ELSEVIER

Journal of Chromatography A, 922 (2001) 385–390

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Short communication

Identification of lipid binders in paintings by gas chromatography Influence of the pigments ☆

J.V. Gimeno-Adelantado[a,*], R. Mateo-Castro[a], M.T. Doménech-Carbó[b], F. Bosch-Reig[a], A. Doménech-Carbó[a], M.J. Casas-Catalán[a], L. Osete-Cortina[a]

[a]*Department of Analytical Chemistry, Faculty of Chemistry, University of Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain*
[b]*Department of Conservation and Restoration, Polytechnical University of Valencia, Camino de Vera 14, 46022, Valencia, Spain*

Received 21 November 2000; received in revised form 12 April 2001; accepted 18 April 2001

Abstract

The influence of the presence and the type of pigments in the lipid binding media of paintings were studied by gas chromatography with flame ionization detector. The drying oils were linseed stand oil, poppy oil and sunflower oil, and the pigments studied were cadmium red, cobalt blue, tin white, lead white, chalk and plaster of Paris, commonly used in paintings. The results indicate that the stearic/palmitic ratio and the presence of pigments are quite stable during ageing. However, some differences in the oleic acid/palmitic acid ratio were found, depending on the type of pigment present in the lipid binding media. These variations are related to the drying effect of the pigments. The proposed method has been applied to the identification of drying oils in two samples from baroque paintings in the ''Basilica de la Virgen de los Desamparados'' of Valencia, Spain.

Keywords: Oils; Art analysis; Lipids; Pigments; Fatty acids

1. Introduction

In the conservation and restoration of paintings, analytical chemistry offers suitable techniques to provide the restorer with the necessary analytical information for conservation treatment [1]. Some of the analytical results, such as identification of the nature of the binding media (which provide cohesion and protect the pigment) or the identification of the pigments present, are valuable data for characterising a painting in a given artistic style, facilitating the choice of reagents to be used in the restoration and even sometimes for assigning a particular period to the work.

There are many factors which make the task of identifying the chemical nature of binding media difficult, such as the use of a small quantity of sample (to avoid deterioration of the work), the lack of purity of the sample (due to the presence of a large proportion of pigments and other substances) and its lack of homogeneity. A suitable technique for applying to this type of samples is gas chromatography, one of its foremost and most successful applications being the determination of fatty acids

☆Presented at the 29th Scientific Meeting of the Spanish Group of Chromatography and Related Techniques, Alcalá de Henares (Madrid), 12–14 July 2000

*Corresponding author. Tel.: +34-963-864-533; fax: +34-968-64-436.

E-mail address: jose.v.gimeno@uv.es (J.V. Gimeno-Adelantado).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)00914-1

(major components in lipoid binding media). Authors such as Mills [2], Stolov and de W. Rogers [3] and Pancella and Bart [4] are forerunners in this type of analysis applied to samples from paintings.

The samples are treated rapidly and efficiently (after hydrolysis) by derivatisation with alkyl chloroformates as proposed by Hušek [5]. Identification of the type of binding media is carried out by calculating the ratio of the chromatographic areas of each fatty acid present with respect to palmitic acid [2,6]. However, as already mentioned, a large quantity of pigment can be present in the binding media.

Some authors have studied the influence of pigments in proteinaceous binding media [7,8], with the conclusion that pigments impede derivatisation of amino acids due to the formation of complexes between amino acids and metallic cations in the pigments during hydrolysis.

Due to the presence of pigments and also because the criteria for sample extraction are based mainly on avoiding the deterioration or aesthetic alteration of the work without giving much importance to the pigment present, the question arises of determining whether the presence of pigment and its composition can interfere with the identification of the binding media.

In this study, a series of lipoid binding media commonly used in paintings such as linseed oil, poppy oil and sunflower oil are identified by the proportion of fatty acids after hydrolysis of each oil. To do this, the relation of the areas of the chromatographic peaks of each derivative against the palmitic derivative is proposed to obtain a typical profile for each oil and the influence on this identification of the presence of several widely used pigments such as cobalt blue, lead white, tin white, chalk, hemhydrite and cadmium red is studied.

