
OOS C57H10606 471893 1.41 420.58 SOS C57H10806 1466773 4.38 1307.28 Linseed oil t ₂ C18:2,0HC18:1,0HP C55H10008 7271040 15.09 3788.97 C18:1,0HC18:2,0HS C57H10408 5063206 10.51 2638.46 SC18:1,0HP C55H10007 11611921 24.10 6051.03 C18:2,0HOP C55H10007 2739991 5.69 1427.82 SC18:1,0HO C57H10607 361686 0.75 188.48 C18:2,0HSP C55H10207 6926453 14.38 3609.41 C18:2,0HSP C57H10807 1242562 2.58 647.50 POP C53H10206 3727982 7.74 1942.67 OOP C55H10206 1930461 4.01 1005.97		OSP	C55H104O6	2346684	7.01	2091.52
SOS C57H10806 1466773 4.38 1307.28 Linseed oil t2 C18:2,OHC18:1,OHP C55H10008 7271040 15.09 3788.97 C18:1,OHC18:2,OHS C57H10408 5063206 10.51 2638.46 SC18:1,OHP C55H10407 11611921 24.10 6051.03 C18:2,OHOP C55H10007 2739991 5.69 1427.82 SC18:1,OHO C57H10607 361686 0.75 188.48 C18:2,OHSP C55H10207 6926453 14.38 3609.41 C18:1,OHSS C57H10807 1242562 2.58 647.50 POP C53H10006 3727982 7.74 1942.67 OOP C55H10207 1930461 4.01 1005.97		00S	C57H106O6	471893	1.41	420.58
Linseed oil t ₂ C _{18:2,OH} C _{18:1,OH} P C55H10008 7271040 15.09 3788.97 C _{18:1,OH} C _{18:2,OH} S C57H10408 5063206 10.51 2638.46 SC _{18:1,OH} P C55H10407 11611921 24.10 6051.03 C _{18:2,OH} OP C55H10007 2739991 5.69 1427.82 SC _{18:1,OH} O C57H10607 361686 0.75 188.48 C _{18:2,OH} SP C55H10207 6926453 14.38 3609.41 C _{18:1,OH} SS C57H10807 1242562 2.58 647.50 POP C53H10006 3727982 7.74 1942.67 OOP C55H10206 1930461 4.01 1005.97		SOS	C57H108O6	1466773	4.38	1307.28
Linseed oil t ₂ C _{18:2,OH} C _{18:1,OH} P C55H10008 7271040 15.09 3788.97 C _{18:1,OH} C _{18:2,OH} S C57H10408 5063206 10.51 2638.46 SC _{18:1,OH} P C55H10407 11611921 24.10 6051.03 C _{18:2,OH} OP C55H10007 2739991 5.69 1427.82 SC _{18:1,OH} O C57H10607 361686 0.75 188.48 C _{18:2,OH} SP C55H10207 6926453 14.38 3609.41 C _{18:2,OH} SS C57H10807 1242562 2.58 647.50 POP C53H10206 3727982 7.74 1942.67 OOP C55H10206 1930461 4.01 1005.97						
C18:1,0HC18:2,0HSC57H10408506320610.512638.46SC18:1,0HC55H104071161192124.106051.03C18:2,0HC55H1000727399915.691427.82SC18:1,0HC57H106073616860.75188.48C18:2,0HSPC55H10207692645314.383609.41C18:1,0HC57H1080712425622.58647.50POPC53H1000637279827.741942.67OOPC55H1020619304614.011005.97	Linseed oil t ₂	C _{18:2,OH} C _{18:1,OH} P	C55H100O8	7271040	15.09	3788.97
SC18:1,0HPC55H104071161192124.106051.03C18:2,0HOPC55H1000727399915.691427.82SC18:1,0HOC57H106073616860.75188.48C18:2,0HSPC55H10207692645314.383609.41C18:1,0HSSC57H1080712425622.58647.50POPC53H1000637279827.741942.67OOPC55H1020619304614.011005.97		C _{18:1,OH} C _{18:2,OH} S	C57H104O8	5063206	10.51	2638.46
C18:2,0HOPC55H1000727399915.691427.82SC18:1,0HOC57H106073616860.75188.48C18:2,0HSPC55H10207692645314.383609.41C18:1,0HSSC57H1080712425622.58647.50POPC53H1000637279827.741942.67OOPC55H1020619304614.011005.97		SC _{18:1,OH} P	C55H104O7	11611921	24.10	6051.03
SC18:1,0HOC57H106073616860.75188.48C18:2,0HSPC55H10207692645314.383609.41C18:1,0HSSC57H1080712425622.58647.50POPC53H1000637279827.741942.67OOPC55H1020619304614.011005.97		C _{18:2,OH} OP	C55H100O7	2739991	5.69	1427.82
C18:2,0HSPC55H10207692645314.383609.41C18:1,0HSSC57H1080712425622.58647.50POPC53H1000637279827.741942.67OOPC55H1020619304614.011005.97		SC _{18:1,OH} O	C57H106O7	361686	0.75	188.48
C18:1,OHSSC57H1080712425622.58647.50POPC53H1000637279827.741942.67OOPC55H1020619304614.011005.97		C _{18:2,OH} SP	C55H102O7	6926453	14.38	3609.41
POP C53H100O6 3727982 7.74 1942.67 OOP C55H102O6 1930461 4.01 1005.97		C _{18:1,OH} SS	C57H108O7	1242562	2.58	647.50
OOP C55H102O6 1930461 4.01 1005.97		РОР	C53H100O6	3727982	7.74	1942.67
		OOP	C55H102O6	1930461	4.01	1005.97

