# Capability of Far-Infrared for the selective identification of red and black pigments in paint layers

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HIGHLIGHTS

- Some inorganic pigments (oxides) change their absorption band position when mixed with oil.
- Detection limits are high for some pigments in oil mixtures and change when applied to canvas.
- Aging of the paint layers produces changes in the carboxylate bands.

GRAPHICAL ABSTRACT
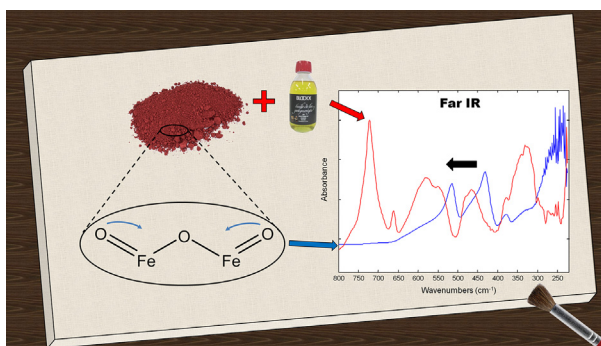
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ABSTRACT

Artworks are complex objects that merit study and preservation. Far-infrared spectroscopy in ATR mode appears to be a suitable technique for this purpose because it enables information to be obtained regarding the material's composition in a non-destructive way. The use of Far-infrared is especially interesting because most organic compounds do not absorb in this energy range, suggesting the possibility of identifying inorganic pigments. Based on works performed by two research groups from the University of Bologna and the University of Tartu, this study attempts to obtain additional information regarding the capabilities and limitations of Far-infrared spectroscopy when it is applied to objects as complex as artworks. This article first studies the capability of the technique for identifying pigments by following the stability of the position of their absorption bands when mixed with linseed oil, the minimum amount of pigment necessary to be detected and how this amount changes when it is part of a paint layer. The consequences of the pigment: linseed oil interaction and the ageing process are also studied through changes in the linseed oil signal absorptions related to the acid carboxylic and carboxylate bands. The entire study leads to the conclusion that Far-Infrared in ATR mode is an interesting option for the selective identification of some inorganic pigments, but their potential application depends on each case considered.

1. Introduction

From a material point of view, artworks are complex objects with challenging material characterisations. Paint layers are an example of this complexity because they include pigments, fillers,

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and binders, which imply the presence of both organic and inorganic compounds. These materials are heterogeneously distributed across layers, and their major and minor constituent compounds are mixed not only with themselves, but also with their degradation products. Nonetheless, the complex composition and interaction of these compounds is very worthy of study due to their aesthetic or stability relevance.

In addition, any attempt at material characterisation must consider the object's physical preservation for the future. Thus, if an artwork is studied, sampling should be avoided or reduced to a minimum, which is a limitation that has sparked an ongoing research effort to develop the least invasive analytical techniques possible. [1].

Among these, Fourier Transform Infrared spectroscopy (FTIR) has stood as a great tool for the analysis of paint layers. In the Mid-Infrared range, this technique is capable of providing information about organic compounds (binders, pigments, and fillers) with a minimal amount of sample (in transmission mode) or even without sampling (in Reflectance or Attenuated Total Reflectance modes) [2–3].

However, some important inorganic pigments, such as oxides and sulphides, do not show absorptions in the Mid-Infrared range. This is a consequence of the mass of the atom involved in the molecule, which leads the vibrations to lower energies in the range corresponding to Far-Infrared.

In the past few years, these instruments have evolved in size portability and electronics, improving their capabilities for artwork analysis. Among them, the development of Deuterated TriGlycine Sulfate (DTGS) detectors allowed for the commercialisation of FTIR equipment capable of acquiring the spectrum in both Mid- and Far-Infrared ranges, enabling the use of both ranges in routine analyses of paint layers.

Two research groups (E.L. Kendix et al. from the University of Bologna and S. Vahur et al. from the University of Tartu) developed important research to evaluate and apply Far-Infrared spectroscopy in attenuated total reflectance (ATR) mode for determining paint layers composition, focused on pigment identification. The work of these two groups has grounded the capability of this approach, but at the same time they have noted difficulties related to the complexity of the samples and the differences between Transmission and ATR modes [4–14].

Despite the significant advantage related to the non-destructivity of the ATR mode, a drawback is that the spectra obtained are not completely equivalent to those acquired by transmission.

The origin of these differences is related to the penetration depth of the evanescent wave in ATR mode. In transmission mode the optical path is constant, whereas in ATR it is variable, as it is the penetration depth that ranges between 0,5 and 2 μm. More specifically, in ATR mode the penetration depth (dp) (or depth equivalent) depends on instrumental parameters, such as the refractive index of the ATR crystal ($\eta 1$), the reflection angle (θ), and the number of reflections in the crystal. However, it also depends on the refractive index of the sample ($\eta 2$) and wavelength, with additional dependence in a nonlinear way, on the refractive index from the wavelength values [15–17]. Consequently, dp and absorption variations lead to the distortion of the ATR spectrum signals, such as increasing their intensity at lower wavenumbers, generating asymmetric bands and shifting their maxima towards lower wavenumbers with regard to the behaviour observed in Transmission mode.

Several algorithms have been developed and applied to correct ATR spectra and lead them to a position and shape equivalent to those obtained with Transmission [3,17]. An important effort has also been made to create an open database of far-Infrared ATR spectra of artwork constituent materials [10–17].

Nonetheless, for some inorganic pigments, such as oxides and sulphides, the refractive index ($\eta 2$) is much higher than the refractive index of the ATR crystal ($\eta 1$), which only allows for approximate corrections on the dp. One option to overcome this difficulty is to mix the pigment with linseed oil (CH–(CH$_2$-O-CO-R)(CH$_2$-O-CO-R')(-O-COR'') were RCOOH can be linoleic, palmitic, oleic or alpha linoleic acid) with the purpose of decreasing the refractive index and improving the quality of the spectra acquired [10]. This option has been shown to result in the appearance of a new effect for some inorganic pigments: a shift of the absorption bands to higher energies (opposite to what could be expected as consequence of a decrease in the refractive index ($\eta 2$)).

At this point, it is interesting to note the studies that explain the formation of soaps in linseed oil paintings as a result of the reaction of linseed oil carboxylic acids with inorganic pigments such as zinc oxide, lead oxide, or iron oxide (($RCOO)_n M$) [7,18–25]. This phenomenon may also be related to the shift to higher energies of the absorption bands when pigments are mixed with linseed oil.

In the Mid-Infrared range, the formation of these metal carboxylates and the linseed oil polymerisation process induce some changes in the registered absorption spectra. These changes are evidence of the saponification process and can be summarised as a decrease or even a disappearance of the carboxylic band at approximately 1710 cm^{-1}, the appearance of carboxylate bands in the range between 1600 and 1500 cm^{-1}, the broadening of the ester band at 1740 cm^{-1}, and the changes in absorption of the double bonds of fatty acids at 1650 cm^{-1} related to the drying process [7,21].

