

# Study of Post-Byzantine Icon Varnishes by Chromatographic and Spectroscopic Methods

C.Vieillescazes, P.Archier and M.S. Pistre

*In 1997, an exhibition entitled 'Treasures of Mount Athos' was organized at the Byzantine Culture Museum in Thessaloniki. Among these treasures were post-Byzantine icons that required thinning of their varnish in order to be exhibited. Varnish samples were taken, using cotton swabs and a mixture of acetone (propanol) and ethanol as solvent, and kept as original control samples. A European project — PLATON, a bilateral Franco-Hellenic programme — was developed by the Universities of Athens (Greece) and Avignon (France) for the scientific study of these varnishes. The specific objective of the project was the rediscovery of the so-called 'secrets' of varnish preparation. In fact, recipes for varnishes such as these were described in the eighteenth century by a monk from Mount Athos, Dionysos of Fournas, and the object of our work was to evaluate these recipes. Two analytical techniques were used: infrared spectroscopy and liquid chromatography with two detectors (UV-visible and fluorimetry). After the development of an analytical corpus by studying fresh natural resins, which are usual components of varnishes, 25 samples were analysed and 24 were identified. The main conclusions were that the resinous composition identified differed from the ancient recipes recorded by Dionysos of Fournas.*

## INTRODUCTION

The term 'icon' means, fundamentally, all religious pictures, portable or fixed, whatever the technique and the scale may be. Both art object and object of worship, the icon is a visual expression of the Orthodox faith. It holds a privileged position in the history of Byzantine art. The Christian icon has its origin at the end of the Hellenic and Roman portrait tradition. No icons are known before the sixth century. At this time, they had a protective value, as people believed that they had a miraculous origin. After the prohibition of images by the iconoclastic emperors, icons multiplied again in the tenth and eleventh centuries due to the growth of the cult of saints. Latin domination from 1204 did not interrupt this production. Cultural contacts were created between the east and the west. Icon painting achieved its highest expression in the Paleologue period (1261–1453), when its development proceeded in parallel with wall painting; in fact, both types of work were often executed by the same artists. At the end of the fourteenth

century and in the fifteenth, Moscow emerged as the main icon painting centre. After the conquest of Constantinople by the Turks in 1453, artistic activity moved to monastic centres, for example Mount Athos [1, 2], where traditions were preserved, the Meteora, or Crete which was under Venetian rule. The post-Byzantine artists combined Byzantine traditions and occidental influences.

The aim of the present research is a better understanding of post-Byzantine techniques of icon painting, especially those of the seventeenth to eighteenth centuries, which are more often found in the Mount Athos monasteries. Moreover, in collaboration with restorers and historians, such a study could contribute to a very precise chemical characterization of natural substances used in art, and to establishing a network between partners involved in the field of cultural heritage conservation.

One of the rare ancient texts describing post-Byzantine painting technique is the *Painter's Manual (Eminia)* written by Dionysios of Fournas, a disciple of the master Panselinos, between 1728 and 1733 [3–5]. This text contains about 70 instructions (how to apply a

*Received February 2003*

gesso, preparation of red bole, how to gild icons, etc.); more particularly, some of them describe different varnish recipes (varnish from *santalozi*, yellow varnish, varnish made from *raki*, etc.). One of them is a heated conifer resin dissolved in hot oil (*peziri*, linseed oil). Depending on the translation, the ancient Greek word for the resin can have different interpretations. For example 'pegoula' can be translated as fir resin [3], pine resin [4], Venice turpentine [5]. Moreover, some recipes mention 'sandarka' as a component, which can be translated as sandarac but which also designated in the past other types of resins [5]. At the end, the artist applied several layers of the hot varnish with the palm of his hand.

So, the purpose of the present study was to evaluate the recipes of the *Erminia*. To this end, 25 varnish samples were studied, from icons coming from five monasteries (Simon Petra, Meghisti Lavra, Nea Skiti, Xenophontos, Xeropotamou). The oldest icon can be dated to the sixteenth–seventeenth century; most of them belong to the seventeenth to eighteenth centuries and one is from the early nineteenth century. Only four of them are dated exactly. There is a high possibility that the varnishes are the original ones, used by the hagiographers, since the icons are not known to have been restored in the past, according to the restorers of the Greek Ministry of Culture.