	000	C57H104O6	922369	1.91	480.65
	OSP	C55H104O6	3521209	7.31	1834.92
	OOS	C57H106O6	797494	1.66	415.58
	SOS	C57H108O6	2056666	4.27	1071.74
					I
Linseed oil t ₃	C _{18:20H} C _{18:10H} P	C55H100O8	3620569	21.86	4049.85
	C _{18:1,OH} C _{18:2,OH} S	C57H104O8	2712290	16.37	3033.88
	PC _{18,OH} C _{18,OH}	C55H106O8	132105	0.80	147.77
	C _{18,OH} PC _{18,OH}	C55H106O8	363705	2.20	406.83
	SC _{18:1,OH} P	C55H104O7	4696958	28.35	5253.87
	С _{18:1,ОН} С _{18:1,ОН} Р	C55H102O8	284375	1.72	318.09
	С _{18:2,ОН} SP	C55H102O7	3061072	18.48	3424.02
	POP	C53H100O6	463212	2.80	518.13
	OOP	C55H102O6	264174	1.59	295.50
	000	C57H104O6	368293	2.22	411.96
	OSP	C55H104O6	400887	2.42	448.42
	SOS	C57H108O6	198503	1.20	222.04
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Linseed oil t ₄	PC _{18,OH} C _{18,OH}	C55H106O8	275284	2.81	304.18
	C _{18:1,OH} C _{18,OH} P	C55H104O8	79495	0.81	87.84
	SC _{18:1,OH} P	C55H104O7	1366120	13.92	1509.52
	C _{18:1,OH} C _{18:1,OH} P	C55H102O8	630339	6.42	696.51
	SC _{18:1,OH} C _{18,OH}	C57H108O8	271237	2.76	299.71
	C _{18:2,OH} SP	C55H102O7	1960995	19.99	2166.85
	C _{18:1,OH} SS	C57H108O7	524299	5.34	579.34
	POP	C53H100O6	781021	7.96	863.01
	OOP	C55H102O6	1206860	12.30	1333.55
	000	C57H104O6	782423	7.97	864.56
	OSP	C55H104O6	437758	4.46	483.71
	OOS	C57H106O6	230922	2.35	255.16
	SOS	C57H108O6	167377	1.71	184.95
Linseed oil t_5	PC _{18,OH} C _{18,OH}	C55H106O8	695141	8.38	413.04
	C _{18,OH} PC _{18,OH}	C55H106O8	828173	9.98	492.08
	C _{18:1,OH} C _{18,OH} P	C55H104O8	329881	3.98	196.01
	C _{18:1,OH} C _{18:1,OH} P	C55H102O8	1668184	20.11	991.20
	SC _{18:1,OH} C _{18,OH}	C57H108O8	257169	3.10	152.80
	C _{18:2,OH} SP	C55H102O7	1033561	12.46	614.12
	C _{18:1,OH} SS	C57H108O7	732293	8.83	435.11
	РОР	C53H100O6	796310	9.60	473.15
	OOP	C55H102O6	1081025	13.03	642.32
	OSP	C55H104O6	500241	6.03	297.23
	OOS	C57H106O6	252630	3.05	150.11
	SOS	C57H108O6	120652	1.45	71.69