Hermans and Baij et al. [18,25] discussed two types of metal carboxylate species: the first was characterised by sharp bands and related to crystalline metal complexes (metal soaps) appearing as spots on the paint surface, and the second was expressed in broad bands shifted to higher energies compared with the first species, corresponding to amorphous metal carboxylate dispersed throughout the binding medium.

The variation in the spectral distribution shape of the carboxylate absorptions, as well as the reactivity and rate of this process for zinc, lead, iron, manganese, cadmium and copper based pigments in linseed oil and egg tempera media, have been summarised [7].

However, several aspects of the saponification process in actual paint layers remain unknown, partially due to the different behaviours observed when natural ageing results are compared with artificial ageing. Van der Weerd [21] noted the different effects of lead white on carboxylate production if the ageing was natural or induced by UV light.

As a whole, the potential interest of Far-Infrared for determining the inorganic pigments is clear, but it is also clear that there is a notable uncertainty associated with band identification as a consequence of the different phenomena concurrent with the signal distortion and the shift related to the use of the ATR mode, the unknown composition of the samples, and the effect of the binder. As a consequence, the goal of this article is to contribute to establishing the capability of Far-Infrared in ATR mode for identifying pigments in linseed oil paint layers.

This work is focused on red and black pigments, and the specific objectives are divided into two steps: a preliminary study aimed to obtain basic information about the pigment band shift as a consequence of the presence of linseed oil and the minimum amount of pigment detectable in this media; and a second step that is focused on evaluating pigment identification in complex linseed oil paint samples, as well as the study of their evolution over time.

2. Experimental

2.1. Materials

The pigments used in this study are presented in Table 1. For the mixtures and linseed oil paintings, polymerised stand linseed oil 358 purchased from Jacques Blockx (Belgium) was used. A commercial canvas F6 (33 × 42 cm) on a stretcher prepared with a white ground made of calcium carbonate and rabbit glue from Piera (2015), was used as a support in the linseed oil paintings.

2.2. Apparatus

Analyses of the infrared spectrometry with Fourier transform were performed using an infrared spectrometer IR Frontier (PerkinElmer), equipped with an accessory of attenuated total reflectance GladiATR (pike Technologies). The detector used is a DTGS with a CsI window and the 3 mm ATR crystal is made of diamond with an incident angle of 45 degrees.

Accelerated ageing was performed in a high-speed exposure unit Sunset CPS+ (Heraus) equipped with air-cooled xenon lamps and controlled black standard temperature.

2.3. Sample preparation

For pigment identification in linseed oil media studies, several mixtures of pigments with linseed oil were prepared. In all cases, the samples were prepared by weight and homogenised by shaking them for 24 h in an end-over-end shaker. The final concentrations obtained for the mixtures of pure pigments used for studying the spectral stability were 9.1% for Red Lead, 8.8% for Iron Red, 8.5% for Rouge Vermillion, 8.8% for Cinnabar, 8.8% for Mars Black, 12.9% for Manganese Black, 11.2% for Vine Black, 10.0% for Ivory Black and 13.0% for Lead White.

In the case of the mixtures prepared for studying the minimum amount of pigment detectable, the single mixtures' final concentrations were: for Red Lead, 9.1, 5.3, 1.9, 1.0 and 0.2%; for Iron Red, 8.8, 4.7, 1.9, 1.1 and 0.1%; for Rouge Vermillion, 8.5, 4.9, 1.9, 0.9 and 0.1%; for Cinnabar, 8.8, 5.7, 1.9, 1.1 and 0.1%; for Mars Black, 8.8, 4.7, 1.9, 1.1 and 0.2%; and for Manganese Black, 12.9, 4.5, 1.9, 1.0 and 0.1%, whereas the binary mixtures final concentrations are presented in Table 2.

For studying the pigment identification in complex paint layers, several binary and ternary mixtures were prepared. In general, 1 g of each pigment was mixed with the necessary amount of linseed oil to paste them. The mixture was then homogenised and used to paint in a traditional manner using a brush in a commercial canvas with calcium carbonate and rabbit glue preparation The layers of paint were applied with successive brush strokes in horizontal and vertical directions to obtain a homogeneous distribution. The area painted for each composition was 5 × 12 cm. The thickness of the paint layer ranges between 100 and 150 μm. Finally, the linseed oil paintings were allowed to stand in room conditions for a period of time, as described in the 2.4 Ageing section. The linseed oil paintings were prepared and its final pigment concentration, in brackets, were NB6: Red Lead (22.5%) and Iron Red (23.1%), NB9: Red Lead (25.2%) and Rouge Vermillion (24.6%), NB20: Red Lead (23.8%), Rouge Vermillion (19.9%) and Lead White (3.7%), NB8: Red Lead (31.1%) and Cinnabar (31.1%), NB16: Rouge Vermillion (14.5%) and Lead White (14.3%), NB10: Cinnabar (32.8%) and Lead White (32.8%), NB13: Red Lead (17.5%), Cinnabar (18.1%) and Lead White (17.4%), NB15: Mars Black (24.1%) and Manganese Black (26.9%) and NB14: Manganese Black (24.7%) and Ivory Black (20.5%).

2.4. Ageing

The prepared linseed oil painting samples were aged using two different methods. First, the paintings were naturally aged for one year in environmental conditions under natural sunlight exposure.

Second, the same samples were artificially aged in the equivalent of an additional year. To do that, a 3 × 3 cm section of the canvas was cut and photodegraded in a high-speed exposure unit at an irradiation power of 765 w/m² with a glass filter cut-off (>295) and a black panel temperature of 45 degreesC for 34 h.

2.5. Measurement conditions

For the different analyses, a small amount of pure pigment or linseed oil pigment mixture was placed in the ATR crystal and pressed against it. In the case of the linseed oil paints in the canvas, a fraction of 1 per 2 cm was cut from the canvas and placed in the crystal, with the paint layer facing it and pressed. In all cases, the spectrum was registered from 4000 to 225 cm^{-1} using 16 scans (as the default acquisition protocol) and each sample was analysed on triplicate. Between each measurement, the crystal surface was cleaned with ethanol, and a blank was measured to check and subtract any possible contamination. The spectra were measured using Spectrum 10™ software with a resolution of 1 cm^{-1}.

2.6. Data treatment

To improve the study of the spectra and to improve the visualisation and recognition of the differences between the spectra, different treatments were applied. In the case of the spectral stability in linseed oil mixture studies, a standard normal variate (SNV)

Table 1
Pigments used in this study and its commercial specifications.