## CHEMICAL COMPOSITION OF RESINS

Resinous materials are complex mixtures varying in their chemical composition as a function of botanical or geographical criteria [6, 7]. It is traditional to classify these materials as gums (polysaccharides), which are water-soluble, and resins, which are soluble in alcohol; so, the application of cotton swabs and an acetone–ethanol mixture enables the varnish to be dissolved and removed for analysis of the resinous component.

Resins of vegetable origin contain terpenic hydrocarbons whose molecular weights correspond to various degrees of condensation. In general, the chemical terpenic hydrocarbon structure can be considered as a derivative of the isoprene or 2-methylbuta-1,3-diene ( $C_5H_8$ ) polymerization.

The diterpenic resins ( $C_{20}$ ) come mainly from various *Coniferae* families, i.e., the *Pinaceae* for colophony or rosin (*Pinus*) and Venice turpentine (*Larix*), the *Cupressaceae* for sandarac (*Tetraclinis*) [8]. They contain predominantly abietane and pimarane acids.

In *Pinaceae* resins, an abietane diterpenoid acid dominates: abietic acid,  $C_{20}H_{30}O_2$ . The rapid conversion

of abietic acid *in situ* leads to dehydroabietic acid. It predominates in old samples and by auto-oxidation produces 7-oxodehydroabietic acid, also present in aged resins. Finally, abietic acid produces retene or 1-methyl, 7-isopropyl phenanthrene ( $C_{18}H_{18}$ ), which is the ultimate degradation product in very old samples [9].

Pimarane compounds are present in the *Cupressaceae* resins. Sandaracopimaric acid characterizes fresh sandarac resin [8].

Triterpenes ( $C_{30}$ ) are the characteristic constituents of several Angiosperm families, such as the *Dipterocarpaceae* with dammar (*Balanocarpus*) and the *Anacardiaceae* with mastic (*Pistacia*); they are also the main components in frankincense, a resin of the *Burseraceae* family [8].

In triterpenes, the basic carbon backbone is euphane; it leads to the ursane- and oleanane-type derivatives, such as oleanolic acid (3-hydroxy, 28-carboxy) and oleanonic acid (3-keto, 28-carboxy), and  $\alpha$ - and  $\beta$ -amyryne (3-hydroxy).

Several tetracyclic compounds of the euphane series, masticadienonic acid and its isomer isomasticadienonic acid, are characteristic of fresh mastic resin. These include oleanonic acid (also present in dammar) and its double bond isomer moronic acid.