	TAG	formula	area	area (%)	area/weight
Sunflower oil t ₀	С _{18:2,ОН} ОР	C55H100O7	3436031	8.16	5488.87
	Unknown 2	C57H102O7	3678557	8.73	5876.28
	C _{18:2,OH} SP	C55H102O7	1197350	2.84	1912.70
	Unknown 3	C57H104O7	4574192	10.86	7307.01
	A00	C59H110O6	299030	0.71	477.68
	POP	C53H100O6	3742996	8.89	5979.23
	OOP	C55H102O6	8283165	19.67	13231.89
	000	C57H104O6	7018828	16.66	11212.18
	OSP	C55H104O6	3322644	7.89	5307.74
	OOS	C57H106O6	4143433	9.84	6618.90
	SOS	C57H108O6	877265	2.08	1401.38
	Unknown 7	C61H116O6	590837	1.40	943.83
Sunflower t ₁	Unknown 3	C57H104O7	1502887	2.93	1155.18
	С _{18:1,ОН} РР	C53H102O7	452789	0.88	348.03
	C _{18:1,OH} OO	C57H104O7	4900181	9.56	3766.47
	С _{18:1,ОН} ОР	C55H102O7	7153112	13.95	5498.16
	SC _{18:1,OH} P	C55H104O7	3877326	7.56	2980.26
	Unknown 4	C57H106O7	4750181	9.27	3651.18
	C _{18:1,OH} SS	C57H108O7	1368068	2.67	1051.55
	POP	C53H100O6	4633876	9.04	3561.78
	OOP	C55H102O6	6570028	12.82	5049.98
	000	C5/H10406	32//165	6.39	2518.96
	OSP	C55H104O6	48/4052	9.51	3746.39
	005	C5/H10606	3795034	7.40	2917.01
	SOS -	C5/H10806	1/85815	3.48	1372.65
	Unknown /	C61H116O6	1019237	1.99	/83.42
Sunflower oil t ₂	C _{18:2,OH} C _{18:1,OH} P		607178	2.61	717.70
	Unknown 1	C55H102O9	321118	1.38	379.57
	C _{18:1,OH} C _{18:1,OH} P	C55H102O8	270258	1.16	319.45
	C _{18:1,OH} C _{18:1,OH} S	C57H106O8	280211	1.21	331.22
	С _{18:2,ОН} ОР	C55H100O7	1787588	7.70	2112.99
	Unknown 2	C57H102O7	142832	0.61	168.83
	Unknown 3	C57H104O7	751498	3.24	888.29
	С _{18:1,ОН} РР	C53H102O7	334980	1.44	395.96
	C _{18:1,OH} OO	C57H104O7	1032570	4.45	1220.53
	С _{18:1,ОН} ОР	C55H102O7	2451246	10.56	2897.45
	SC _{18:1,OH} P	C55H104O7	1753269	7.55	2072.42
	Unknown 4	C57H106O7	1521073	6.55	1797.96
	C _{18:1,OH} SS	C57H108O7	650381	2.80	768.77
	РОР	C53H100O6	2249074	9.69	2658.48
	OOP	C55H102O6	2290271	9.86	2707.18
	000	C57H104O6	860531	3.71	1017.18
	OSP	C55H104O6	2307063	9.94	2727.02
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	OOS	C57H106O6	1303573	5.61	1540.87
	SOS	C57H108O6	675141	2.91	798.04
	Unknown 6	C57H104O8	610980	2.63	722.20
	Unknown 7	C61H116O6	346054	1.49	409.047
Sunflower t ₃	C _{18:2,OH} C _{18:1,OH} P	C55H100O8	2957859	9.19	3211.57
	Unknown 1	C55H102O9	3198960	9.94	3473.35
	C _{18:1,OH} C _{18:1,OH} S	C57H106O8	2565467	7.97	2785.52
	С _{18:2,ОН} SP	C55H102O7	1463676	4.55	1589.22
	Unknown 3	C57H104O7	399535	1.24	433.80
	С _{18:1,ОН} РР	C53H102O7	715569	2.22	776.95
	С _{18:1,ОН} ОО	C57H104O7	724164	2.25	786.28
	С _{18:1,ОН} ОР	C55H102O7	3858989	12	4189.99
	SC _{18:1,OH} P	C55H104O7	5135280	15.96	5575.76
	Unknown 4	C57H106O7	2192146	6.81	2380.18
	C _{18:1,OH} SS	C57H108O7	1818754	5.65	1974.76
	POP	C53H100O6	1335767	4.15	1450.34
	OOP	C55H102O6	660533	2.05	717.19
	000	C57H104O6	142412	0.44	154.63
	OSP	C55H104O6	1378433	4.28	1496.67
	00S	C57H106O6	400097	1.24	434.41
	SOS	C57H108O6	453198	1.41	492.07
	Unknown 6	C57H104O8	462609	1.44	502.29
	Unknown 7	C61H116O6	373182	1.16	405.19
Sunflower oil t ₄	C _{18:2,OH} C _{18:1,OH} P	C55H100O8	2252426	7.58	1333.58
	Unknown 1	C55H102O9	6147850	20.68	3639.93
	C _{18:1,OH} C _{18:1,OH} S	C57H106O8	3040999	10.23	1800.47
	C _{18:2,OH} SP	C55H102O7	1651792	5.56	977.97
	С _{18:1,ОН} РР	C53H102O7	1236760	4.16	732.24
	C _{18:1,OH} OO	C57H104O7	245444	0.82	145.32
	С _{18:1,ОН} ОР	C55H102O7	1442592	4.85	854.11
	SC _{18:1,OH} P	C55H104O7	7379840	24.83	4369.35
	Unknown 4	C57H106O7	905915	3.05	536.36
	C _{18:1,OH} SS	C57H108O7	2593015	8.72	1535.24
	РОР	C53H100O6	656813	2.21	388.88
	OOP	C55H102O6	77296	0.26	45.76
	OSP	C55H104O6	667344	2.24	395.11
	005	C57H106O6	61928	0.21	36.66
	SOS	C57H108O6	229163	0.77	135.68
	Unknown 7	C61H116O6	258340	0.87	152.95
	Γ				
Sunflower oil t₅	C _{18:2,OH} SP	C55H102O7	839570	55.19	861.10
	С _{18:1,ОН} ОР	C55H102O7	147150	9.67	150.92

	SC _{18:1,OH} P	C55H104O7	343130	22.55	351.93
	C _{18:1,OH} SS	C57H108O7	80699	5.30	82.77
	Unknown 7	C61H116O6	110783	7.28	113.62
Sunflower oil t ₆	C _{18:1,OH} C _{18:1,OH} P	C55H102O8	4437408	68.19	4437.41
	C _{18:1,OH} OP	C55H102O7	318699	4.90	318.70
	C _{18:1,OH} PP	C53H102O7	1367744	21.02	1367.74
	SC _{18:1,OH} P	C55H104O7	383504	5.89	383.50