Pigment	Commercial name	Reference	Manufacturer	Composition [a]
Red Lead	Red Lead, Minium	42,500	Kremer (Germany)	Pb_3O_4 (96%) PbO_2 (3.35%)
Iron Red	Iron Oxide Red 120 M	48,120	Kremer (Germany)	Fe_2O_3 (96%) $SiO_2 + Al_2O_3$ (3%)
Rouge Vermillion	French vermilion Subst.	675	Sennelier (France)	Azoic pigments mineral fillers
Cinnabar	Natural Cinnabar	10,620	Kremer (Germany)	HgS
Mars Black	Iron Oxide Black 318, high tinting	48,400	Kremer (Germany)	Fe_3O_4
Manganese Black	Manganese Black	47,501	Kremer (Germany)	$(Fe,Mn)_3O_4$
Vine Black	Vine Black, German	47,000	Kremer (Germany)	C
Ivory Black	Ivory Black JU	47,200	Kremer (Germany)	Bone charcoal
Lead White	Cremnitz White	46,000	Kremer (Germany)	$2PbCO_3 \bullet Pb(OH)_2$

[a] According to the manufacturer

Table 2
Concentration of the binary red and black mixtures prepared for the study of the minimum amount of pigment detectable, the remaining percentage corresponds to linseed oil.

Pigment Concentration (%) (w/w)													
Mixture 1		Mixture 2		Mixture 3		Mixture 4		Mixture 5		Mixture 6		Mixture 7	
Red Lead	Lead White	Red Lead	Iron Red	Red Lead	Rouge Vermillion	Mars Black	Vine Black	Mars Black	Ivory Black	Manganese Black	Vine Black	Manganese Black	Ivory Black
8.5	9.7	7.4	7.4	8.0	8.0	8.1	8.7	8.3	8.5	8.2	8.1	8.2	8.0
4.4	8.7	6.3	4.5	4.7	4.1	4.3	8.7	5.9	8.6	4.2	8.9	4.3	8.7
1.8	9.4	1.9	1.9	1.9	2.3	1.8	8.6	1.9	8.9	1.8	8.5	1.8	8.7
0.9	8.9	1.3	1.0	1.1	1.0	1.1	8.4	0.9	9.2	1.3	9.1	0.9	8.8
0.1	9.1	0.1	0.1	0.2	0.2	0.1	8.1	0.1	9.6	0.1	8.5	0.1	8.5

algorithm was applied to normalise their intensities. For the study of the minimum amount of pigment detectable, no treatment was applied to avoid distortions in the intensity of the spectral bands. Finally, in the case of the linseed oil paintings, the spectra were normalised to a linseed oil band of 1740 cm^{-1} to obtain a constant height on this band. This procedure was also followed when the linseed oil spectrum was subtracted to ensure that the band at 1740 cm^{-1} was the same height in the linseed oil spectrum and in the original spectrum of the pigment mixed with linseed oil.

For calculating the band intensity, the common procedure of IR analysis was applied, to the spectra without treatment, which consists of the correction of the height of the band from a baseline created between the valleys of the band.

All these data treatment procedures were performed using MATLAB 2009 software [26].

3. Results and discussion

The content of this section is divided into two parts, following the specific objectives: a preliminary study aimed to obtain basic information for pigment identification in linseed oil media; and a second part focused on the capability to identify pigments in complex paint layers.

The pigments selected in this study were reds (Red Lead, Iron Red, Rouge Vermillion and Cinnabar) and blacks (Mars Black, Manganese Black, Vine Black and Ivory Black) due to their wide use in painting and because among them there are inorganic and organic compounds, which enable us to show the different behaviours of oxide materials. Lead White was also included because it is often part of the composition of the paint layers. The concentrations used were those in the range that could be presented in real paintings.

All spectra shown were acquired in ATR mode.

3.1. *Pigment identification in* linseed *oil media.*

The goal of the preliminary study was to determine the characteristics and limitations of Far-Infrared spectroscopy in ATR mode for the analysis of red and black pigments in linseed oil media. For this purpose, first, the behaviour of the pigment absorption bands when they were mixed with linseed oil was studied. Second, the minimal amount of pigment that produces detectable bands was established.

3.1.1. *Spectra stability in* linseed *oil mixtures*

The spectra of the pure pigments, as well as the spectra of the pigments mixed with linseed oil (in a proportion of approximately 10%), were acquired in Far-Infrared and Mid-Infrared in ATR mode. For all of the spectra obtained, pigment-related bands for both types of samples were established for the two IR regions considered. In some cases, the overlapping of the pigment's bands with those of the linseed oil spectrum did not make identifying the pre-

sent bands easy, as was the case of Rouge Vermillion (Fig. 1a). In those cases, the pure linseed oil spectrum was subtracted, obtaining a net spectrum (Fig. 1b) where the pigment bands became evident. This procedure was applied for the Rouge Vermillion, Cinnabar, Manganese Black, Vine Black Ivory Black and Lead White pigments. The most important bands observed in the pure pigments were, for Red Lead, the Pb-O stretching band at 488 cm^{-1}, for Iron Red, the Fe-O bending band at 431 cm^{-1} and stretching band at 515 cm^{-1}, in the case of Rouge Vermillion, the C-N stretching vibration of the azoic group at 1196 cm^{-1} and for Cinnabar, the three Hg-S stretching bands at 247, 286 and 346 cm^{-1}. In the case of black pigments, the most important bands observed were, the Fe-O stretching vibration band at 543 cm^{-1} for Mars Black, the Mn-O stretching bands at 464 and 515 cm^{-1}, for Manganese Black, the Fe-O stretching bands at 468 and 530 cm^{-1} and Si-O stretching bands at 798 and 1007 cm^{-1}, for Vine Black and the P-O bending at 600 cm^{-1}, the Si-O stretching at 961 cm^{-1} and the P-O stretching at 1023 cm^{-1} for Ivory Black. Finally, in the case of Lead White, the C-O rocking at 678 cm^{-1} and the C-O stretching bands at 1045 and 1392 cm^{-1}, were observed. Additionally, a band under 300 cm^{-1} can be attributed to water, as this region is not used for identification, but more importantly the samples from real artworks do not allow the application of treatments to remove this water, the abovementioned region was not taken into account.

Based on the observed bands, two groups of pigments could be distinguished (Table 3): those with a shift of the spectral bands when mixed with linseed oil (Fig. 2), and those with no shift in their positions (Fig. 1). This band movement was only observed in pigments composed of oxides (Red Lead, Iron Red, Mars Black and Manganese Black), where all their bands shifted towards higher energies, whereas the other pigments' bands remained in the same position. It is important to note that, although the bands shifted, the general shape of the spectra remained the same.

The shift towards higher energies when the pigments are mixed with linseed oil has also been observed by other authors. Nonetheless, the extent of this movement is different from that observed in this study; as an example, Tartu's group database [10] (Table 3) presents a smaller shift in their measurements, also performed in ATR mode. Consequently, the results presented here introduce a certain degree of uncertainty in establishing the position of each band and its subsequent use for pigment identification.

This behaviour could be related to the sample preparation. According to the description provided [5,10–12], the linseed oil pigment samples of the database had thicknesses between 20 and 100 μm, and as Harrick [12] indicated, for thin films the effective thickness was independent of the penetration depth, and the acquired spectra appeared to be less distorted. These results illustrate the dependence of the spectral positions and the movement of the different bands on the experimental conditions.

