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Non-invasive detection of lead carboxylates in oil paintings by in situ infrared spectroscopy how far can we go?

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Abstract:	<p>This paper demonstrates the efficacy of portable mid-infrared spectroscopy as a diagnostic tool for revealing the presence of lead carboxylates on artworks, in situ, without sampling. Samples of cerussite and hydrocerussite -the main components of lead white- were separately mixed with linseed oil, and artificially aged in two phases. Their compositional changes have been monitored over time by infrared spectroscopy in two investigation modes: absorption (benchtop instrument) and reflection (portable instrument), and by XRD spectroscopy.</p> <p>Each component of lead white showed different behavior depending on aging conditions, giving important information about the degradation products which are found in real cases.</p> <p>The accordance of results obtained in both modalities demonstrates that portable FT-MIR is a reliable technique for individuating and identifying lead carboxylates directly on paintings.</p> <p>Examples of the efficacy of this application are provided, by studying paintings from the 17th and 18th centuries.</p>
Suggested Reviewers:	<p>Marco Malagodi, PhD professor, University of Pavia marco.malagodi@unipv.it good experience on organic materials used on paintings</p> <p>Sophia Sotiropoulou, PhD professor, Foundation of Research and Technology Hellas sophiaso@iesl.forth.gr She has been specialized in applying optical and spectroscopic methods for the analysis of materials, the study of mechanisms of natural aging and the characterization of paint surfaces of heritage objects.</p>



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Perugia, March 4 2023

Dear Editors,

I am submitting to your consideration a research paper titled “**Non-invasive detection of lead carboxylates in oil paintings by *in situ* infrared spectroscopy: how far can we go?**” by M. Vagnini, C Anselmi, R. Vivani and A. Sgamellotti, for publication in the Microchemical Journal.

In this paper, we demonstrated the efficacy of portable mid-infrared spectroscopy in revealing the presence of lead carboxylates on artworks, *in situ*, without sampling, by studying their formation starting from lead white, one of the most employed pigment ever. Metal carboxylates, or metal soaps, are one of the most complex degradation phenomena shown by oil paintings and leads to severe damages for artworks.

The presence of metal carboxylates in oil paintings is usually revealed by invasive techniques on samples taken from their surface. By demonstrating the accordance between portable mid-infrared spectrometer and the bench-top one on purposely prepared samples confirmed by XRD measurements, we showed that is possible to monitoring the conservation state of the artworks directly in the museums or wherever the artworks are located, without sampling. Moreover, the study of lead carboxylates formation from lead white, by separating its two components, namely cerussite and hydrocerussite, lead us to discover two different processes of degradation involving the two components. Each component of lead white showed different behavior depending on aging conditions, giving important information about the conditions in which the artworks has been stored,

and also explaining the various discrepancies often found in literature concerning the different lead carboxylates found on the artworks surface.

We thank you for your kind attention and looking forward to receiving your response.

Sincerely yours,
Manuela Vagnini



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Highlights:

- Portable mid-FTIR spectroscopy are used as diagnostic tool for identification of lead carboxylates
- Kinetics of lead carboxylates formation on mock-ups by ATR-FTIR and portable mid-FTIR are analysed
- The aging processes of the hydrocerussite and cerussite on the formation of lead carboxylates on paintings are investigated
- Lead azelate is identified by portable mid-FTIR spectroscopy

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Non-invasive detection of lead carboxylates in oil paintings by *in situ* infrared spectroscopy: how far can we go?

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Keywords: lead carboxylates, FTIR reflectance mode, FTIR-ATR, infrared spectroscopy, oil paintings degradation

Abstract

This paper demonstrates the efficacy of portable mid-infrared spectroscopy as a diagnostic tool for revealing the presence of lead carboxylates on artworks, *in situ*, without sampling. Samples of cerussite and hydrocerussite -the main components of lead white- were separately mixed with linseed oil, and artificially aged in two phases. Their compositional changes have been monitored over time by infrared spectroscopy in two investigation modes: absorption (benchtop instrument) and reflection (portable instrument), and by XRD spectroscopy.

Each component of lead white showed different behavior depending on aging conditions, giving important information about the degradation products which are found in real cases.

The accordance of results obtained in both modalities demonstrates that portable FT-MIR is a reliable technique for individuating and identifying lead carboxylates directly on paintings.