	TAG	formula	area	area (%)	area/weight
Safflower oil t ₀	Unknown 1	C53H92O7	251983	0.64	245.12
	LnLnP	C55H94O6	5186163	13.26	5044.91
	SC _{18:1,OH} P	C55H104O7	984811	2.52	957.99
	LLnP	C55H96O6	5498866	14.06	5349.09
	C _{18:2,OH} SP	C55H102O7	1256919	3.21	1222.68
	Unknown 2	C57H100O6	2181172	5.58	2121.76
	С _{18:1,ОН} ОР	C55H102O7	1213095	3.10	1180.05
	SC _{18:1,OH} P	C55H104O7	2351419	6.01	2287.37
	C _{18:1,OH} SS	C57H108O7	1343847	3.43	1307.24
	POP	C53H100O6	5298998	13.55	5154.67
	OOP	C55H102O6	3259877	8.33	3171.09
	000	C57H104O6	936486	2.39	910.98
	OSP	C55H104O6	4546045	11.62	4422.22
	OOS	C57H106O6	1558241	3.98	1515.80
	Unknown 6	C55H106O6	456646	1.17	444.21
	SOS	C57H108O6	2405589	6.15	2340.07
	Unknown 8	C61H116O6	381585	0.97	371.19
Safflower oil t_1	Unknown 1	C53H92O7	141226	0.29	74.06
	LnLnP	C55H94O6	1494140	3.09	783.50
	SC _{18:1,OH} P	C55H104O7	7020017	14.50	3681.18
	LLnP	C55H96O6	3412325	7.05	1789.37
	C _{18:2,OH} SP	C55H102O7	942155	1.95	494.05
	Unknown 2	C57H100O6	1379414	2.85	723.34
	С _{18:1,ОН} ОР	C55H102O7	3098342	6.40	1624.72
	SC _{18:1,OH} P	C55H104O7	7875831	16.27	4129.96
	C _{18:1,OH} SS	C57H108O7	4832818	9.98	2534.25
	POP	C53H100O6	4801048	9.92	2517.59
	OOP	C55H102O6	1799059	3.72	943.40
	000	C57H104O6	459919	0.95	241.17
	OSP	C55H104O6	5079974	10.49	2663.86
	OOS	C57H106O6	990853	2.05	519.59
	Unknown 6	C55H106O6	921109	1.90	483.01
	SOS	C57H108O6	3509586	7.25	1840.37

	Unknown 8	C61H116O6	645110	1.33	338.29
<u>C. (()</u>		055140000	1107252	2.54	045.22
Sattiower oll t ₂	PC _{18,OH} C _{18,OH}	C55H10608	120527	3.51	845.23
	C _{18:2,OH} PP	C53H10007	120527	0.38	92.01
	SC _{18:1,OH} P	C55H10407	1126279	3.57	859.75
		C55H96O6	1029279	3.26	/85./1
	C _{18:2,OH} SP	C55H10207	2124977	6.74	1622.12
	С _{18:1,ОН} ОР	C55H10207	810690	2.57	618.85
	SC _{18:1,OH} P	C55H104O7	7928365	25.14	6052.19
	C _{18:1,OH} SS	C57H108O7	5110481	16.21	3901.13
	Unknown 3	C50H94O7	1171882	3.72	894.57
	POP	C53H100O6	3515365	11.15	2683.48
	OOP	C55H102O6	872458	2.77	666.00
	000	C57H104O6	149794	0.47	114.35
	OSP	C55H104O6	3252071	10.31	2482.50
	00S	C57H106O6	470136	1.49	358.88
	Unknown 6	C55H106O6	698887	2.22	533.50
	SOS	C57H108O6	1704091	5.40	1300.83
	Unknown 8	C61H116O6	339880	1.08	259.45
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Safflower oil t ₃	PC _{18,OH} C _{18,OH}	C55H106O8	1485109	4.14	1289.16
	SC _{18:1,OH} P	C55H104O7	4107772	11.46	3565.77
	C _{18:2,OH} SP	C55H102O7	2656171	7.41	2305.70
	С _{18:1,ОН} РР	C53H102O7	1866821	5.21	1620.50
	С _{18:1,ОН} ОР	C55H102O7	551465	1.54	478.70
	SC _{18:1,OH} P	C55H104O7	12103060	33.77	10506.13
	C _{18:1,OH} SS	C57H108O7	6507583	18.16	5648.94
	Unknown 3	C50H94O7	1393402	3.89	1209.55
	РОР	C53H100O6	1703354	4.75	1478.61
	OOP	C55H102O6	215916	0.60	187.43
	000	C57H104O6	86319	0.24	74.93
	OSP	C55H104O6	1575848	4.40	1367.92
	005	C57H106O6	110565	0.31	95.98
	Unknown 6	C55H106O6	705863	1.97	612.73
	SOS	C57H108O6	766741	2.14	665.57
Safflower oil t ₄	PC _{18,OH} C _{18,OH}	C55H106O8	1268455	5.67	1268.46
	SC _{18:1.0H} P	C55H104O7	3086848	13.80	3086.85
	LLnP	C55H96O6	1923060	8.59	1923.06
	C _{18:2,OH} SP	C55H102O7	1769257	7.91	1769.26
	С _{18:1,ОН} РР	C53H102O7	704628	3.15	704.63
	С _{18:1,ОН} ОР	C55H102O7	1769257	7.91	1769.26
	SC _{18:1.0H} P	C55H104O7	5157851	23.05	5157.85
	C _{18:1,OH} SS	C57H108O7	2740334	12.25	2740.33
	Unknown 3	C50H94O7	1344839	6.01	1344.84
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Appendix B