In any case, the shift to higher energies observed in the samples prepared in this study cannot be attributed to a decrease in the refractive index of the pigment-linseed oil mixture, since the movement was towards higher energies. A possible hypothesis
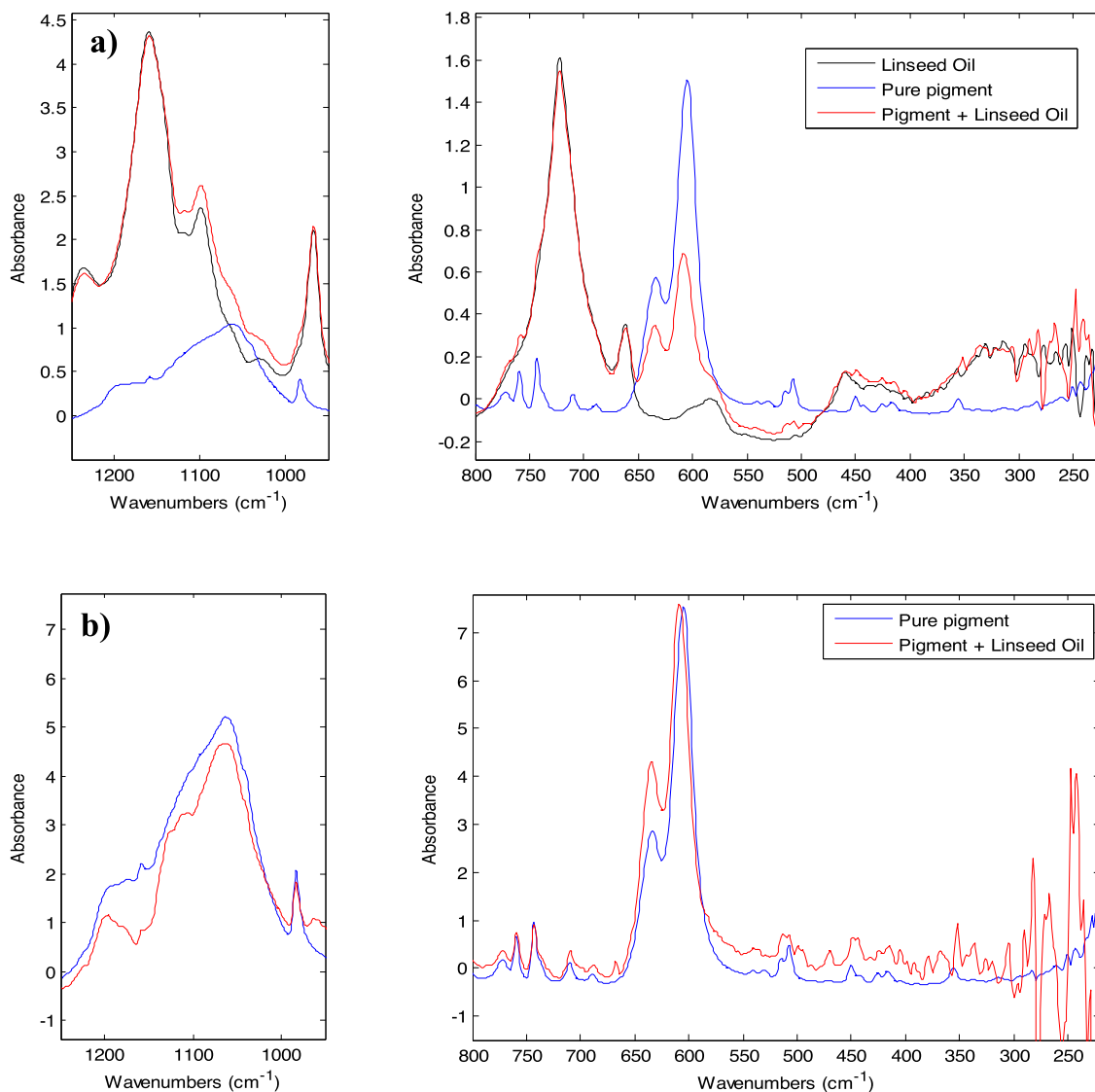
Fig. 1. Spectra of Rouge Vermillion pure and mixed with linseed oil as well as the pure linseed oil spectra (a) without treatment and (b) with the linseed oil subtracted.

to explain this phenomenon is that this behaviour is related to the reactivity of these oxides with the carboxylic acid of the linseed oil. This reactivity has been widely studied and would lead to an "apparent decrease" in the reduced atomic mass included in Hook's equation. Then, this reduction would correspond to the anharmonic oscillator model, which would imply higher vibration frequency values and thus higher energy positions in the spectra.

Table 3
Principal bands of the different pigments analysed, pure and mixed with linseed oil, measured in this study and presented in [10] both in ATR mode.

Pigment	Measured		Database University Tartu [10]	
	Pure Pigment bands (cm^{-1})	Mixed with linseed oil bands (cm^{-1})	Pure Pigment bands (cm^{-1})	Mixed with linseed oil bands (cm^{-1})
Red Lead	240, 299, 355, 419, 510	281, 325, 380, 443, 528	277, 317, 373, 428, 511, 527	277, 311, 371, 427, 532
Iron Red	240/275, 327, 379, 431, 515	327, 345, 379, 475, 558	275	345
Rouge Vermillion	609, 634, 1064, 1196	609, 634, 1064, 1196		
Cinnabar	247, 286, 346	247, 286, 346	274, 329	279, 339
Mars Black	323, 543	371, 570	540	346, 544
Manganese Black	374, 464, 515	405, 546, 575		
Vine Black	415, 468, 530, 742, 798, 1007	415, 468, 530, 742, 798, 1007		348, 420, 468, 535, 724, 804, 977
Ivory Black	250, 560, 600, 961, 1023	250, 560, 600, 961, 1023	263, 339, 470, 561, 599,961, 1024	
Lead White	395, 678, 768, 1045, 1392	395, 678, 768, 1045, 1392	358, 386, 411, 628, 691, 762, 1045, 1397	360, 387, 680, 771, 1045, 1159, 1398
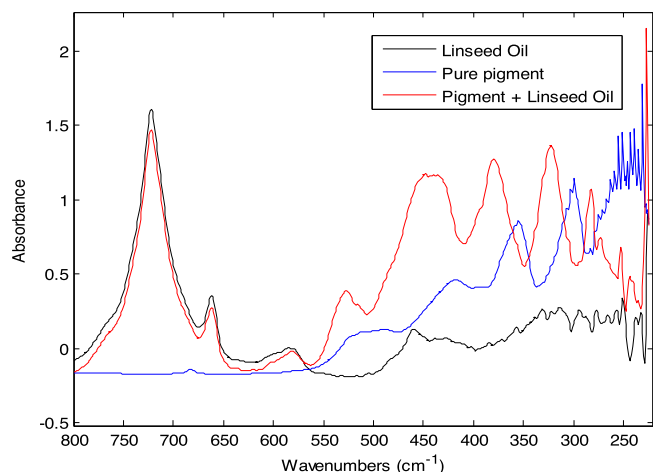
Fig. 2. Spectra of Red Lead pure and mixed with linseed oil as well as the pure linseed oil spectra.

