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Studies of organic paint binders by NMR spectroscopy

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ABSTRACT Nuclear magnetic resonance spectroscopy is applied to the study of aged binding media used in paintings, namely linseed oil, egg tempera and an acrylic medium. High resolution 1D and 2D NMR experiments establish the state of hydrolysis and oxidation of the linseed and egg tempera binders after five years of aging, by determining several markers sensitive to the hydrolytic and oxidative processes of the binder lipid fraction. The composition of the acrylic binder co-polymer is determined by 2D NMR spectroscopy, while the identification of a surfactant, poly(ethylene glycol), found in greater amounts in aged acrylic medium, is reported.

The non-destructive nature of the proposed analytical NMR methodology, and minimization of the amount of binder material needed through the use of sophisticated cryoprobes and hyphenated LC-NMR techniques, make NMR attractive for the arts analyst, in view of its rapid nature and experimental simplicity.

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1 Introduction

A paint consists of pigments, in the form of a fine powder, dispersed in a suitable matrix called the binding medium, which can be of proteinaceous oil or a synthetic polymer nature [1]. Linseed, poppyseed and walnut oils have traditionally found most use in western European painting practice as the binding media of oil paints, while egg tempera and animal glue are commonly encountered in proteinaceous binding media. The solidification of oil paints during drying is effected by cross-polymerization of the triglyceride unsaturated fatty acids, while in egg-tempera paints a large polyamide–lipid crosslink network is formed. During the last fifty years, acrylic polymers have been used extensively as binders in water-soluble acrylic emulsion paints. Drying of acrylic paints is attained by polymer particle fusion during water evaporation, and does not involve as significant a chemical modification of the binder as in oil and egg tempera based binders.

Chromatographic analytical instrumental techniques are very important in the identification of organic binders in paintings [2, 3]. Gas chromatography–mass spectrometry, GC-MS, in combination with various off-line [4–8] or on-line [9] derivatization procedures, pyrolysis-GC-MS [10, 11], direct temperature resolved mass spectrometry and laser desorption ionisation mass spectrometry [12] have been used extensively to study the composition and degradation of organic paint binders. GC-MS has also been successfully applied for the identification of the type of drying oil used in oil paintings by analysis of the oil's fatty acid composition after derivatization [7, 13, 14]. Despite its established and prominent role in materials analysis and characterization [15], the use of nuclear magnetic resonance (NMR) spectroscopy for the analysis of painted artwork has only recently received attention [16]. NMR spectroscopy exploits the dependence of the magnetic properties of spin 1/2 nuclei, such as ^{1}H and ^{13}C, on their immediate chemical environment. Since ^{1}H and ^{13}C nuclei are abundant in all organic materials, NMR spectroscopy is ideal for the identification of organic molecules in complex multicomponent mixtures, such as paint materials. Gradient 2D NMR spectroscopy further increases the analytical capabilities of this methodology, by spreading information in two spectral dimensions.

In this report we present a comparative NMR study of binders used frequently in painted works of art, namely linseed oil, egg tempera and acrylic polymer, using an analytical protocol that involves no chemical preparation, and utilizes sonication in deuterated acetone for the direct extraction of organic material from the binding medium. The composition of the acetone-extracted fraction will be determined by NMR spectroscopy, in an attempt to (a) assess the level of degradation of the aged binders, and (b) verify the ability of the NMR methodology to differentiate between the three different binding media.

The main advantage of NMR spectroscopy over GC-MS analytical methods involving derivatization procedures that have been used to study solvent extracts of paints [4–8], is its non-destructive character. Complications that may arise from incomplete derivatization reactions or side products during chemical preparation are avoided, and the whole of the paint sample can be reclaimed and made available for further analysis upon completion of the NMR experiments, if required. The ability to apply a series of different analytical methodologies is important, since the amount of chemical information

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obtainable from limited quantities of original material from works of art is thus maximized.

2 Experimental

Deuterated acetone-d_6 was obtained from Aldrich. The acrylic base studied was commercially available (Lukas N-2267, Düsseldorf, Germany). The egg tempera binding medium was prepared in the laboratory using egg yolk and vinegar [1]. Films of approx. 0.1 mm thickness were prepared by spreading out linseed oil (LO), egg tempera (ET) and acrylic medium (AM) on glass slides. These model films were kept under room temperature conditions for five years. Before being studied, the binding material was dissolved in 0.6 mL of acetone-d_6 and extracted for 30 min in a sonicator. The solvent was then filtered through glass wool directly into a 5 mm NMR tube.