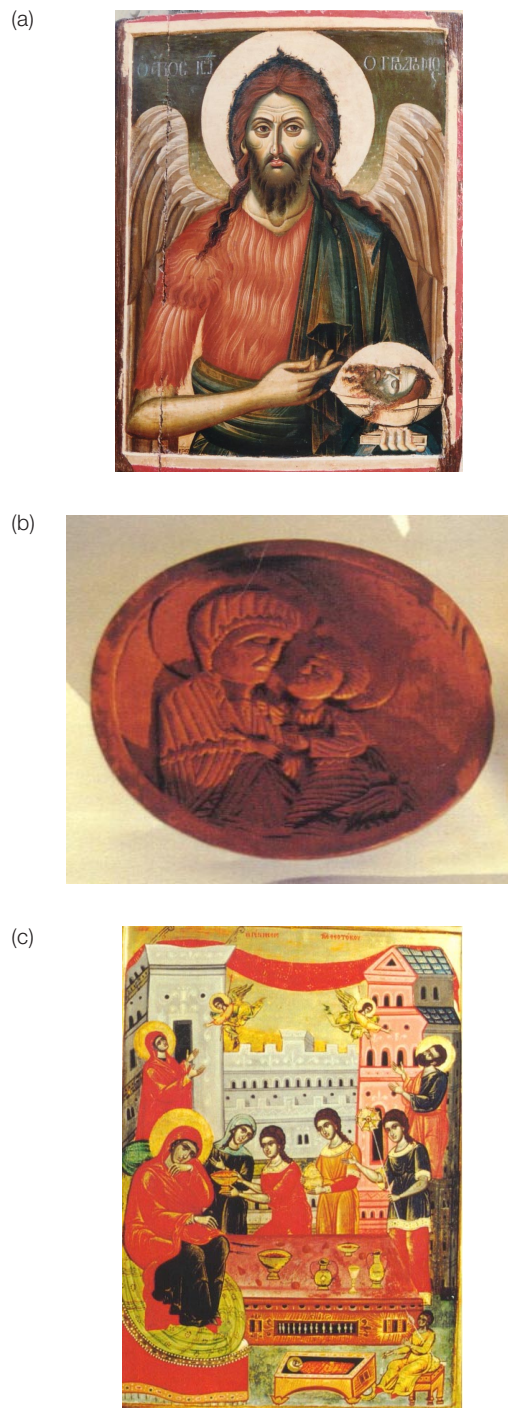
The composition of dammar consists largely of compounds of the tetracyclic dammarane family, the pentacyclic compound ursonic acid, and  $\beta$ -resene (polymeric fraction, insoluble in alcohol). Like dammar, mastic also contains a proportion of polymeric hydrocarbon [6].

Both di- and triterpenes are characteristic of specific botanical families; they are present in fresh resins, where they can be studied, as well as in aged samples, where they still can be detected. Some markers are not present in fresh resins and only appear on aging (7-oxodehydroabietic acid or retene, for example, in the case of diterpenes). Such compounds must be considered as markers of degradation [10].

## MATERIALS AND EXPERIMENTAL TECHNIQUES

### Icons

The icons studied (Figure 1) are painted on wood panels. Table 1 summarizes, for each icon, the monastery of origin, the subject represented, the date of production and the size. The *Panaghia* representations (icons 3, 4, 5) are small, round-format (diameter about 10 cm) painted works or sculpted wood of the same period. The varnish samples were removed with a mixture of acetone (propanone) and ethanol (1:1).



**Figure 1** Some icons studied. (a) St John the Baptist (icon 24), (b) Panaghiaro (recto - icon 3), (c) Birth of the Virgin

#### *Analytical procedure*

Each cotton swab was extracted with 2 ml of HPLC grade methanol, without any further treatment, except filtration on a Dynacard cartridge. The filtered solution was directly injected for HPLC (high performance liquid chromatography), coupled with UV-visible (photodiode array) and fluorimetric detection.

For FTIR (Fourier-transform infrared) study, the solvent was first evaporated. Samples were analysed with potassium bromide as micropellets (microgram quantities of sample with a 20-fold excess of anhydrous KBr).

#### *Fourier-transform infrared absorption spectrometry*

Equipment and conditions: Fourier-transform spectrophotometer (Mattson series 1000); FIRST software; data acquisition: 50 scans; data processing: pattern mode and correlation coefficient algorithm.

#### *High performance liquid chromatography*

The HPLC equipment consisted of a ternary pump (Spectraphysics SP 8800) and an injection loop of 20  $\mu$ L. Two columns were tested: Merck's Lichrocart cartridge 250-4 Superspher 100 RP 18 and Nova-Pak C18; in both cases the analysis was done at constant temperature (22°C) for a better reproduction of retention times. UV detection was performed with a Waters 996 photodiode array detector (Millennium 2010 computer). At the same time, a Waters 470 scanning fluorescent detector (PN 31300) was used, with a 150 watt xenon lamp as excitation source and a D-2000 Hitachi driver. The elution solvent was a binary mixture of distilled water and HPLC-grade methanol; the gradient conditions are described below for both columns.

It quickly appeared that these two columns present a very similar retention power and degree of hydrophobicity. After many trials, the following conditions summarized in Table 2 were adopted 2). These conditions remained the same for every material studied, to permit comparative study. The eluted compounds go first through the UV and then through the fluorimetric detector; the chromatograms were recorded in both detection modes.