The reaction between the inorganic pigments and the linseed oil, together with the polymerisation process of the linseed oil, should also produce changes in the vibrations related to the existing linseed oil bands (ester absorption at 1740 cm^{-1} and carboxylic acid at 1708 cm^{-1}) and the appearance of new signals due to the carboxylates generated in the range 1550 – 1500 cm^{-1}.

To observe these changes, the spectra of pigments with and without band shifts (taking Red Lead and Cinnabar as examples, respectively) were studied (Fig. 3). It is possible to observe that, in almost all cases, the ester band at 1740 cm^{-1} became wider and the weak carboxylic acid shoulder at 1708 cm^{-1} decreased or even disappeared, with these changes being small, probably due to the high proportion of linseed oil regarding the pigment. The decrease in the carboxylic acid band in the first group of pigments is produced as a consequence of the saponification reaction. Conversely, in the second group it may be related to the combined effect of the low intensity of the initial signal of carboxylic acid and the broadening of the ester band during the drying process. In the case of the new carboxylate band at 1530 cm^{-1}, it appeared exclusively in the spectra of Red Lead and Lead White, and even if it did not show band shifting, its production of lead soaps is widely described in the literature [7,19–20]. This carboxylate band supports the hypothesis of the linseed oil reaction with the metallic

pigments; however, it is difficult to extend this conclusion to the rest of them, as this band was not observed, probably due to the linseed oil:pigment ratio, the slower reaction rate, or both.

3.1.2. Minimum amount of pigment detectable

The second step in studying the capability of Far-Infrared for identifying pigments in linseed oil paint mixtures was to establish the minimum amount of pigment capable of producing a band in the spectra that could be distinguishable. For this purpose, a set of samples composed of one or two red or black pigments mixed with linseed oil at five different concentrations (containing approximately 10, 5, 2, 1 and 0.1%) were prepared and analysed on triplicate.

3.1.2.1. Single mixtures. To establish the minimum amount of pigment detectable, first a spectral band not overlapping with any other band of the linseed oil or other pigments that could be present in a mixture was selected. Next, the net height of this band for the different concentrations was calculated, as is commonly performed, by using the union of valleys located on each side of the band as a baseline. Finally, the mean and standard deviation for the three replicates at each concentration level were calculated (Table 4). As an example, the spectra for the Red Lead pigment are presented (Fig. 4). In this case, the 380 cm^{-1} band was selected. The concentrations of 0.1 and 1% showed negative values in the band (Table 4), as could be expected, taking the shape of both spectra into account (Fig. 4). The intensity value at 2% was positive but small and lower than their standard deviation, which is a reflection of the spectra that shows a small visible band, but only in some of the cases. Therefore, the minimum amount had to be higher than this value. Finally, the two highest concentrations showed positive intensities in all replicates with values larger than their standard deviations. These results indicated that at these concentrations the bands were easily observed, and therefore 5% was selected as the minimum amount of pigment detectable.

Following this procedure, minimum amounts of pigment detectable were determined at 5% for Red Lead and Cinnabar and 1% for Rouge Vermillion and Iron Red.

In the case of black pigments, two bands were selected for each pigment due to potential overlapping with other components of the paint layer. A minimum amount of 5% was established for Mars Black and Manganese Black when the signals at 371 cm^{-1} and 405 cm^{-1}, respectively, were considered. When the bands located at approximately 570 cm^{-1} were analysed, the detection capability seemed to improve to 0.1% for both pigments. However, this result
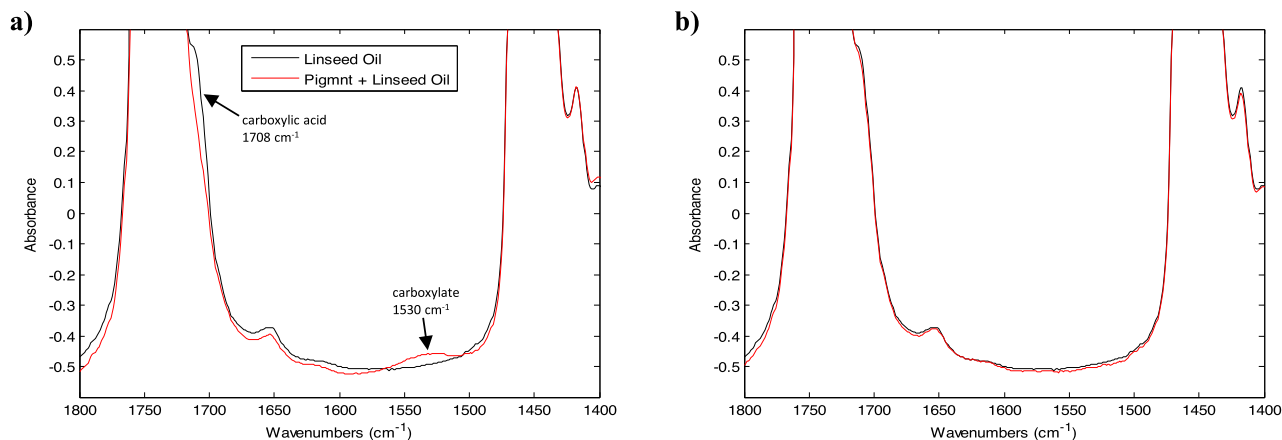
Fig. 3. Mid IR spectra comparison of the linseed oil bands for the linseed oil and the pigments mixed with linseed oil for a) spectrum with band shift (Red Lead) and b) without band shift (Cinnabar) in the far IR bands.

Table 4
Mean and standard deviation, in brackets, of the band height for the different pigments studied. The band used for the measurement are indicated. The results obtained with the net spectra, after linseed oil spectra subtraction, are presented after the dash.

Pigment	Red Lead	Iron Red	Rouge Vermillion	Cinnabar	Mars Black		Manganese Black	
Content level (%)	380 cm⁻¹	558 cm⁻¹	609 cm⁻¹	346 cm⁻¹	571 cm⁻¹	371 cm⁻¹	575 cm⁻¹	405 cm⁻¹
10	0.022(8)	0.029(10)	0.020	0.0051(7)	0.035(2) / 0.034(2)	0.018(2) / 0.028(3)	0.012(4) / 0.009(4)	0.003(1) / 0.004(1)
5	0.0111(7)	0.014(5)	0.012(1)	0.0030(7)	0.018(3) / 0.017(3)	0.008(2) / 0.016(2)	0.0060(7) / 0.0030(6)	0.0023(9) / 0.0030(9)
2	0.001(3)	0.007(1)	0.0038(5)	0.0007(7)	0.0077(4) / 0.0068(4)	−0.001(2) / 0.005(2)	0.0041(4) / 0.0011(5)	0.0004(3) / 0.0011(3)
1	−0.0001(7)	0.004(1)	0.0019(5)	0.001(1)	0.0042(1) / 0.0033(1)	−0.002(1) / 0.004(2)	0.0036(4) / 0.0005(4)	−0.0001(7) / 0.0005(7)
0.1	−0.0024(2)	−0.0013(3)	0.00002(10)	0.0002(4)	0.014(2) / 0.0005(2)	−0.0031(5) / 0.0017(9)	0.0026(6) / −0.0004(7)	0.0005(5) / 0.0011(4)
Minimum amount detectable	5%	1%	1%	5%	—ᵃ / 1%	5% / 1%	—ᵃ / 2%	5% / 5%

ᵃ Overlap of the oil band

did not correspond to the measurement of the pigment band, but to the overlapping of the linseed oil band located in the same area. Following the previous procedure of linseed oil spectrum subtraction, the new limits became 1% and 2% for Mars Black and Manganese Black, respectively, which evidenced the removal of linseed oil interference. This subtraction also improves the minimum amount of pigment detectable for Mars Black to 1% using the other band (371 cm⁻¹) due to its partial overlap with linseed oil.