^{1}H and ^{13}C-NMR 1D spectra were obtained on either a Bruker MSL-300 or a Bruker AMX-500 spectrometer using standard instrument software and pulse sequences [17], at a probe temperature of 299 K. Quantitative ^{13}C NMR spectra were acquired using a low (30°) flip angle and a long relaxation delay (10 seconds). For the ^{13}C NMR spectra, a line-broadening of 1 Hz and drift correction were applied prior to Fourier transformation. Polynomial fourth-order baseline correction was performed before manual integration of all NMR spectra. Chemical shifts in acetone-d_6 are referenced to the solvent peak (δ 2.02/29.8). ^{1}H-^{1}H homonuclear gradient COSY 2D NMR spectra [16, 17] were obtained using 256 increments of 1 K data points, 16 scans and 4 dummy scans with a recycle delay of 1 s. ^{1}H-^{13}C heteronuclear gradient multiple quantum correlation [gHMQC] and multiple bond correlation [gHMBC] 2D NMR spectra were obtained using 128 increments of 1 K data points, 16 scans and 4 dummy scans with a recycle delay of 1 s. The gHMQC experiment was optimized for one bond ^{1}H–^{13}C couplings of 140 Hz by setting the evolution delay to 3 ms. The HMBC experiment used an evolution delay of 60 ms optimized for long range ^{1}H–^{13}C J-couplings of $\sim$ 8 Hz [17]. Before Fourier transformation all 2D data sets were zero-filled to a 1 K × 1 K matrix, and a square-sinusoidal window function was used for processing.

3 Results and discussion

Figures 1 and 2 present the ^{1}H and ^{13}C NMR spectra, respectively, of the acetone-d_6 extract of aged linseed oil, egg tempera and acrylic medium binders. The ^{1}H and ^{13}C NMR spectrum of LO binder extract are dominated by peaks originating from triglyceride (TG), diglyceride (DG), monoglyceride (MG), free fatty acid (FA), diacids (DA) and hydroxy- (and/or oxo-) acid (HA) moieties [16]. Apart from TG, the rest of the molecules are products of ongoing hydrolysis and degradation of the binder as a result of aging.

The NMR spectra of the egg tempera binder in Figs. 1 and 2 are similar to those of LO, indicating that acetone solvent successfully separates the lipid fraction (approx. 33% in freshly prepared egg tempera medium [1]) from the egg tempera binder, while extracting practically none of the proteinaceous material or its degradation products, which are presumably of a much greater polarity. Table 1 summarizes the ^{1}H and ^{13}C NMR chemical shift data of

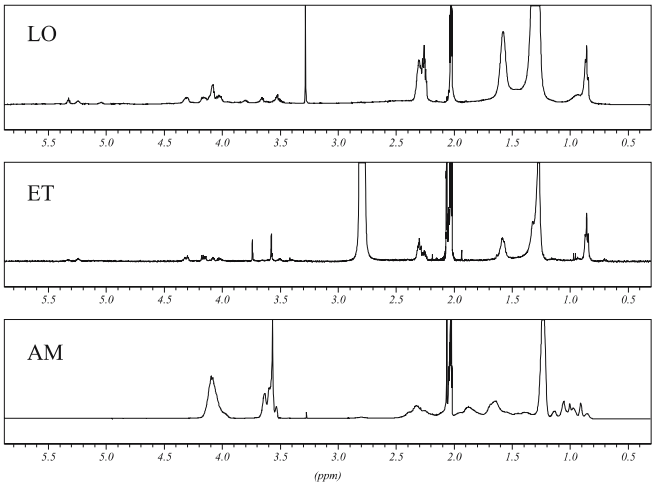

FIGURE 1 ^{1}H NMR spectra of binding material extracted from aged linseed (LO), egg tempera (ET) and acrylic medium (AM) films in acetone-d_6 solvent