2. Experimental

2.1. Solvents and reagents

The following reagents were used to treat the samples: ethyl chloroformate (ECF) (purity >98% GC) and absolute pyridine (Fluka, Buchs, Switzerland). HCl at 37% for analysis (Scharlau, Barcelona, Spain), chloroform at 98% (Acros, Cambridge, USA) and absolute ethanol for analysis (Panreac, Barcelona, Spain).

The drying oils used as standards were Linseed Stand Oil 73200, Poppy Oil 73600 and Sunflower Oil 7362, all from Kremer Pigmente (Aichstten, Allgaü, Germany). The pigments studied were cobalt blue (CoO, Al_2O_3, H_3PO_4), zinc white (ZnO), lead white ($PbCO_3$), chalk ($CaCO_3$), plaster of Paris ($CaSO_4 \cdot 1/2\ H_2O$) and cadmium red (three parts of CdS to two parts of CdSe). All from Kremer Pigmente.

2.2. Samples

The drying oils were mixed with each of the pigments (in a proportion of 20–40%, w/w) and were spread as thin layers on glass slides. They were dried at room temperature (during 15 days) and kept in the fridge until analysis.

Work of art samples were taken from paintings from Palomino's vault (painted in 1701) in the ''Basilica de la Virgen de los Desamparados'', Valencia, Spain.

2.3. Apparatus

Analysis of the fatty acids was performed in a Hewlett-Packard 6890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA) with flame ionisation detector. Inlet and detector temperatures were 250°C and 300°C, respectively. Separation of ethyl esters was achieved in a HP 1701 fused-silica capillary column, 14% cyano-propyl-phenyl-methylsilicone (30 m×250 μm I.D., 0.14 μm film thickness) (Hewlett-Packard). The oven temperature was programmed from 100°C to 275°C (maintained for 8 min) with a ramp of 40°C/min. The carrier gas was He, with inlet pressure of 115 kPa and 1:20 split ratio. The volume of sample injected was 1.5 μl.

To confirm the results, a Trio 1000 mass spectrometer was used coupled to a Fisons 8000 gas chromatograph (Fisons Instruments, Manchester, UK). Chromatographic separation was carried out in the same HP 1701 capillary column. Inlet temperature was 250°C and the oven temperature was programmed from 100°C to 275°C (maintained for 8 min) with a ramp of 30°C/min. Electronic impact (EI) was used as ionisation technique with an

electronic energy of 70 eV and a spectrometer scan rate of 0.5 s/scan with m/z range between 15 and 750. The carrier gas was He with inlet pressure of 47 kPa and 1:20 split ratio.

2.4. Procedure

The samples of binding media (0.5–1 mg) were put into 0.3 ml minivials (Supelco, Bellefonte, PA, USA) and hydrolysed with 100 μl of HC1 6 *M* for 24 h at 110°C in Ar atmosphere. The resulting solution was evaporated to dryness to eliminate excess acid. After adding 100 μl of water, the fatty acids resulting from hydrolysis were extracted with 100 μl of chloroform. The organic layer obtained was taken to dryness and then redissolved with 50 μl of a water–ethanol–pyridine (5:4:1) mixture for derivatisation with 8 μl of ECF After vigorous shaking for 10 s, the reaction mixture was extracted with 50 μ1 of 1% ECF in chloroform; then 50 μ1 of $NaHCO_3$ saturated solution was added. Two layers, aqueous and chloroformic were formed and an aliquot of 1.5 μ1 was taken from the chloroformic layer for injection into the gas chromatograph.

3. Results and discussion

3.1. Identification of lipoid binding media

The three types of lipoid binding media studied (linseed stand oil, sunflower oil and poppy oil) were analysed by the procedure described above and the ratios between the areas of each fatty acid ethyl ester, [azelaic (*A*), myristic (*M*), oleic (*O*) and stearic (*S*) acids] and the area of palmitic acid ethyl ester were calculated. This method makes it possible to study the changes which take place during the ageing process whereas the method proposed by Mills is based on the calculation of the areas of palmitic and stearic acids (P/S) only, which are more stable during ageing as they are saturated [2]. The identification of the fatty acids was confirmed by GC–MS. Fig. 1 shows the chromatograms for poppy oil and linseed oil.