#### *Standards*

The following standards were studied; for each one the retention time, the  $\lambda_{\text{max}}$  in UV and the fluorimetric conditions are given in Table 3. The  $\lambda_{\text{max}}$  were

**Table 1** Origin, age, size and name of the icons studied [1]

No.	Monastery	Date	Name	Dimensions (cm)
1	Simon Petra	19th C.	Panagion	158 × 139 × 4
2		17th–18th C.	Birth of the Virgin	69 × 51.1 × 4.5
3		17th–18th C.	Panaghiario	diameter: 9.5
4		17th–18th C.	Panaghiario	diameter: 10
5		17th–18th C.	Panaghiario	diameter: 10
6		17th–18th C.	Birth of the Virgin	69 × 51.1 × 4.5
7		17th–18th C.	St Anthony	unknown
8		18th C.	St Christopher	unknown
9		16th–17th C.	Deisis	unknown
10		17th–18th C.	40 saints	unknown
11		16th–17th C.	St George	87 × 62 × 4
12		17th C.	Pantocrator	87 × 61 × 4
13		17th C.	Pantocrator	87 × 62 × 4
14		16th–17th C.	St George	87 × 62 × 4
15		17th C.	Apostoli	unknown
16	Nea Skiti	1768	The first Ecumenical Council	34.5 × 26.5 × 2.5
17		1766	SS Anthony, Euthymios & Sabbas	29.5 × 21.5 × 2
18		18th C.	SS Stephen & Paul of Xeropotamou	66 × 48 × 4.5
19		1770	All Saints	52 × 32.5 × 2.5
20	Xenophontos	17th C.	The three Hierarchs	61 × 43 × 4
21		18th C.	Our Lady of Succour	54.5 × 32 × 4
22		17th C.	Pantocrator	41 × 35.5 × 4
23		18th C.	Apostoli	21.5 × 30.5 × 3.5
24	Xeropotamou	1747	St John the Baptist	54.5 × 32.5 × 4

**Table 2**

t (min)	0	14	34	37	70
CH <sub>3</sub> OH (%)	15	85	85	100	100
H <sub>2</sub> O (%)	85	15	15	0	0

Nova-Pak C18, flow rate 0.7 mL.min<sup>-1</sup>

measured on the peak corresponding to each standard on the chromatogram. The fluorimetric conditions were determined as follows:

- For the molecular standards, the cell of the fluorimetric detector was filled with a methanolic solution; the optimal  $\lambda_{\text{excitation}}$  and  $\lambda_{\text{emission}}$  were adjusted.
- when no standard was available, a methanolic solution of the resin was used. Mastic showed a fluorimetric response ( $\lambda_{\text{excitation}} = 300$  nm,  $\lambda_{\text{emission}} = 360$  nm) while dammar gave none. These results, observed with fresh resins, present the same characteristics in aged samples.

## RESULTS AND DISCUSSION

Table 4 summarizes the experimental results from the above-mentioned two investigative methods combined [11].

## FTIR

The main IR application was a comparative analysis of the samples with a databank using specific software. The study showed, first, the resinous nature of these varnishes and second, the presence of oil in some cases; this had been suspected following preliminary hot-plate tests.

There is no characteristic peptidic binding band of proteins in any sample (near 1650 cm<sup>-1</sup> for  $\nu_{\text{C=O}}$  and 1550 cm<sup>-1</sup> for  $\nu_{\text{NH}_2}$ ) [12], so neither egg (except for one sample) nor animal glue was detected in these specimens. On the other hand, the presence of oil was demonstrated in various samples ( $\nu_{\text{C-H}}$  at 2850–2820 cm<sup>-1</sup>,  $\nu_{\text{C=O}}$  at 1740 cm<sup>-1</sup>). The Greek team confirmed this identification of oil (and sometimes wax) by the detection of azelaic acid using gas-chromatography.

## HPLC

The analytical efficiency of high performance liquid chromatography has led to its use to determine complex organic mixtures; since 1988, we have analysed terpenic resins using this technique with UV-visible detection [13].