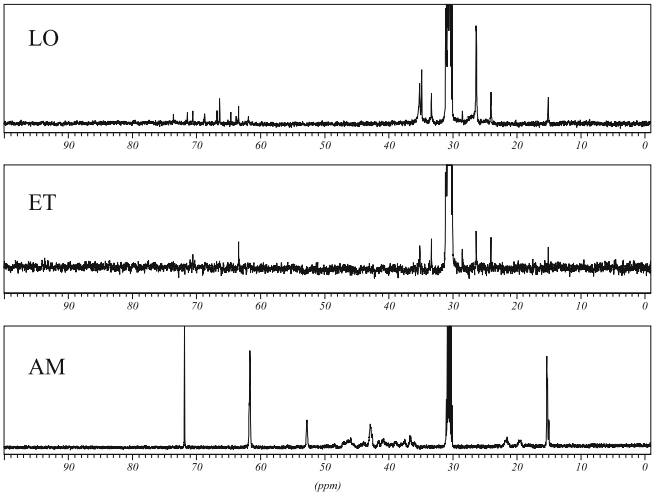

FIGURE 2 ^{13}C NMR spectra (aliphatic region) of binding material extracted from aged linseed (LO), egg tempera (ET) and acrylic medium (AM) films in acetone-d_6 solvent

glycerides (TG, DG, MG), free fatty acids (FA), diacids (DA), and hydroxy- (and/or oxo-) acid (HA) moieties that contribute to the spectra of linseed and egg tempera binder extracts [16].

The ^{1}H NMR spectra of the two lipid-containing binders can be further analyzed through peak integration, in order to provide quantitative information regarding the extent of hydrolysis and degradation of the lipid fraction, by evaluating several markers that have been recently proposed [16]. The values of these markers for the LO and ET binder extracts are provided in Table 2, and are defined as follows: B_f/B, the ratio of free to total carboxyl groups in the binder sample; HFA, indicating the extent of triglyceride hydrolysis; IV, the iodine value of the lipid extract; Di/FA, a measure of the amount of diacids and HA/FA, a measure of the amount of hydroxyacids in the paint binder extracts.

Inspection of Table 2 allows several conclusions to be made with respect to the chemical composition of the two lipid binder extracts: (a) both binders still retain a large amount of unsaturated fatty acid units, as evidenced by the

TABLE 1 Chemical shifts (δ) of the main resonances in the ^{1}H and ^{13}C NMR spectra of binding material extracted from aged linseed, egg tempera and acrylic medium films in acetone-d_6 solvent

δ (ppm)		Group	Assignment
^{1}H	^{13}C		
5.33	130.5	C*H*=CH	unsaturated vinyl protons
5.25	69.9	*CH*–OCOR	triglycerides
5.05	73.0	*CH*–OCOR	1,2-diglycerides
4.09	61.0	CH_2CH_3	PEA
4.32/4.16	62.8	CH_2–OCOR	triglycerides
4.34/4.13	63.1	CH_2–OCOR	1,2-diglycerides
4.1	65.7	CH_2–OCOR	1,3-diglycerides
	66.1		1-monoglycerides
4.06	68.1	*CH*–OH	1,3-diglycerides
		CH–O–	hydroxy- and oxo-acids
3.8	70.8	*CH*–OH	1-monoglycerides
3.66	61.2	CH_2–OH	1,2-diglycerides
3.61	52.1	COOCH_3	PMMA
3.56	71.2	CH_2O	PEG
3.5	64.0	CH_2–OH	1-monoglycerides
2.32	42.2	–CH_2–CH–	PEA
2.30	34.6	CH_2COOR	sn-2 esterified acids and diacids
	34.5		sn-1,3
2.24	34.2	CH_2COOH	free fatty acids and diacids
2.02	27.8	CH_2CH=	unsaturated fatty acids
1.6–1.9	35.1–37.4	–CH_2–*CH*–	PEA
1.57	26.3	CH_2CH_2COO–	all fatty acids and diacids
1.3–1.5	44.5–46.8	–*CH*$_2$–C–	PMMA
1.23	14.6	CH_2CH_3	PEA
1.2–1.4	28–30	$(CH_2)_x$	all fatty acids and diacids
1.2–1.4	32.6	$CH_2CH_2CH_3$	oleic/linoleic acid
1.2–1.4	23.3	CH_2CH_3	oleic/linoleic acid
0.85–1.05	20.8, 18.8	*CH*$_3$–C–	PMMA
0.83-0.98	14.4	*CH*$_3$	all fatty acids