	POP	C53H100O6	829164	3.70	829.16
	OOP	C55H102O6	85712	0.38	85.71
	OSP	C55H104O6	706787	3.16	706.79
	Unknown 6	C55H106O6	625945	2.80	625.95
	SOS	C57H108O6	350213	1.56	350.21
Safflower oil t_5	PC _{18,OH} C _{18,OH}	C55H106O8	939656	13.38	951.07
	SC _{18:1,OH} P	C55H104O7	682405	9.72	690.69
	LLnP	C55H96O6	747693	10.65	756.77
	C _{18:2,OH} SP	C55H102O7	641743	9.14	649.54
	С _{18:1,ОН} ОР	C55H102O7	61984	0.88	62.74
	SC _{18:1,OH} P	C55H104O7	1501249	21.38	1519.48
	C _{18:1,OH} SS	C57H108O7	885149	12.61	895.90
	Unknown 3	C50H94O7	1017287	14.49	1029.64
	OOS	C57H106O6	55612	0.79	56.29
	Unknown 6	C55H106O6	488128	6.95	494.06
Safflower oil t_6	PC _{18,OH} C _{18,OH}	C55H106O8	378214	49.20	520.96
	Unknown 2	C57H100O6	44139	5.74	60.80
	SC _{18:1,OH} P	C55H104O7	346407	45.06	477.14

	TAG	formula	area	area (%)	area/weight
Soybean oil t _o	LnLnP	C55H94O6	46481361	9.35	64827.56
	C _{18:1,OH} C _{18:1,OH} S	C57H106O8	7477958	1.50	10429.51
	С _{18:2,ОН} ОР	C55H100O7	39123985	7.87	54566.23
	LLnP	C55H96O6	31107260	6.26	43385.30
	LLO	C57H100O6	14839637	2.99	20696.84
	С _{18:1,ОН} ОР	C55H102O7	21723286	4.37	30297.47
	SC _{18:1,OH} P	C55H104O7	13212645	2.66	18427.68
	POP	C53H100O6	56449460	11.35	78730.07
	OOP	C55H102O6	77182445	15.53	107646.37
	C _{18:1,OH} SS	C57H108O7	6085956	1.22	8488.08
	000	C57H104O6	34407012	6.92	47987.46
	OSP	C55H104O6	60058693	12.08	83763.87
	00S	C57H106O6	45638083	9.18	63651.44
	SOS	C57H108O6	29920616	6.02	41730.29
	Unknown 7	C61H116O6	4225050	0.85	5892.68
Soybean oil t ₁	LnLnP	C55H94O6	16773053	4.632	13022.56
	С _{18:2,ОН} ОР	C55H100O7	54400636	15.023	42236.52
	С _{18:1,ОН} ОР	C55H102O7	6147714	1.698	4773.07
	POP	C53H100O6	61607240	17.014	47831.71
	OOP	C55H102O6	61365096	16.947	47643.71
	000	C57H104O6	19415402	5.362	15074.07

	OSP	C55H104O6	65862654	18.189	51135.60
	00S	C57H106O6	35597728	9.831	27637.99
	Unknown 4	C55H106O6	2751673	0.760	2136.39
	SOS	C57H108O6	33333766	9.206	25880.25
	Unknown 7	C61H116O6	4849309	1.339	3764.99
Soybean oil t ₂	C _{18:1,OH} C _{18:1,OH} P	C55H102O8	4047585	2.07	2525.01
	C _{18:1,OH} C _{18:1,OH} S	C57H106O8	2143352	1.10	1337.09
	С _{18:1,ОН} РР	C53H102O7	3187922	1.63	1988.72
	С _{18:1,ОН} О Р	C55H102O7	19976384	10.23	12461.87
	SC _{18:1,OH} P	C55H104O7	26833115	13.75	16739.31
	РОР	C53H100O6	30070318	15.41	18758.78
	OOP	C55H102O6	21027877	10.77	13117.83
	C _{18:1,OH} SS	C57H108O7	13651799	6.99	8516.41
	000	C57H104O6	4190910	2.15	2614.42
	OSP	C55H104O6	33030088	16.92	20605.17
	00S	C57H106O6	12119873	6.21	7560.74
	SOS	C57H108O6	16371985	8.39	10213.34
	Unknown 7	C61H116O6	2211785	1.13	1379.78
				1	
Soybean oil t ₃	LLnP	C55H96O6	11264904	12.56	5538.30
	LLO	C57H100O6	4311448	4.81	2119.69
	С _{18:1,ОН} О Р	C55H102O7	24187475	26.97	11891.58
	РОР	C53H100O6	12158624	13.56	5977.69
	OOP	C55H102O6	3421596	3.82	1682.20
	OSP	C55H104O6	17145275	19.12	8429.34
	00S	C57H106O6	2316981	2.58	1139.13
	Unknown 4	C55H106O6	2588896	2.89	1272.81
	SOS	C57H108O6	8986935	10.02	4418.36
	Unknown 7	C61H116O6	1301871	1.45	640.05
Soybean oil t ₄	LLnP	C55H96O6	3222640	7.542	3083.87
	С _{18:1,ОН} РР	C53H102O7	1794804	4.201	1717.52
	С _{18:1,ОН} О Р	C55H102O7	8015582	18.760	7670.41
	SC _{18:1,OH} P	C55H104O7	14452501	33.825	13830.14
	РОР	C53H100O6	2644998	6.190	2531.10
	OOP	C55H102O6	319610	0.748	305.85
	C _{18:1,OH} SS	C57H108O7	6456699	15.111	6178.66
	OSP	C55H104O6	3096335	7.247	2963.00
	Unknown 4	C55H106O6	1367415	3.200	1308.53
	SOS	C57H108O6	1356510	3.175	1298.10
	L				
Soybean oil t ₅	PC _{18,OH} C _{18,OH}	C55H106O8	5111172	6.91	1762.47
	LLnP	C55H96O6	3523204	4.76	1214.90
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	C _{18:1,OH} PP	C53H102O7	4709772	6.37	1624.06
	SC _{18:1,OH} P	C55H104O7	33195318	44.87	11446.66
	C _{18:1,OH} SS	C57H108O7	18766821	25.37	6471.32
	Unknown 4	C55H106O6	3219937	4.35	1110.32
Soybean oil t ₆	PC _{18,OH} C _{18,OH}	C55H106O8	913951	11.00	492.17
	С _{18:1,ОН} О Р	C55H102O7	1176221	14.16	633.40
	C _{18:1,OH} SS	C57H108O7	5529135	66.57	2977.46
	Unknown 4	C55H106O6	686094	8.26	369.46