Examples of the efficacy of this application are provided, by studying paintings from the 17th and 18th centuries.

Introduction

The formation of metal carboxylates – commonly called metal soaps- is one of the most complex degradation phenomena shown by oil paintings, and identified for the first time in *The anatomy Lesson of Dr. Nicolaes Tulp* painted by Rembrandt van Rijn in 1632 [1].

It involves the saponification of the triglycerides of the oil by hydrolysis of the ester bonds, leading to a network of carboxylate groups bearing the metal ions from pigments as counterions.

Triglycerides are esters composed of glycerol and three (different or not) fatty acids. Fatty acids are the main component of siccative oils used as binders in paintings, such as linseed oil, whose main fatty acids are palmitic, stearic, oleic, linoleic, linolenic acid, and in a small amount, lauric and myristic acid. Among these, saturated fatty acids (SFAs) are about 10-15% of the total linseed oil composition, the rest is composed of monounsaturated and polyunsaturated fatty acids (MUFAs and PUFAs, respectively) [2].

The formation and growth of metal carboxylates is a multi-step process strongly affected by environmental conditions such as high temperature and relative humidity [3]. The key reactions of this process are hydrolysis and (auto)-oxidation whose sequence is still under debate, although thoroughly studied, and most likely dependent on the particular conditions of each painting [4, 5]

The presence of metal carboxylates in oil paintings is usually revealed on samples taken from the artworks by invasive, sometimes destructive, techniques: infrared (IR) and mass spectrometry (MS). [6, 7] whilst the kind of fatty acid involved in metal carboxylate formation (stearic, palmitic, azelaic) is mostly identified by mass spectrometry techniques [6].

Non-invasive FT-MIR still encounters difficulties in becoming a routinary tool for metal carboxylates detection although it has been demonstrated that this technique allows the identification of metal carboxylates [8]. The limited penetration capacity of the radiation which is often adduced as its major drawback can be bypassed by carrying out measurements on cleaning assays where, once the superficial varnish has been removed, it is possible to identify the presence of the carboxylates.

The real difficulty in identifying metal carboxylates through non-invasive FT-MIR concerns its operational mode, i.e. the reflection modality. When spectra are acquired in reflection mode, the bands' shape may be distorted due to the presence of *reststrahlen* effects [9] which can modify the appearance of the signals, thus affecting the readability of the spectra.

In a previous work [8] we already showed how metal carboxylates can be individuated by portable FT-MIR and how the use of artificially aged samples could help in interpreting the signal obtained in reflection mode. However, in that case, the samples were prepared with a strong excess of pigment to promote the metal coordination with the free carboxylic group to assure their individuation.

In this work, we focused our attention on one of the most frequently encountered types of carboxylates, i.e. lead ones, by proving the efficacy of portable FT-MIR to identify and follow their evolution both on artificially aged samples and, *in situ*, directly on artworks.

In literature, many cases are reported of lead carboxylates individuation by invasive techniques on prepared samples, and being the experimental conditions very different from each other it is quite difficult to get an overview of the rules governing their genesis [10, 11, 12]. Moreover, when the samples are taken from artworks, it is even more complicated to reconstruct their formation because of the unknown conditions of aging to which they have been subjected.

For these reasons, we decided to study the development of lead carboxylates starting from the probably most used lead-based pigment among oil paintings, i.e. lead white.

In particular, we studied separately the behavior of its two main components i.e. cerussite and hydrocerussite, each one mixed in a 1:1 ratio with linseed oil, upon artificial aging.

We decided to carry out the artificial aging in two phases: the first was characterized by mild conditions of air drying at RT and 45-50%RH for 40 days, and the second one by harsher conditions of 40°C and 93%RH for a further 100 days.

This strong difference was chosen to better highlight any difference in their aging process.

The evolution of each mixture was followed by ATR and portable FT-MIR at fixed time intervals and by XRD spectroscopy. Lead carboxylates of the main fatty acids of linseed oil were separately synthesized and characterized with the same techniques for comparison with the real samples.

The non-invasive study of three oil paintings of the 17th and 18th centuries is reported as a successful example of *in situ* application.