The subtraction procedure shows an improvement in detecting linseed oil overlapping bands and no effect in the other cases, such as Iron Red or Manganese Black band at 405 cm⁻¹, despite the fact that in a real situation of painting analysis the results would be more unpredictable due to the variability derived to the unknown composition of the matrix, it could provide some improvement in pigment identification if the matrix is known.

In absolute terms, the minimum amount of red pigments detectable was approximately 1 mg, considering the quantity added to the ATR crystal. This value is not far from the limit of detection of 0.04 mg for Malaquite established by Kendix [4] in ATR mode when pigment powder is directly measured.

3.1.2.2. Binary mixtures. A step forward to study the real complexity of paint samples is to consider the possibility that several pigments of the same colour were included in the same paint layer to induce some chromatic effects. This complex composition may lead to spectra where the bands of the different pigments appear overlapped. For this purpose, three different pigment mixtures of red pigments and two black pigments were studied following the same procedure described before (Table 5).

The results obtained were similar to those achieved with the single mixtures. For Red Lead, the detection limit remains at 5% (mixtures with Lead White and mixtures with Rouge Vermillion), except for the mixtures with Iron Red, which were improved up to 2%. For the other two red pigments studied, Iron Red and Rouge Vermillion the minimum detectable amount remained at 1%, the same value obtained with the single mixtures (Table 5).

In the case of black pigments, as in the case of red pigments, the minimum amounts achieved were similar to those obtained for single mixtures of Mars Black and Manganese Black pigments. In the presence of Ivory Black, the minimum amount detectable for Mars Black (371 cm⁻¹) increased up to 2%, whereas for Manganese Black (405 cm⁻¹), it remained at 5%. The situation is the opposite in the presence of Vine Black (the 570 cm⁻¹ band was used for both pigments); the minimum amount for Mars Black remained at 1%, whereas for Manganese Black, it increased to 5%.

These results show that the mixture of the two pigments did not affect the values obtained, and only small variations, probably due to the experimental conditions, were observed.

3.2. Pigment identification in complex paint layers

The mixtures of pigments and linseed oil used in the previous sections were used to study some of the consequences of the saponification process on the Far-Infrared spectra. However, the complexity of real paint layers, in composition and material distribution, recommended to go further by studying the capability of pigment identification for this spectral range in canvas paint samples of known compositions exposed to natural and artificial ageing processes.

For this purpose, a set of linseed oil paints on canvas, including binary and ternary mixtures of pigments that showed or did not show shift of the bands when mixed with linseed oil, were prepared (Table 6). Mixtures of red and black pigments, together with Lead White pigments, were considered. The concentrations chosen for the pigments in these mixtures had no other purpose than to be in the same range used by the artists (when a pigment is pasted with linseed oil).

The discussion first focused on the band positions and their signal intensities in the linseed oil paintings and second on the effect of the ageing of these signals.
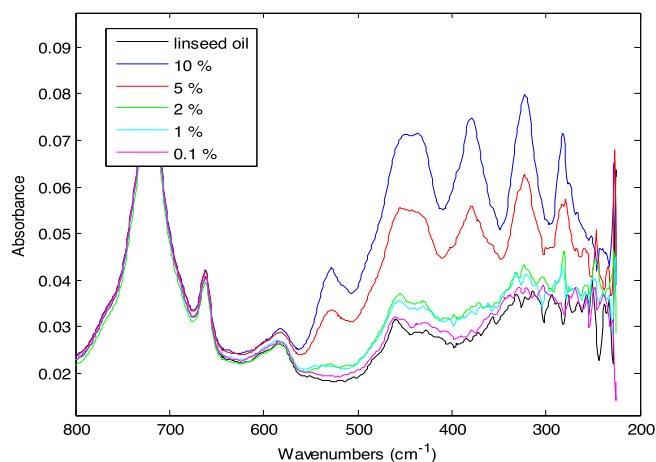
Fig. 4. Spectra of Red Lead mixed with linseed oil at different proportions ranging from 10 to 0.1% as well as the pure linseed oil spectrum.

Table 5
Mean and standard deviation, in brackets, of the band height for the different pigments studied. The band used for the measurement are indicated. When the pigment is in a constant proportion and no calculation with them was performed is presented in italics.

Pigment	Red Lead + *Lead White*	Red Lead +	Iron Red	Red Lead +	Rouge Vermillion	Mars Black[a] + *Ivory Black*	Mars Black[a] + *Vine Black*	Manganese Black + *Ivory Black*	Manganese Black[a] + *Vine Black*
Content level (%)	380 cm^{-1}	380 cm^{-1}	558 cm^{-1}	380 cm^{-1}	609 cm^{-1}	371 cm^{-1}	571 cm^{-1}	405 cm^{-1}	575 cm^{-1}
10	0.030(4)	0.023(3)	0.037(4)	0.026(2)	0.020(2)	0.028(1)	0.033(1)	0.003(2)	0.011(1)
5	0.0132(8)	0.0204(9)	0.035(3)	0.0104(7)	0.0110(3)	0.020(3)	0.0176(8)	0.0015(4)	0.0039(12)
2	0.003(2)	0.004(1)	0.008(2)	0.002(2)	0.0032(7)	0.007(2)	0.0066(5)	0.00004(81)	0.0006(6)
1	−0.0003(6)	0.0009(8)	0.0018(5)	−0.0007(15)	0.0018(5)	0.003(2)	0.0042(2)	0.001(1)	0.0009(1)
0.1	−0.0019(3)	−0.0015(5)	−0.0028(3)	−0.0031(9)	0.00003(18)	−0.0005(37)	0.0002(5)	−0.0008(9)	−0.0003(3)
Minimum amount detectable	5%	2%	1%	5%	1%	2%	1%	5%	5%

[a] Subtracted heights

3.2.1. Spectra stability and signal intensity. A systematic procedure to study the stability of the spectra and the intensity of the signals of the linseed oil paint mixtures on canvas was used. First, the different bands observed in the spectrum were determined and attributed to the pigments present in the mixture (Table 6). Next, the net heights of each band, using the union of valleys as the baseline, were calculated for the same nonoverlapping bands described in the previous section. To compare the results obtained in this section with those of the minimum amount obtained for each pigment when only the mixture with linseed oil was considered, the pigment band intensities were normalised regarding the linseed oil intensity registered in the same spectrum at 1740 cm^{-1}. Intensity ratios were compared taking as a reference value the ratio obtained in the previous section from the single mixtures with a pigment concentration of approximately 10%.