Both sandarac and colophony derive from conifers and are essentially composed of diterpenoids. Fresh resins are different and, of course, easy to distinguish by UV-visible

**Table 3** Standards characteristics

Standard	T <sub>R</sub> (min)	λ <sub>max</sub> (nm)	fluorimetric conditions (nm) λ <sub>excitation</sub> /λ <sub>emission</sub>
7-oxodehydroabietic acid	22.8	210, 255, 303	no response
abietic acid	43.1	240	271/576
dehydroabietic acid	25.2	211, 265	220/290, 271/576
neoabietic acid	43.7	248	no response
palustric acid	41.8	263	204/290
pimaric acid	42.4	204, 251	290/360
isopimaric acid	42.7	203	290/360
sandaracopimaric acid	42.8	211	280/310, 290/360
retene	43.8	211, 255, 298	250/400

**Table 4** Main results summarized

	FTIR results		HPLC results	
	Vegetable oil	Other	Diterpenoid	Triterpenoid
1	yes		colophony	dammar
2	yes		colophony	
3	yes		colophony	
4	yes		unidentified	
5	yes		colophony	mastic
6	yes		colophony	
7	yes		colophony	
8	yes		colophony	
9	yes		colophony	
10	yes		colophony	dammar
11	yes	wax	colophony	
12	yes	wax	colophony	
13	yes	wax	colophony	
14	yes	wax + egg	colophony	
15			colophony	
16			Venice turpentine	mastic
17			colophony	mastic
18			colophony	
19			colophony	
20			Venice turpentine	
21			colophony	
22			colophony	
23			colophony	
24	yes		colophony	

detection; it is not so easy in aged samples and in this case fluorimetry can be necessary.

When analysed by HPLC/PDA detection, several samples present the same chromatographic pattern, at various wavelengths. This has allowed us to classify them as belonging to the same family. Precise identification is based on the retention time and UV-visible spectra of reference materials stored in databases. For example, all these different chromatograms present a peak at  $t_R = 22.8$  min whose UV-visible spectrum corresponds to 7-oxodehydroabietic acid (Figure 2). In two samples of this family (coming from the same icon, the Birth of the Virgin, Table I, samples 2, 6) dehydroabietic acid was

also detected. All these results allow us to identify the whole family of samples with a diterpenic resin, more precisely a conifer resin. The absence of pimaranes indicates that the resins come from conifers of the *Pinaceae* family [6, 8].

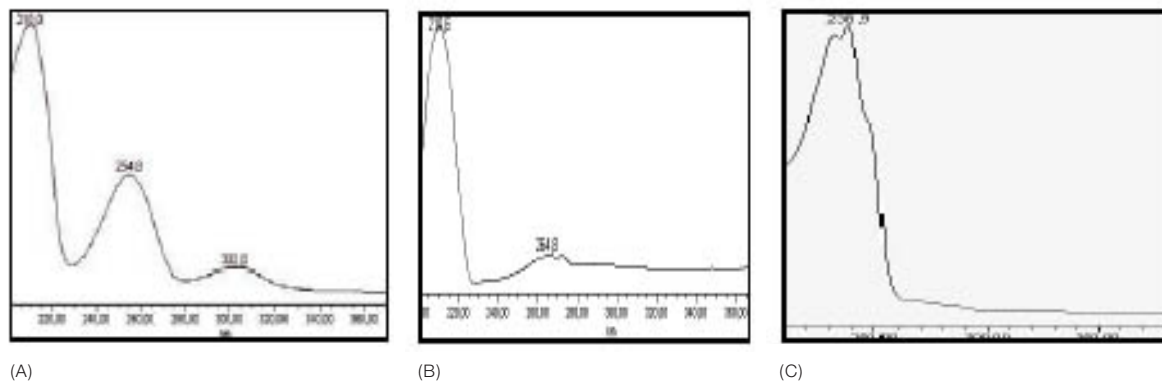
In some cases the UV detection was not efficient enough to provide reliable results. Nevertheless, when the fluorimetric detection conditions of dehydroabietic acid are correctly adjusted ( $\lambda_{excitation} = 271$  nm,  $\lambda_{emission} = 576$  nm), the chromatograms allow an unequivocal distinction between sandarac (pattern with one peak) and colophony (pattern with four peaks). This distinction remains for aged diterpenoid resins; the authors have compared the fresh resins with naturally aged archaeological samples [14]. In the case of the analysed varnish samples, the chromatograms are identical to colophony, in the same conditions, whereas they are different from sandarac.