The results shown in Table 1 suggest that identification of these binding media is feasible due to the different proportions (profile) of fatty acids. These results are similar to those obtained by other authors [9] since the S/P ratio is 0.62 for linseed oil and 0.22 for poppy oil.

The M/P quotient cannot be used for identification purposes since myristic acid is found in very small proportions in the three drying oils in this study. Nor is the A/P quotient useful due to the fact that as azelaic acid is more polar than the other fatty acids it is distributed in both the aqueous and chloroformic layers (which are separated according to the proposed procedure) and therefore it is not possible to determine its total content. However, separation into layers makes it possible to isolate more polar compounds such as amino acids in the aqueous layer and therefore with the same procedure to detect lipoid binding media in the presence of proteinaceous binding media or viceversa.

The S/P ratio is useful for differentiating linseed stand oil and poppy oil (the latter has a lower ratio) but the O/P ratio is needed to distinguish between sunflower and linseed oil, since the ratio does not go above 0.07 for sunflower oil, but is higher than 0.10 for linseed oil [9].

3.2. Study of the influence of pigments

To confirm whether or not pigments have any influence on the analysis of the lipoid binding media studied, a variation in the experimental procedure was introduced proposed in a previous work [6] This modification consists in taking the hydrolysed to dryness, evaporating the excess of HC1 instead of neutralizing the solution with $CaCO_3$ as this addition would saturate the solution with Ca^{2+} ions, thus masking the effect produced by pigments on the sample. The Ca^{2+} ions themselves could also interfere in the analysis of the binding media.

The results found for the identification of binding media in the presence of pigments (in Table 1), show that the S/P ratio does not differ significantly in the case of the oils with pigments present and those without pigment. This corroborates the fact that this ratio is the most appropriate for identification purposes [2] due to the stability of saturated fatty acids versus ageing and also versus the presence of different pigments. The O/P ratio is however affected by the presence of pigments and differences become more acute in the case of cadmium red