relatively high IV values. This is also corroborated by the appearance of a peak with δ 27.8 in the ^{13}C NMR spectra of the binders in Fig. 2, which is due to methylene carbons directly attached to an unsaturated double carbon–carbon bond [16]; (b) triglyceride hydrolysis in the LO binder is more advanced (higher B_f/B, and HFA values) than in the egg tempera binder. This is also evident in the ^{13}C NMR spectra of the binders, where the carbon peak at δ 34.2 due to methylene carbons next to free carboxylic groups is evident for LO, but weak for ET; (c) the levels of hydroxy-acids in the two binders are similar, but LO contains far more diacids, indicating that fatty acid degradation in LO is more advanced.

It is interesting to note that the ET spectrum in Fig. 1 shows a peak at δ 0.70 which is not present in the LO binder spectrum, tentatively attributed to sterically-hindered methyl groups present in sterols. Since linseed oil does not contain any significant amounts of sterols, while cholesterol constitutes about 0.5% of whole eggs [1], we are currently exploring the ^{1}H peak at δ 0.70 as a possible identifier that may be used to differentiate between linseed and egg tempera binders using NMR spectroscopy.

Binder	B_f/B	HFA	IV	Di/FA	HA/FA
Linseed oil	0.47	0.32	4.9	0.62	0.09
Egg tempera	0.22	0.18	17.3	0.00	0.11

TABLE 2 Characteristic parameters (markers) determined from the ^{1}H and ^{13}C NMR spectra of binding material extracted from aged linseed and egg tempera binder films with acetone-d_6 solvent. For abbreviations used see text

The ^{1}H and ^{13}C NMR spectra of aged acrylic base are depicted in Figs. 1 and 2, and are significantly different from the spectra of both LO and ET binders. Thus, analysis of the NMR spectra of acetone extracts can be used to easily conclude whether an acrylic medium has been used in a painting either originally by the artist, or subsequently during restoration work performed by conservators. The acrylic media available to artists usually consists of a blend of different acrylic and non-acrylic polymers and various additives, such as surfactants, colloids or stabilizers depending on the medium producer. NMR spectroscopy can be used for the identification of the composition of an acrylic medium by identifying the different polymeric components present. This can also be useful for introducing time constraints for dating purposes, since some acrylic formulations were developed only recently. Figure 3 presents the ^{1}H-^{1}H homonuclear gradient COSY (a) and ^{1}H-^{13}C heteronuclear gradient multiple quantum correlation [gHMQC] 2D NMR spectra of the acetone extract of the acrylic base. Off-diagonal cross-peaks in the ^{1}H-^{1}H homonuclear 2D COSY spectrum indicate correlation of protons by J-coupling due to their close proximity in the carbon skeleton of the polymer. However, the peaks in the heteronuclear gHMQC 2D NMR spectrum correlate carbon nuclei with their directly bonded protons. A heteronuclear gHMBC 2D experiment tracing the long range J-coupling correlation of carbon nuclei with protons two to four bonds away in the carbon polymer chain was also obtained (not shown). The analysis of the 2D NMR spectra led to the total assignment of all peaks present in the ^{1}H and ^{13}C 1D NMR