Materials and methods

Mixtures of linseed oil with cerussite and hydrocerussite in a 1:1 ratio were applied on aluminum plates. After 40 days of drying at room temperature and 40-50%RH, the paint films were artificially aged at 40°C and 93% of relative humidity, assured by the presence of a KNO₃-saturated solution in the aging chamber. Cerussite and hydrocerussite were purchased by Sigma-Aldrich, and the linseed oil from Zecchi (Firenze, Italy).

Lead palmitate, lead stearate, and lead azelate synthesis

Palmitic, stearic, and azelaic acids and PbNO_3 were purchased by Sigma-Aldrich. Pure lead palmitate and stearate standards were synthesized in the laboratory according to methods reported elsewhere [13]. A mixture of 30 mL of lead nitrate 0.02 M solution (water, ethanol, methanol 5:5:2) and 12.5 mL of 0.02M solution of palmitic or stearic acid in methanol was prepared and left in an ultrasonic bath for 30 minutes. The obtained crystallized solid was filtered, washed with ethanol and ethyl ether, and then vacuum-dried.

Lead azelate was prepared by a 0.005M solution of azelaic acid in water solubilized at 65°C. Thereafter, 240 mg of hydrocerussite was added to the solution and maintained at 65°C for 24 hours [13]. The obtained crystallized solid was filtered and dried in an oven for 24 hours.

ATR and micro-FTIR spectroscopy

The medium infrared analyses were carried out by a JASCO FTIR 4100 infrared spectrophotometer, equipped with a ceramic light source, a Michelson interferometer, DLATGS, and MCT (Mercury Cadmium Telluride) detectors. The spectra were recorded covering the range 4000 – 400 cm^{-1} at a spectral resolution of 2 cm^{-1} using KBr pellets.

Micro-FTIR analyses were carried out with a Jasco FTIR 4100 spectrophotometer, equipped with a nitrogen-cooled mercury cadmium telluride detector and an IMV4000 optical microscope. Measurements were performed in reflectance geometry (Cassegrain 16x objective) on paint films with contact diamond ATR objective.

Portable FT-MIR

Reflectance FT-MIR spectra were recorded using a portable JASCO VIR 9500 spectrophotometer equipped with a Remspec mid-infrared fiber-optic sampling probe. The bench was made up of a Midac Illuminator IR radiation source, a Michelson interferometer, and liquid nitrogen cooled MCT (Mercury Cadmium Telluride). The fiber optic probe was a bifurcated cable containing 19 chalcogenide glass fibers which allow the collection of spectra from 6500 to 900 cm^{-1} with an excellent signal-to-noise ratio throughout the range, except in the 2200 - 2050 cm^{-1} region, due to the glass fiber Se-H stretching absorption. In the present study typically 400 interferograms were collected covering a spectral range from 6500 to 900 cm^{-1} at a resolution of 4 cm^{-1} . The fiber optic probe was kept perpendicular to the sample surface (0°/0° geometry). The investigated sample area width was about 4 mm as determined by the probe diameter.

X-ray diffraction

X-ray diffraction data were collected directly on the samples surface in theta-theta reflection geometry with the CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$) on a PANalytical X'PERT PRO diffractometer, PW3050 goniometer equipped with an X'Celerator fast detector. The *Long Fine Focus* tube operated at 40KV, 40mA. Data were collected using a step size of 0.017° and a count time of 10 s per step. Positions of diffraction maxima for phase identification were determined by the second derivative method and the results processed with the PANalytical X'Pert Highscore search - match program with the help of the ICDD-PDF database.

Results and discussion

Characterization of standard fatty acids and pure linseed oil by ATR and XRD spectroscopy

To better understand the nature of the lead carboxylates and their kinetics of formation, standards of pure linseed oil as well as of lead-azelate, lead-stearate and lead-palmitate were characterized by micro-FTIR in ATR mode (Figure 1) and XRD spectroscopy (Figure 2).