	TAG	formula	area	area (%)	area/weight
Tung oil t ₀	Unknown 2	C57H90O6	554595	5.56	452.73
	С _{18:2,ОН} ОР	C55H94O6	888456	8.90	725.27
	С _{18:1,ОН} ОР	C55H102O7	1302632	13.05	1063.37
	LLnP	C55H96O6	1136710	11.39	927.93
	РОР	C53H100O6	1453195	14.56	1186.28
	OOP	C55H102O6	1088094	10.90	888.24
	000	C57H104O6	427027	4.28	348.59
	OSP	C55H104O6	1582778	15.85	1292.06
	OOS	C57H106O6	770056	7.71	628.62
	SOS	C57H108O6	779984	7.81	636.72
Tung oil t ₁	РОР	C53H100O6	972675	12.86	1226.58
	OOP	C55H102O6	1813109	23.97	2286.39
	000	C57H104O6	1496186	19.78	1886.74
	OSP	C55H104O6	1164339	15.39	1468.27
	OOS	C57H106O6	1489300	19.69	1878.06
	SOS	C57H108O6	630041	8.33	794.50
Tung oil t ₂	РОР	C53H100O6	1651564	15.25	1298.40
	OOP	C55H102O6	2475621	22.85	1946.24
	000	C57H104O6	1587850	14.66	1248.31
	OSP	C55H104O6	1996161	18.43	1569.31
	OOS	C57H106O6	1925416	17.77	1513.69
	SOS	C57H108O6	1196086	11.04	940.32
Tung oil t ₃	РОР	C53H100O6	1751833	13.15	1369.69
	OOP	C55H102O6	3064663	23.00	2396.14
	000	C57H104O6	2753392	20.66	2152.77
	OSP	C55H104O6	2069797	15.53	1618.29
	OOS	C57H106O6	2488934	18.68	1946.00
	SOS	C57H108O6	1197154	8.98	936.01
Tung oil t_4	POP	C53H100O6	210866	37.03	262.93

	000	C57H104O6	43068	7.56	53.70
	OSP	C55H104O6	232463	40.83	289.85
	SOS	C57H108O6	83005	14.58	103.50
Tung oil t ₅	POP	C53H100O6	339019	17.39	253.19
	OOP	C55H102O6	397411	20.38	296.80
	000	C57H104O6	254341	13.04	189.95
	OSP	C55H104O6	419248	21.50	313.11
	OOS	C57H106O6	330661	16.96	246.95
	SOS	C57H108O6	209327	10.73	156.33
Tung oil t ₆	С _{18:1,ОН} ОР	C55H102O7	861530	14.71	433.80
	C _{18:1,OH} OO	C57H104O7	975998	16.67	491.44
	SC _{18:1,OH} P	C55H104O7	892661	15.25	449.48
	OOP	C55H102O6	1081762	18.47	544.69
	000	C57H104O6	2043406	34.90	1028.91