It should be noted that fluorimetric detection presents two advantages compared with the PDA response: on the one hand, the detection limit is improved for some compounds; on the other hand, fluorescent compounds can sometimes be detected, which are not visible by PDA detection [15].

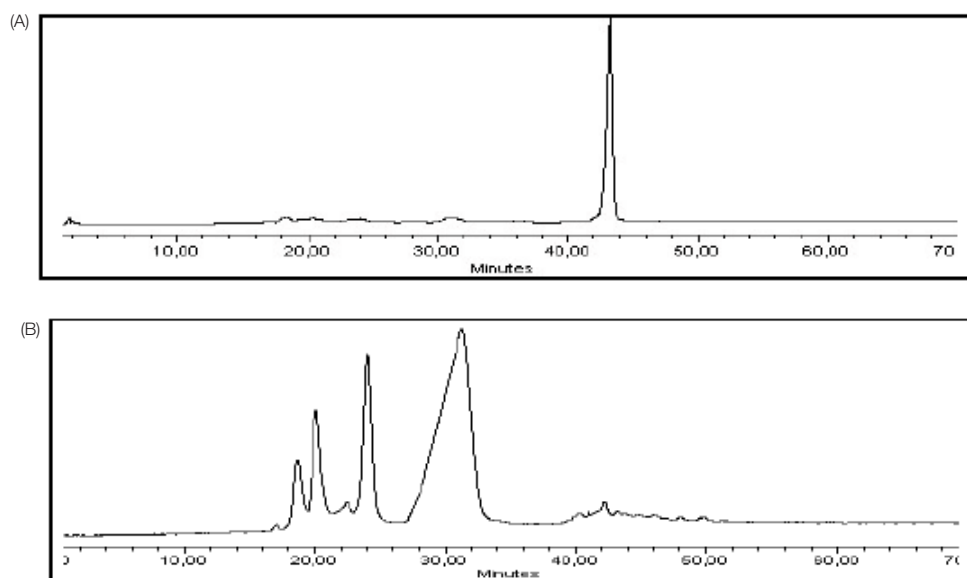
In summary, in 20 icons colophony was identified in the varnish (by the presence of its degradation markers: 7-oxodehydroabietic and dehydroabietic acid), while in two samples Venice turpentine was identified. This material is not detected by using *larixol* family standards [16] but by comparison of the chromatograms with fresh and artificial aged resin, in UV-visible and fluorimetric detection; in this last case, Venice turpentine presents a characteristic fingerprint (Figure 3). Both colophony and Venice turpentine are resins of the *Coniferae* family (*Pinaceae* for colophony, *Larix* for Venice turpentine).

Sandarac was not identified in any sample; this result is particularly interesting, because it contradicts some aspects of the recipes of Dionysios of Fourna.





**Figure 2** UV spectra of major components in the chromatogram of colophony: (a) 7-oxodehydroabietic acid ( $t_R = 23$  min,  $\lambda_{max} = 210-254-302$  nm), (b) dehydroabietic acid ( $t_R = 25$  min,  $\lambda_{max} = 210-265$  nm), (c) abietic acid ( $t_R = 43$  min,  $\lambda_{max} = 240$  nm)