ATR spectroscopy

As reported in the literature lead palmitate and lead stearate present very similar infrared signals [6, 14,15, 16] with a characteristic double band at $1540\text{-}1513 \text{ cm}^{-1}$ (figure 1a) ascribed to the carboxyl asymmetric stretching, and multiple bands of regular spacing ($\sim 20 \text{ cm}^{-1}$) in the $1180\text{-}1350 \text{ cm}^{-1}$ region (insert in Figure 1a). The number of bands in the progression increases as a function of the chain length [17]. These bands are assigned to the wagging and twisting-rocking vibrations of methylene groups [17] or the coupling of CH_2 wagging modes with the carboxyl vibrations [15]. In the spectrum of lead azelate, the carboxyl asymmetric stretching occurs at 1512 cm^{-1} as a broad and intense band (Figure 1b) and, differently from lead palmitate and lead stearate, the lack of any regular spacing is observed in the region between 1180 and 1350 cm^{-1} (Figure 1b). These bands together with the 1340cm^{-1} peak, allow distinguishing lead azelate from lead palmitate and lead stearate (Figure 1a). The aging of pure linseed oil makes the carbonyl band shift to lower wave numbers, from 1737 cm^{-1} to 1703 cm^{-1} , while a broadening of a shoulder at 1640 cm^{-1} occurs (Figure 1c). As mentioned above, these bands are due to the formation of fatty acids, as well as of other types of carbonyls (e.g. ketones, lactones, aldehydes), and unsaturations (i.e. double bonds $\text{C}=\text{C}$ in fatty acids), which take place during the aging of linseed oil [18, 19, 20]. The presence of unsaturations is confirmed by the signals at 725

cm^{-1} , due to the cis CH out-of-plane deformation, and at 976 cm^{-1} most likely attributed to the double bond isomerization from *cis* to *trans* configuration [19].

It is worth noting that in pure linseed oil, no signals appear in the $1500\text{-}1550\text{ cm}^{-1}$ range (Figure 1c).

XRD spectroscopy

Diffraction analyses of pure synthesized standards (lead palmitate, lead stearate, and lead azelate) are reported in Figure 2. Their intense characteristic signals are at low angles ($2\theta < 15$) and are equidistant for lead palmitate and lead stearate, while lead azelate shows one very intense signal at $2\theta = 5.99$ and other less intense ones at $2\theta > 10$, but not equally spaced. Diffraction peaks of lead stearate and lead palmitate are separated and then distinguishable while the most intense signal of lead azelate is partially overlapped with the peak of lead palmitate.

Characterization of mixtures of hydrocerussite and cerussite with linseed oil by ATR, portable FT-MIR, and XRD spectroscopy

The samples were first exposed to air at RT and 40-50%RH for 40 days, and then put at then 40°C and 93%RH for a further 100 days. Analyses of the samples were carried out after 40 days at RT and then at regular intervals after exposure at increased temperature and relative humidity.

ATR spectroscopy

The artificially aged mixture of linseed oil/hydrocerussite 1:1 (Figure 3A-left) shows a broad band centered at 1535 cm^{-1} arising after 40 days at RT, becoming more and more intense and sharp with time, shifting finally at 1508 cm^{-1} -with two shoulders at 1520 and 1538 cm^{-1} - after 140 days of aging (Figure 3A-right).

In the case of linseed oil/cerussite 1:1 (Figure 3B-left), a broad carboxylate band appears at 1508 cm^{-1} after 40 days, becoming sharper and more intense, but not shifted, after 140 days of aging, with two shoulders at 1520 and 1538 cm^{-1} (Figure 3B-right). The intense and sharp band at 1508 cm^{-1} is ascribable to the presence of lead azelate that in the reference compound shows a broad band centered at 1510 cm^{-1} (Figure 1a). The presence of a shoulder at 1445 cm^{-1} , and the bands at 1340 , 988 , 940 , 768 , and 665 cm^{-1} which are specific for lead azelate, give further confirmation of its presence. In both mixtures, the weak shoulder at 1538 cm^{-1} is due to the presence of lead palmitate and/or lead stearate, confirmed also by other signals below 1370 cm^{-1} .

XRD spectroscopy

XRD patterns of the aged mixtures of linseed oil with cerussite and hydrocerussite show the signals at low angles ($2\theta < 15$) arising during the aging and ascribable to organic compounds with a crystalline nature (Figure 4). Comparing the diffraction spectra of mixtures with those of synthetic organic lead salts (Figure 2), the signals at low angles, being broader than the standard ones, can be attributed to a mixture of lead stearate/palmitate and lead azelate. Other signals revealed in the X-ray diffraction spectra are attributable to the presence of lead oxides.