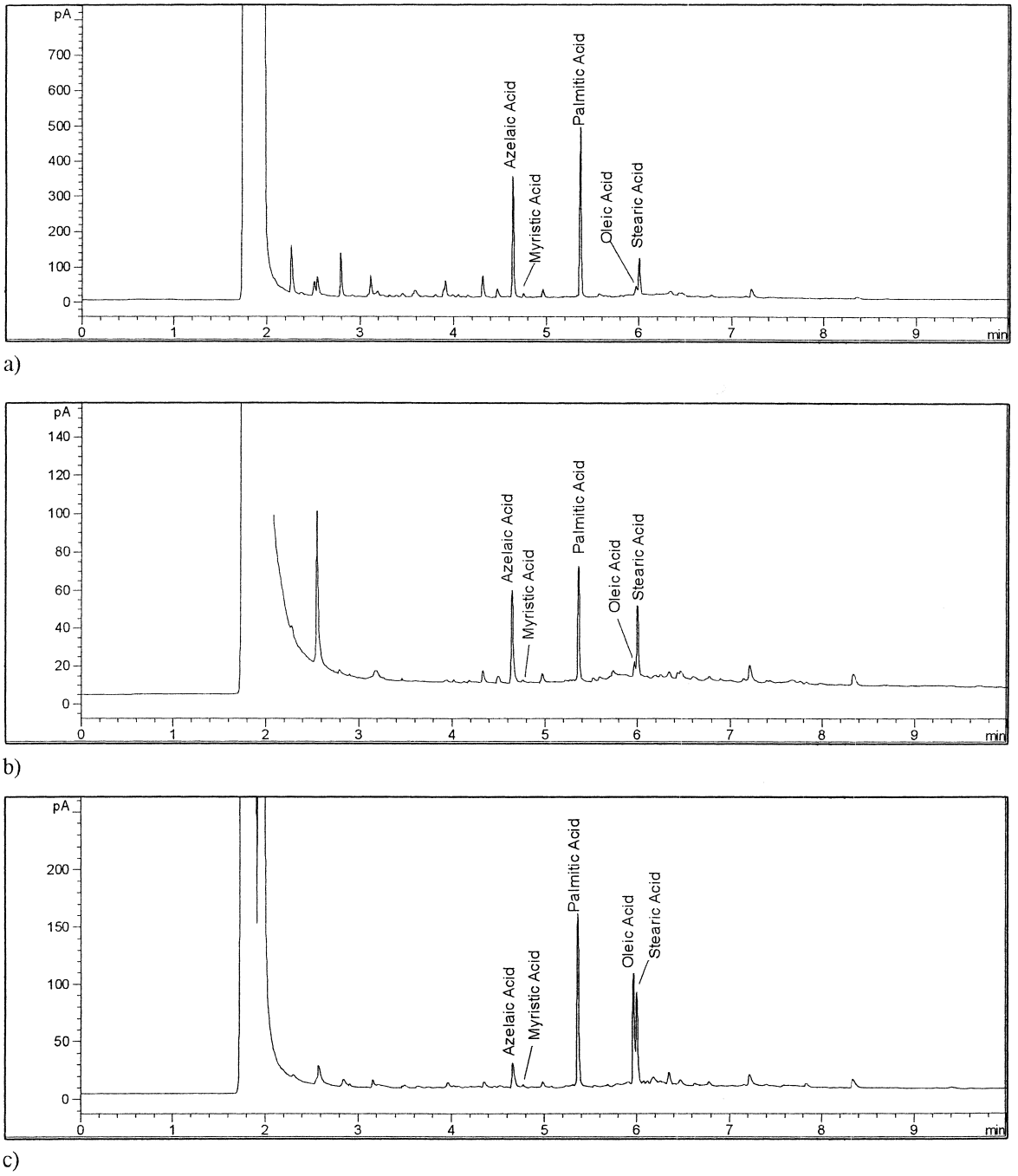

Fig. 1. Chromatograms of ethyl esters of fatty acids from drying oils: (a) poppy oil, (b) linseed stand oil and (c) linseed stand oil in presence of cadmium red pigment.

Table 1
Ratios of the fatty acid ethyl esters relative to palmitic acid ethyl ester in three lipid binding media in the presence and absence of various pigments[a]

Oil	Pigment	A/P Ratio	M/P Ratio	O/P Ratio	S/P Ratio
Poppy		0.78±0.09	0.02±0.01	0.06±0.01	0.22±0.01
	Chalk	0.7±0.1	0.01±0.01	0.01±0.01	0.20±0.03
	Co blue	0.6±0.2	0.01±0.01	0.02±0.01	0.19±0.01
	Cd red	0.9±0.3	0.01±0.01	0.12±0.01	0.18±0.01
	Zn white	1.5±0.3	0.01±0.01	0.06±0.01	0.19±0.01
	Pb white	0.6±0.3	0.01±0.01	0.02±0.01	0.20±0.03
	Plaster of Paris	0.8±0.3	0.01±0.01	0.04±0.01	0.21±0.01
Linseed		0.16±0.05	0.02±0.01	0.18±0.06	0.62±0.04
	Chalk	1.1±0.2	0.01±0.01	0.10±0.03	0.56±0.07
	Co blue	0.17±0.03	0.01±0.01	0.10±0.03	0.62±0.02
	Cd red	0.26±0.05	0.01±0.01	0.60±0.02	0.61±0.06
	Zn white	0.37±0.07	0.02±0.01	0.25±0.05	0.60±0.01
	Pb white	0.29±0. 08	–	0.30±0.06	0.63±0.07
	Plaster of Paris	0.32±0.07	0.01±0.01	0.15±0.04	0.55±0.04
Sunflower		1.2±0.2	0.02±0.01	0.06±0.01	0.57±0.01
	Chalk	2.0±0.2	0.01±0.01	0.02±0.01	0.53±0.04
	Co blue	0.8±0.1	0.02±0.01	0.05±0.01	0.62±0.03
	Cd red	1.4±0.2	0.01±0.01	0.05±0.02	0.55±0.04
	Zn white	0.47±0.08	0.01±0.01	0.02±0.01	0.60±0.02
	Pb white	1.8±0.2	–	0.02±0.01	0.54±0.04
	Plaster of Paris	2.5±0.2	0.02±0.01	0.02±0.01	0.55±0.03

[a] $n=3$.

pigment, where this proportion increases significantly (doubling and even tripling in the case of linseed oil). It can also be seen that in some cases the effect of the pigments is the opposite, giving rise to a decrease in the O/P ratio. This can be explained by the different drying capacities of each pigment [10,11]. In some cases, pigments can accelerate and in other cases impede the drying process in the different oils (at this stage the unsaturated fatty acids such as oleic acid oxidise to become a polymeric film by forming cross links which protect the paint from deterioration) [10].