	TAG	formula	area	area (%)	area/weight
Castor oil t ₀	C _{18:1,OH} C _{18:1,OH} O	C57H104O10	21957550	1.85	24397.28
	RnRnRn	C57H104O9	107795944	9.07	119773.27
	RnRnL	C57H102O8	236032285	19.86	262258.09
	С _{18:1,ОН} С _{18:1,ОН} Р	C55H102O8	105799221	8.90	117554.69
	RnRnO	C57H104O8	214533022	18.05	238370.02
	RnRnS	C57H106O8	157240308	13.23	174711.45
	RnLL	C57H100O7	64697793	5.44	71886.44
	RnLO	C57H102O7	81040779	6.82	90045.31
	С _{18:2,ОН} ОР	C55H100O7	35645717	3.00	39606.35
	С _{18:1,ОН} ОР	C55H102O7	20229184	1.70	22476.87
	RnLS	C57H104O7	66713391	5.61	74125.99
	SC _{18:1,OH} P	C55H104O7	3196383	0.27	3551.54
	OOL	C57H102O6	3162287	0.27	3513.65
	OOP	C55H102O6	1246057	0.10	1384.51
	000	C57H104O6	2224452	0.19	2471.61
	OOS	C57H106O6	637721	0.05	708.58
Castor oil t ₁	C _{18:1,2OH} C _{18:1,OH} O	C57H104O10	18375233	2.57	26250.33
	RnRnL	C57H102O8	167449819	23.43	239214.03
	С _{18:1,ОН} С _{18:1,ОН} Р	C55H102O8	79328365	11.10	113326.24
	RnRnO	C57H104O8	158522708	22.18	226461.01
	RnRnL	C57H102O8	18040973	2.52	25772.82
	RnRnS	C57H106O8	126013569	17.63	180019.38
	RnLL	C57H100O7	21249581	2.97	30356.54

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	RnLO	C57H102O7	47068773	6.59	67241.10
	С _{18:2,ОН} ОР	C55H100O7	19468637	2.72	27812.34
	С _{18:1,ОН} ОР	C55H102O7	17058825	2.39	24369.75
	SC _{18:1,OH} P	C55H104O7	2407912	0.34	3439.87
	00L	C57H102O6	2083723	0.29	2976.75
	OOP	C55H102O6	1192465	0.17	1703.52
	000	C57H104O6	2484732	0.35	3549.62
	00S	C57H106O6	959915	0.13	1371.31
Castor oil t ₂	Unknown 3	C57H102O9	36290597	4.39	45363.25
	RnRnRn	C57H104O9	285420940	34.55	356776.18
	RnRnL	C57H102O8	46654786	5.65	58318.48
	C _{18:1,OH} C _{18:1,OH} P	C55H102O8	92753753	11.23	115942.19
	RnRnO	C57H104O8	157219001	19.03	196523.75
	RnRnL	C57H102O8	6085748	0.74	7607.19
	RnRnS	C57H106O8	122195517	14.79	152744.40
	RnLO	C57H102O7	6984862	0.85	8731.08
	С _{18:2,ОН} ОР	C55H100O7	3386564	0.41	4233.21
	С _{18:1,ОН} ОР	C55H102O7	10705872	1.30	13382.34
	RnLS	C57H104O7	22376608	2.71	27970.76
	SC _{18:1,OH} P	C55H104O7	1723186	0.21	2153.98
	РОР	C53H100O6	232994	0.03	291.24
	OOP	C55H102O6	802236	0.10	1002.80
	000	C57H104O6	1221350	0.15	1526.69
	OOS	C57H106O6	490921	0.06	613.65
Castor oil t_3	C _{18:1,2OH} C _{18:1,OH} O	C57H104O10	15840293	1.71	9317.82
	Unknown 3	C57H102O9	121692549	13.13	71583.85
	RnRnRn	C57H104O9	214975909	23.20	126456.42
	RnRnL	C57H102O8	19110388	2.06	11241.40
	C _{18:1,OH} C _{18:1,OH} P	C55H102O8	103287414	11.14	60757.30
	RnRnO	C57H104O8	173685762	18.74	102168.10
	C _{18:2,OH} C _{18:1,OH} P	C55H100O8	27258789	2.94	16034.58
	RnRnL	C57H102O8	49368057	5.33	29040.03
	RnRnS	C57H106O8	159170043	17.17	93629.44
	RnLO	C57H102O7	2858333	0.31	1681.37
	С _{18:1,ОН} ОР	C55H102O7	12262213	1.32	7213.07

	OOP	C55H102O6	838010	0.09	492.95
	000	C57H104O6	1165054	0.13	685.33
	OOS	C57H106O6	540129	0.06	317.72
Castor oil t ₄	C _{18:1,20H} C _{18:1,0H} O	C57H104O10	96627011	15.03	32209.00
	C _{18:1,2OH} C _{18:1,2OH} C _{18:1,OH}	C57H104O11	59763340	9.29	19921.11