The different bands detected are presented in Table 6. A common trend is that the absorption bands observed for the different pigments remained stable with regard to those achieved after the shift process related to their mixture with linseed oil. This trend

could not be found, in any case, for Manganese Black and only in some cases for Cinnabar, because no pigment-related bands were detected in the corresponding paintings. These results indicated the capability of this technique for pigment identification, as the bands remained in the same position but they also noted the influence of the matrix on the intensity of the bands of the different pigments, and therefore the minimum amount of detectable pigment.

Regarding the bands intensity, a general increase in the relative height of the signals was observed, which would correspond to concentrations from 1.3 to 4.4 times higher than the actual ones, regarding the theoretical value according to the relationship observed in section 3.1.2. (Table 6). The results did not enable an establishment of a relationship between this trend and a specific pigment or mixture, despite the fact that the physical and chemical composition of components should be one of the factors involved in the process. Two outstanding pigments were Cinnabar and Manganese Black because the tendency towards an increasing height was not followed. In the case of Manganese Black, as explained previously, no signal related to this pigment could be observed (NB15

Table 6
Concentration, bands mean and standard deviation, in brackets, of the height ratio between the selected band of the pigment and the linseed oil band at 1740 cm-1 for the different pigments present in the mixtures studied. The pure pigments mixed with linseed oil were also presented as reference showing just the bands used for the calculation.

Name	Pigment	Concentration (%)	Bands (cm-1)	Pigment/oil height ratio	Apparent signal increase
NB6	Red Lead	22.5	531 455 380	0.24(2)	1.4
	Iron Red	23.1	558 455 307	0.914(7)	3.5
NB9	Red Lead	25.2	381 325 379 443 528	0.33(3)	1.7
	Rouge Vermillion	24.6	609 634	0.47(1)	2.3
NB20	Red Lead	23.8	381 325 379 443 528	0.37(6)	2.0
	Rouge Vermillion	19.9	609 634	0.42(4)	2.6
	Lead White	3.7	276 678	0.104(9)	4.4
NB8	Red Lead	31.1	281 325 379 443 528	0.33(5)	1.4
	Cinnabar	31.1	–	0.01(2)	–
NB16	Rouge Vermillion	14.5	609 634	0.193(2)	1.6
	Lead White	14.3	395 678 768	0.149(3)	1.3
NB10	Cinnabar	32.8	286 346	0.14(1)	2.1
	Lead White	32.8	395 678 768	0.412(6)	2.0
NB13	Red Lead	17.5	281 325 379 528	0.17(2)	1.3
	Cinnabar	18.1	247	0.004(5)	–
	Lead White	17.4	678 768	0.311(7)	2.8
NB15	Mars Black	24.1	543 305	0.705(8)	2.2
	Manganese Black	26.9	–	−0.08(1)	–
NB14	Manganese Black	24.7	–	−0.01(2)	–
	Ivory Black	20.5	470 560 600	0.204(7)	2.5
Red Lead		9.1	380	0.07(3)	–
Iron Red		8.8	558	0.10(4)	–
Rouge Vermillion		8.5	609	0.070	–
Cinnabar		8.8	346	0.018(3)	–
Mars Black		8.8	571	0.116(7)	–
Manganese Black		12.9	405	0.011(5)	–
Ivory Black		10	599	0.040(5)	–
Lead White		13	680	0.083(5)	–

and NB14). In the case of Cinnabar, the bands were detected in the mixture with Lead White (NB10) doubling its intensity, whereas in the mixture with Red Lead and Lead White, only the band at 247 cm^{-1} was detected (NB13) and no bands were detected when mixed with Red Lead (NB8).

This behaviour could be related to a heterogeneous distribution of pigments inside the paint layer once it had been applied to the canvas. This distribution may depend on the chemical nature and physical morphology of the pigment particles, which lead to a different location of the pigment within the paint layer, for example, far from the surface and therefore more difficult to detect via ATR. It could also contribute to the increase in the observed concentration, the absorption of the linseed oil in the preparation layer or the dry process of the linseed oil, which would increase the concentration of the pigment.

Summarising these results, it is clear that the inclusion of the pigments in a complex and real context as a paint layer changes the minimum amount of pigment detectable and therefore the capability to identify them through Far Infrared spectroscopy in ATR mode, whereas no change in the position of the bands regarding the pigment mixed with linseed oil is observed. The change in the signal intensity compared to the values obtained in simple pigment: linseed oil mixtures depended on the paint layer composition. In some cases, the concentration required to obtain a detectable band was similar, whereas for some pigments the necessary quantity decreased (such as Iron Red or Mars Black), whereas for others (such as Cinnabar or Manganese Black), they were not detected at concentrations as high as 25%. This behaviour implies a limitation in the identification of pigments included in a paint layer, as some of them will only be detected when present in high amounts [27–28].

3.2.2. Ageing effect. Artistic paintings are preserved over time, and during this period they are affected by chemical and physical changes that may also modify the capabilities of the Far-Infrared technique in ATR mode for pigment detection. The linseed oil dries due to its autoxidation but also experiments the hydrolysis of the ester bonds, the formation of new functional groups, oxidative cleavage of the fatty acid hydrocarbon chains, and metal-ion coordination of the fatty acid groups [25,29].

To study these potential changes on the analytical performances of Far-Infrared ATR, the prepared linseed oil paints on canvas were aged first in a natural way, exposing them in a room to environmental conditions for one year. After this, they were exposed in an artificial way, exposing them to UV light and humidity conditions for the equivalent of another year.

The results obtained were discussed in terms of the band position and intensity of the pigments as well as the linseed oil signals.

In the spectra obtained, it is possible to observe that, in all cases, ageing did not produce any shift in the position of the pigment band, as shown in paint NB6 (Red Lead and Iron Red) (Fig. 5). However, in some pigments, ageing led to an increase in the intensity of the absorption bands. This was especially evident in the mixtures including Cinnabar (NB8 and NB13), in which this pigment did not show any detectable absorption, and after ageing the signal appeared and increased following the ageing sequence. For example, in NB13 the signal intensity ratios of Cinnabar (346 cm^{-1}) were 0.004(5) initially, 0.025(6) after 1 year of natural ageing and 0.05 (1) after the equivalent of 2 years of ageing. However, for Manganese Black, even after the ageing process the bands were not detectable in either of the two paints, which included this pigment (NB15 and NB14).