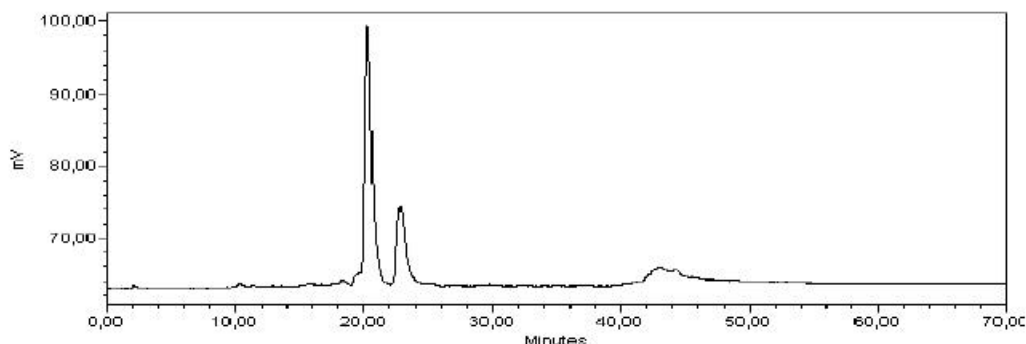


**Figure 3** (a) Chromatogram of Venice turpentine in UV detection at 240 nm. (b) Chromatogram of Venice turpentine in fluorimetric detection ( $\lambda_{excitation} = 271$  nm,  $\lambda_{emission} = 573$  nm).

Five samples contained triterpenoids in addition to diterpene compounds. The presence of triterpenes in these samples was confirmed by the use of gas-chromatography (GC) analysis by the Greek team. Mastic was not detected by the presence of moronic acid, as often by GC [17], but by its characteristic fingerprint in fluorimetry ( $\lambda_{excitation} = 300$  nm,  $\lambda_{emission} = 360$  nm, Figure 4). This fingerprint remains unchanged in

aged as in fresh mastic resin; dammar cannot be identified by a fluorometric fingerprint.

It must be noted that the presence of dammar is suspected, not because of the identification of markers, but by the presence of triterpenes associated with a total absence of response in fluorimetry under any condition whatever. The presence of dammar would certainly prove that the analysed varnish is not the original one,



**Figure 4** Fluorimetric chromatogram of mastic ( $\lambda_{\text{excitation}} = 300 \text{ nm}$ ,  $\lambda_{\text{emission}} = 360 \text{ nm}$ ).

according to the current state of knowledge about the use of this material [18].

## CONCLUSION

Thanks to its chemical composition, the authors have been able to identify the botanical origin of the resin present in varnishes. It has been shown that important differences or misinterpretations exist between the historical sources and the actual varnish composition. It is hoped that these results will help restorers to a good understanding of these icons and permit their better conservation.

The necessity of carrying out chemical studies for the identification of materials and techniques in the Byzantine and post-Byzantine iconographic tradition has already been reported elsewhere [19]. Moreover, in collaboration with botanists, artists and historians, such a technique could contribute to a better chemical characterization of natural substances used in art.

## ACKNOWLEDGEMENTS

The authors would like to express their gratitude to John Paganis, conservator-restorer in Athens, and Professor E. Ioakimoglou of the Technological Institute of Education – Department of Conservation of Works of Art and Antiquities, Athens.

## COMMERCIAL PRODUCTS

Molecular standards: Extrasynthèse SA, BP 62, ZI Lyon nord, rue Jacquard, 69730 Genay, France.

Resins: Ets Laverdure et Fils, 58 rue Traversière, 75012 Paris, France.