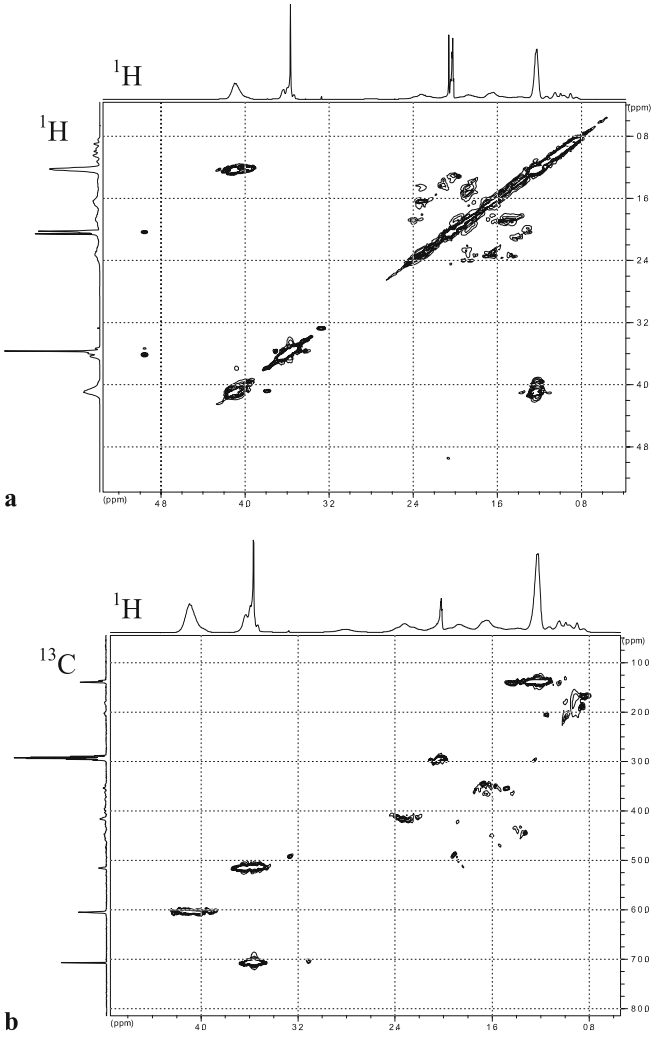

FIGURE 3 ^{1}H-^{1}H homonuclear gradient COSY (**a**) and ^{1}H-^{13}C heteronuclear gradient HMQC (**b**) 2D NMR spectra of the acetone-d_6 extract of aged acrylic medium

spectra of Fig. 1, and the identification of the polymeric constituents of the acrylic base as a co-polymer of ethyl acrylate EA, and methyl methacrylate MMA units, and poly(ethylene glycol), PEG [12]. PEG is a well known non-polar surfactant, used to prevent association of acrylic particles before drying.

Table 1 shows the ^{1}H and ^{13}C NMR chemical shift data of polymeric constituents of the acrylic base obtained from Figs. 1 and 2. Once the chemical structure of the acrylic binder is known, integration of the ^{1}H NMR spectrum provided the molar fraction of MMA units in the acrylic copolymer as 0.29, and the molar fraction of PEG in the aged acrylic medium as 0.08, in good agreement with a study of another acrylic medium [12]. It is worth noting that analysis of the NMR spectra of the acetone extract of a freshly prepared acrylic base film provided the same acrylic copolymer composition, but a larger PEG mole fraction of 0.125. Since PEG has low volatility, further work is needed to show whether PEG microseparation effects are involved during aging of the acrylic base, or being water-soluble, that PEG is exuding to the surface of the film.

4 Conclusions

The experimental results presented show that NMR spectroscopy is a valuable analytical tool in the study of organic paint binders. The study of solvent extracts of aged binding material of oil, proteinaceous or synthetic polymer origin reveals important information regarding the level of deterioration of the organic binder. The acetone extracts of lipid-containing binders contain chemical molecules characteristic of the ongoing processes of TG hydrolysis and oxidation, such as mono- and diglycerides, free fatty acids and diacids. For similar aging conditions, the linseed binder seems to suffer greater lipid hydrolysis and degradation than the egg tempera binder. The presence of small quantities of acrylic medium in paints can be easily detected by NMR spectroscopy, because of their different spectral characteristics in both ^{13}C and ^{1}H spectra. Furthermore, we have shown that 2D NMR spectroscopy can be used efficiently to determine the copolymer composition of acrylic media, and identify the presence of various additives included in their formulation.

The use of deuterated solvents of higher polarity, such as D_2O, for the extraction and NMR analysis of proteinaceous binders, and the study of aging in egg tempera paintings is currently under way in our laboratory. Finally, it should be stressed that the use of cryogenically cooled NMR probes and microprobes [18, 19], offers the chance to minimize the amount of material needed to perform NMR analysis down to the μg scale, and is making NMR spectroscopy a favourable technique for the analyst, in view of its rapid nature and experimental simplicity. Thus, we believe NMR spectroscopy has the potential to become an important analytic tool in the study of painted art works.

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