The action of Co(II) used in the dryers is well known [11]. Table 1 shows that the presence of cobalt blue pigment causes the O/P ratio to decrease. On the other hand, the large increase in this ratio when cadmium red pigment is present shows that Cd(II) delay or impede the drying process in the oil (in Fig. 1c it can be seen the chromatograms of the linseed oil with and without cadmium red pigment). Sunflower oil, however, shows no significant changes in the O/P ratio for the different pigments, this is due to the fact that sunflower oil has a low drying capacity which prevents observation of the effect caused by different pigments.

3.3. Analysis of real samples

As applications to suggested method for the identification of drying oils in works of art, two samples from Palomino's vault in the ''Basilica de la Virgen de los Desamparados'' in Valencia (Spain) have been analysed. One of them was taken from Virgin mantle motif, it contain cobalt blue as an inorganic pigment, the results showed the following ratios: $O/P=0.10$ and $S/P=0.68$, the combination of both values points to the presence of linseed oil. The other sample was taken from a pictorial cloud motif containing lead white as an inorganic pigment, the O/P and S/P ratios obtained were 0.30 and 0.63 respectively, which indicate the presence of linseed oil as the most probable drying oil used by the artist.

4. Conclusions

Identification of the lipoid binding media studied by calculating the ratio between the areas of stearic and palmitic acid peaks (S/P) for linseed stand oil and poppy oil is possible. However, the ratio between oleic and palmitic acids (O/P) is also necessary for differentiating linseed oil and sunflower oil, because both oils have very similar S/P ratios.

The study of the influence of the presence of the six pigments (chalk, Co blue, Cd red, Zn white, plaster of Paris) in this identification, shows that there are significant variations in the O/P ratio depending on the type of pigment. These differences may be due to the drying effect of the pigments. According to the results, the cobalt blue pigment has an accelerating effect on the drying process and the cadmium red pigment has a delaying action. In spite of this the differentiation of the three lipoid binding media studied by their S/P and O/P ratios in presence of the pigments is still possible.

Furthermore, due to the complexity of samples from works of art (various pigments are usually present) it is necessary to study the influence of the mixture of pigments in the identification of the lipoid binding media.

Acknowledgements

Financial support from the Valencian Government, project GV97-RN-14-11, is gratefully acknowledged.

References

[1] G. Colalucci, Scienza e Tecnica, Mondatori, Milan, 1988.
[2] J.S. Mills, Stud. Conserv. 11 (1966) 92.
[3] N. Stolov, G. De W. Rogers, in: Boston: Museum of Fine Arts, Vol. 15, 1973, p. 213.
[4] R. Pancella, R. Bart, Kunsttechnol. Konservierung 3 (1989) 101.
[5] P. Hušek, J. Chromatogr. B 717 (1997) 57.
[6] P. Hušek, J. Chromatogr. A 615 (1993) 334.
[7] R. Aruga, P. Mirti, A. Casoli, G. Palla, Fresenius' J. Anal. Chem. 365 (1999) 559.
[8] R. Mateo, M.T. Doménech, V. Peris, J.V. Gimeno, F. Bosch, J. Chromatogr. A 778 (1997) 373.
[9] A. Casoli, G. Palla, P. Musini, J. Chromatogr. A 731 (1996) 237.
[10] M.R. Schilling, H.P. Khanjian, in: ICOM Committee For Conserv., Vol. 1, 1996, p. 220.
[11] J.S. Mills, R. White, The Organic Chemist of Museum Objects, Butterworths-Heinemann, Oxford, 1994.