## REFERENCES

- 1 *Treasures of Mount Athos*, B' Edition, Thessaloniki (1997).
- 2 Paleologue, A., *Le Mont Athos: merveille du christianisme byzantin*, Découvertes Gallimard – Religions (1997).
- 3 Didron, M., 'Manuel d'iconographie chrétienne, grecque et latine', translation of P. Durand, *Manuscrit Byzantin: le guide de la peinture du moine Denys*, Imprimerie Royale, Paris (1846).
- 4 Hetherington, P., *The Painter's Manual of Dionysius of Furna*, Sagittarius Press, London (1981).
- 5 Politis, P., 'Interprétation sur les techniques de peintures Byzantines', *Dionysios de Phournas*, unpublished, School of Conservation-Restoration, Avignon (2002).
- 6 Mills, J.S., and White, R., *The Organic Chemistry of Museum Objects*, Butterworth Heinemann, 2nd edition (1994) 95–128.
- 7 van den Berg, K.J., Pastorova, I., Spetter, L., and Boon, J.J., 'State of oxidation of diterpenoid Pinaceae resins in varnish, wax lining material, 18th century resin oil paint, and a recent copper resinate glaze', in *ICOM-CC 11th Triennial Meeting, Edinburgh, Scotland, 1–6 September 1996*, Preprints, James & James, London (1996) 930–937.
- 8 Mills, J.S., and White, R., 'Natural resins of art and archaeology; their sources, chemistry and identification', *Studies in Conservation* **22** (1977) 12–31.
- 9 Otto, A., and Simoneit, A., 'Chemosystematics and diagenesis of terpenoids in fossil conifer species and sediment from the Eocene Zeitz formation', *Geochimica and Cosmochimica Acta* **65** (2001) 3505–3527.
- 10 Evershed, R.P., Jerman, K., and Eglinton, G., 'Pine wood from the Mary Rose', *Nature* **314** (1985) 528–530.
- 11 Pistre, M.S., 'Contribution à l'étude d'icônes et de peintures post-byzantines par différentes techniques chromatographiques et spectroscopiques', PhD thesis, University of Avignon (2001).
- 12 Bellamy, L.J., *The Infra-red Spectra of Complex Molecules*, London (1966).
- 13 Vieillescazes, C., and Coen, S., 'Caractérisation de quelques résines utilisées en Egypte ancienne', *Studies in Conservation* **38** (1993) 255–264.
- 14 Martin, P., Archier, P., Vieillescazes, C., and Pistre, M.S., 'HPLC coupled with fluorimetric detection for the

- identification of natural resins in archaeological materials', *Chromatographia* **53** (7/8) (2001) 380–384.
- 15 Albani, J.R., *Absorption et fluorescence*, Tec & Doc Edition, Paris (2001) 53–83.
  - 16 Scalarone, D., Lazzari, M., and Chiantore, O., 'Ageing behaviour and pyrolytic characterisation of diterpenic resins used as art materials: colophony and Venice turpentine', *Journal of Analytical and Applied Pyrolysis* (2002) in press.
  - 17 van der Doelen, G.A., van der Berg, K.J., and Boon J.J., 'Comparative chromatographic and mass-spectrometric studies of triterpenoid varnishes: fresh material and aged samples from paintings', *Studies in Conservation* **43** (1998) 249–264.
  - 18 Whitmore, P.M., *Contributions to Conservation Science: A Collection of Robert Feller's Published Studies on Artists' Paints, Paper and Varnishes*, Pittsburgh (2002) 21–31.
  - 19 Ioakimoglou, E., Yanovits, N., Paganis, J., Tziamourani, E., and Terlixi, A.V., 'Analytical characterization of varnishes used in Byzantine icons by gas chromatography and gas chromatography/mass spectrometry', in *Physics in Culture I*, Aristotle University Publication, Thessaloniki (2000) 128–135.

## AUTHORS

CATHERINE VIEILLES CAZES: doctor specialized in organic chemistry (Avignon, 1983). Professor, University of Avignon, since 1988. Head of the department of chemistry applied to art and archaeology. *Address: Laboratoire de Chimie Bio-organique, Faculté des Sciences, 33 rue L. Pasteur, 84000 Avignon, France. Email: cathy.vieillescazes@univ-avignon.fr*

PAUL ARCHIER: doctor specialized in organic chemistry (Avignon, 1971). Taught chemistry in Moroccan universities. 'Maître de conférences' at the University of Avignon since 1986, he participates in research applied to art and archaeology. *Address: same as Vieillescazes.*

MARIE-STÉPHEN PISTRE: DEA, 'Histoire, civilisation et archéologie des mondes antiques' (Bordeaux III). Doctor specialized in organic chemistry (2001), working in the laboratory of CRITT DIAC. *Address: avenue G. Pompidou, 81100 Castres, France.*