This general trend of increasing the signal intensity of pigments could be attributed to the same physical and chemical mechanisms
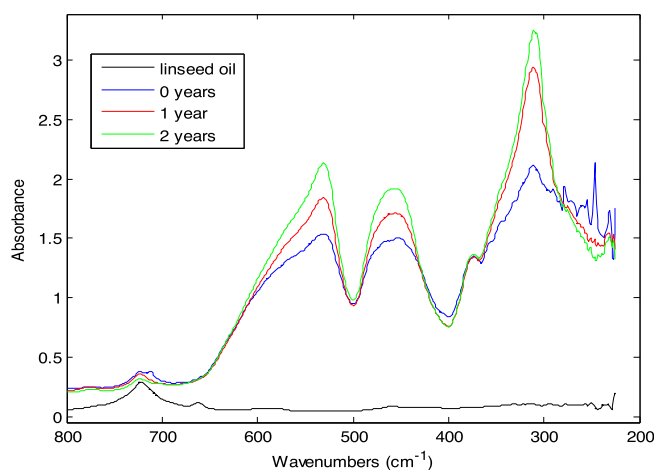
Fig. 5. Far IR spectra of the linseed oil paint on canvas prepared with a mixture of Red Lead and Iron Red measured few weeks after its preparation, after one year of natural ageing and after an additional ageing treatment equivalent to another year.

proposed in the previous section That can change the availability of the pigments on the paint layer surface for the interaction of the evanescent waves in the ATR mode, thus changing its detectability.

Ageing also produced changes in the signals related to the linseed oil spectrum, ester absorption at 1740 cm^{-1}, carboxylic acid band at 1710 cm^{-1} and carboxylate bands at approximately 1550 cm^{-1}.

For all the red paints, the ester absorption at 1740 cm^{-1} became broad as a consequence of the linseed oil drying process, hindering the spectral range of the carboxylic acid absorption (Fig. 6). As a consequence of this band widening, the carboxylic acid signal could not be observed, perhaps due to overlapping or perhaps due to the disappearance of the carboxylic acid by the saponification reaction. For black paint mixtures, this broadening was even more important with the singularity that seemed composed of a double band of similar intensities at 1735 and 1710 cm^{-1}.

For both types of paintings, reds and blacks, the absorption located at 1650 cm^{-1} was difficult to identify.

Regarding the carboxylate band at 1530 cm^{-1}, it was possible to observe this band in all red paints; however, for black pigments broad absorption between 1650 cm^{-1} and 1550 cm^{-1} made it difficult to establish the presence of the band, although the literature indicates the formation of carboxylates with manganese pigments (Burnt Sienna and Burnt Amber) [7]. Nevertheless, the general trend of this band was to increase the height with ageing, with the exception of the mixtures that contained Lead White. In these paints, the intensity increased when natural ageing was applied and decreased to values even lower than those of the non-aged paints when the ageing was artificial, including UV light, corroborating the contradictory behaviour observed for Lead White as a catalyser or inhibitor of the drying linseed oil process [21]. These results would indicate that a saponification reaction occurred for all the mixtures in which lead pigments were involved (Red Lead and White Lead), which is in agreement with the literature [7]. However, the absence of mixtures without these pigments did not allow us to go further in the discussion, and therefore did not help in understanding the relationship between the shift in the bands for each pigment and carboxylate formation.
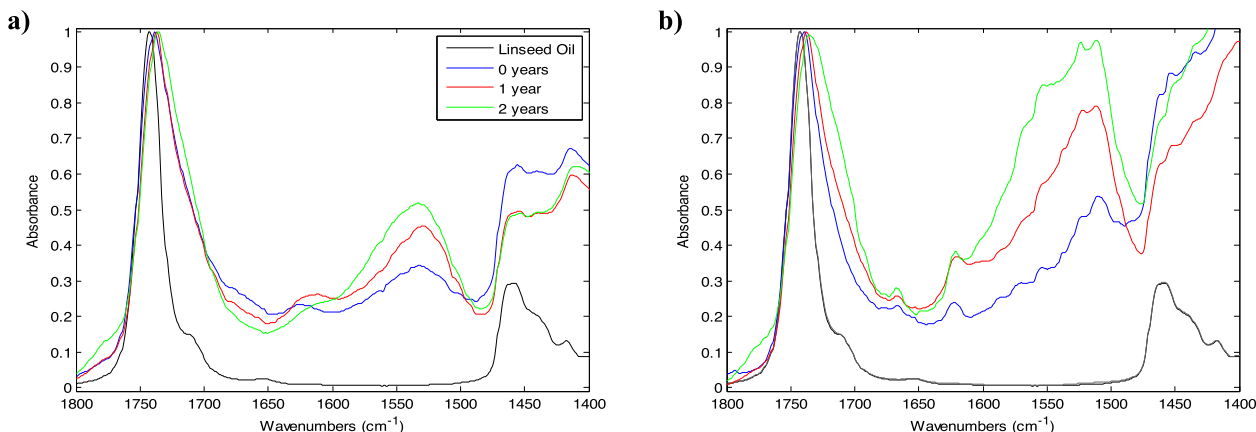
Fig. 6. Spectra of Mid IR of the linseed oil bands for the linseed oil paint on canvas for the mixtures of (a) Red Lead and Iron Red and (c) Red Lead, Rouge Vermillion and Lead White measured few weeks after its preparation, after one year of natural ageing and after an additional ageing treatment equivalent to another year.

4. Conclusions

The obtained results show a shift in the positions of the absorption band characteristics of the oxide pigments as a consequence of their interaction with the linseed oil matrix, which remains constant with ageing. The differences observed with the published databases recommend specifying the experimental conditions of the measurement to use as reference those databases in which measurements are performed under similar conditions.

For spectra with bands overlapping with the linseed oil, the subtraction of the linseed oil spectrum improves the capacities of Far-Infrared for identifying the pigments.

The paint layers in the canvas show differences in the relative band intensity regarding the pigments mixed with linseed oil, leading in most cases to an improvement in their detectability. However, no changes in the band position were observed, allowing pigment identification of the pigments in the paint layer.

The values of this minimum amount of pigment detectable may be quite high in some particular cases and result in the nonidentification of major components.

The pigments with a shift in the characteristic bands in the Far-Infrared range also show an increase in the carboxylate band in the Mid-IR.

Finally, the ageing of the paint layers produces an increase in the carboxylate bands, except in those mixtures with Lead White, in which artificial ageing results in a decrease in the intensity.

The potential of Far-Infrared in ATR mode as a tool for identifying some inorganic pigments is notable. These techniques represent an interesting approach to painting chemical analysis, thanks to their capacity to analyse paint layers in a non-destructive manner. Nonetheless, widespread applicability should be considered carefully and evaluated specifically for each case under study.

CRediT authorship contribution statement

P. Giménez: Investigation, Formal analysis, Data curation. **A. Linares:** Investigation, Formal analysis, Data curation. **C. Sessa:** Conceptualization, Methodology, Validation, Supervision. **H. Bagán:** Methodology, Software, Data curation, Writing – review & editing, Visualization. **J.F. García:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.saa.2021.120411.

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