C57H104O7

C55H10407

22264472

2456133

2.40

0.27

13096.75

1444.78

RnLS

SC_{18:1,OH}P

					пррепал в
	Unknown 3	C57H102O9	56574848	8.80	18858.28
	RnRnRn	C57H104O9	110363139	17.16	36787.71
	С _{18:1,ОН} С _{18:1,ОН} Р	C55H102O8	47307592	7.36	15769.20
	RnRnO	C57H104O8	75229716	11.70	25076.57
	Unknown 10	C57H106O9	22952694	3.57	7650.90
	С _{18:2,ОН} С _{18:1,ОН} Р	C55H100O8	20395407	3.17	6798.47
	RnRnL	C57H102O8	24268157	3.77	8089.39
	RnRnS	C57H106O8	90632382	14.10	30210.79
	С _{18:1,ОН} ОР	C55H102O7	7663141	1.19	2554.38
	RnLS	C57H104O7	9504887	1.48	3168.30
	SC _{18:1,OH} P	C55H104O7	2509249	0.39	836.42
	POP	C53H100O6	360398	0.06	120.13
	OOP	C55H102O6	1107861	0.17	369.29
	000	C57H104O6	1450396	0.23	483.47
	OOS	C57H106O6	614838	0.10	204.95
Castor oil t_5	C _{18:1,2OH} C _{18:1,OH} O	C57H104O10	41057096	21.97	41057.10
	$C_{18:1,2OH}C_{18:1,2OH}C_{18:1,OH}$	C57H104O11	56246165	30.10	56246.17
	RnRnRn	C57H104O9	9321185	4.99	9321.19
	Unknown 8	C59H102O7	28547733	15.28	28547.73
	Unknown 11	C57H104O10	14813060	7.93	14813.06
	RnRnS	C57H106O8	632849	0.34	632.85
	LOP	C55H100O6	1272480	0.68	1272.48
					•
Castor oil t_6	Unknown 8	C59H102O7	823726	6.72	823.73
	Unknown 10	C57H106O9	820893	6.69	820.89
	Unknown 11	C57H104O10	364919	2.98	364.92
	С _{18:2,ОН} ОР	C55H100O7	12572	0.10	12.57
	OOL	C57H102O6	1115135	9.09	1115.14
	POP	C53H100O6	1819110	14.83	1819.11
	OOP	C55H102O6	2739068	22.33	2739.07
	000	C57H104O6	4225807	34.45	4225.81
	LOP	C55H100O6	249300	2.03	249.30
	OOS	C57H106O6	94201	0.77	94.20
	L				

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List of publications, participations in schools, conferences, and internships abroad

Publications.

- La Nasa J., Ghelardi E., Degano I., Modugno F., Colombini M.P. Core shell stationary phases for a novel separation of triglycerides in plant oils by high performance liquid chromatography with electrospray-quadrupole-time of flight mass spectrometer. *Journal of Chromatography A*, 1308 (2013), 114-124.
- Ghelardi E., Degano I., Colombini M.P., Mazurek J., Schilling M., Learner T. Py-GC/MS applied to the analysis of synthetic organic pigments: characterization and identification in paint samples, accepted by *Analytical and Bioanalytical Chemistry*, in press.

Participations in schools.

- LC-MS school 2012: Advanced course on the coupling of mass spectrometry with liquid-phase separation techniques. Lucca, June 11-14/2012.

Conferences.

- M.P. Colombini, L. Dei, I. Degano, F. Modugno, E. Ghelardi, M. Potenza, "Analysis of Contemporary Art Materials: Synthetic Pigments and Binders of Ri de Pomme by Julian Schnabel at the Pecci Museum, Prato", XXIII Congresso Nazionale della Divisione di Chimica Analitica della Società Chimica Italiana, September 16-20/2012, Isola d'Elba poster.
- M.P. Colombini, L. Dei, I. Degano, F. Modugno, E. Ghelardi, M. Potenza, "Analysis of Contemporary Art Materials: Synthetic Pigments and Binders of Ri de Pomme by Julian Schnabel at the Pecci Museum, Prato", Issues in Contemporary Paint Symposium, March 28-29/2013, Amersfoort, The Netherlands poster.
- E. Ghelardi, E. Carretti, L. Dei, "Sistemi Supramolecolari Costituiti da Polivinilalcol, Tensioattivi e Microemulsioni: Proprietà e Applicazioni nel Campo della Pulitura di Beni Artistico/Architettonici", Scientia ad Artem II, May 11-12/2013, Florence – poster.

- E. Carretti, E. Ghelardi, C. Matarrese, I. Natali, M. Bonini, E. Fratini, L. Dei, P. Baglioni, "Supramolecular Systems Based on Polyvinyl alcohol, Surfactants and Microemulsions: Property and Applications for the Cleaning of Artistic/Architectural Heritage", XIV Congresso Nazionale della Divisione di Chimica dell'Ambiente e dei Beni Culturali della Società Chimica Italiana, June 2-5/2013, Rimini poster.
- J. La Nasa, E. Ghelardi, I. Degano, F. Modugno, M.P. Colombini, "Core shell stationary phases for a novel separation of triglycerides in plant oils by high performance liquid chromatography with electrospray-quadrupole-time of flight mass spectrometer", XXIV Congresso Nazionale della Divisione di Chimica Analitica della Società Chimica Italiana, September 15-19/2013, Sestri Levante – poster.
- E. Ghelardi, I. Degano, M.P. Colombini, J. Mazurek, M. Schilling, T. Learner, "Dyes and materials in Contemporary Art: a combined approach between analytical chemistry and the surface science", Ph.D. Day 5, May 29/2014, Sesto Fiorentino, Florence - poster.

Oral contributions.

- E. Ghelardi, I. Degano, M.P. Colombini, J. Mazurek, M. Schilling, T. Learner, "Synthetic organic pigments: detection in paint samples and ageing study", Ph.D.
 Day 5, May 29/2014, Sesto Fiorentino, Florence.
- E. Ghelardi, I. Degano, F. Modugno, M.P. Colombini, "The chemical evidence of a disputed restoration: Ri de Pomme by Julian Schnabel", at the Workshop "Restaurare l'arte contemporanea?", December 11-12/2014, Lucca.

Internships abroad.

During the second year of the PhD programme, I spent six months (January-August 2013) at the Getty Conservation Institute of Los Angeles, CA, USA.