Portable FT-MIR spectroscopy

Once identified the type and the rapidity of carboxylate formation, we switched the methodology towards the reflection mode, by using a portable FT-MIR, to verify if the same information collected by ATR is achievable also through a non-invasive approach aimed at *in situ* application.

Figure 5 shows the FT-MIR reflectance spectra of the linseed oil/hydrocerussite 1:1 mixture, monitored at different times. After 40 days, an inverted broad band starts to appear at 1530cm^{-1} , becoming a shoulder after 80 days, and then a sharp band at 1508cm^{-1} after 140 days of aging.

By what is seen in ATR mode, the initial formation of lead stearate and/or lead palmitate occurs, and then later, the lead azelate band prevails.

In this case, it must be noted that the reflection mode, while providing the same results as ATR, weakens the transition from 1530 to 1508cm^{-1} due to the presence of *reststrahlen* bands, whose shape partially alters the readability. For the same reason, signals between 1460 and 1320cm^{-1} cannot be easily observed. In the case of linseed oil/cerussite 1:1, the outcome of the reflection mode is the same as the absorption one. The band at 1506cm^{-1} which appears after 40 days, becomes more and more intense as the aging time increases until 140 days, with shoulders at 1513cm^{-1} and 1531cm^{-1} . It must be noted that the final spectral outcome after 140 days of aging, is the same for both the mixtures and for both the methodologies of analysis.

Comparing the aging process of the two mixtures, some interesting features emerged. Hydrocerussite and cerussite behave very differently in the short run, and their different chemical compositions seem to promote two different pathways.

During the initial phase of the aging process, when mild conditions are employed (40 days at RT and 40-50%RH), hydrocerussite fosters the hydrolysis by producing lead stearate/palmitate (broad band centered at 1530cm^{-1} after 40 days), whilst cerussite in the same conditions preferably speeds the oxidative pattern by forming lead azelate (1508cm^{-1})

When aging conditions become harsher (up to 100 days at 40°C and 93%RH), both the samples show, at the end of the observation period, the same composition, i.e. the prevalence of lead azelate signal flanked by those of lead palmitate and lead stearate.

The mild conditions of the first phase of aging bring out the kinetically favored products which are lead palmitate and lead stearate for hydrocerussite, and lead azelate for cerussite.

It is frequently reported that autoxidation within the paint layer takes place before hydrolysis [21, 22, 23], and for this reason, the boost of hydrolysis step operated by hydrocerussite at the apparent expenses of autoxidation processes, results quite interesting because so far it has never been reported. The strong oxidative action operated by cerussite deserves also attention. Although the autoxidation process is the first-occurring step in metal-carboxylates development, the formation of lead azelate requests many steps to be completed because azelaic acid is a dicarboxylic acid generated by autoxidation at the Δ^9 double bond of the unsaturated component of linseed oil (MUFAs and PUFAs), then hydrolysis step and coordination with Pb ions need to occur to reveal lead azelate.

The ready and selective formation of lead azelate under mild conditions, and in the presence of other competing reactions, is a marker of cerussite presence.

In the second phase of aging, the conditions have been deliberately worsened by increasing both the temperature and the relative humidity to 40°C and 93% respectively, for encouraging the formation of thermodynamically favored product/s.

At the end of observation time (140 days total), the same mixture was obtained for both samples with a fundamental difference: for cerussite, no significant changes were observed for the “mild aging”, being lead azelate peak the predominant one, only little sharpened with time.

For hydrocerussite instead, at the end of the experiment, occurred a substantial shift of the main peak which under mild aging was assigned to lead palmitate and lead stearate, and after “harsh aging” becomes lead azelate, being lead palmitate and lead stearate only weak shoulders, as confirmed by XRD. Moreover, it must be noted that for hydrocerussite, the appearance of lead azelate peak occurs only at the end of harsh aging, i.e. after 100 days at 40°C and 93%RH, whilst after 40 days of harsh aging (80days total) no lead azelate signal is yet visible.

Such difficulty in lead azelate formation starting from hydrocerussite even at high values of relative humidity is in accordance with examples of hydrocerussite artificial aging which even at 70%RH showed no evidence of lead azelate [10]; our data could also explain those real cases in which after hundreds of aging, no traces of lead azelate are reported [11]: in both cases, probably no cerussite was present in the lead white component of the artwork.

It must be considered, that the pigment called “lead white” may consist either of a single component (cerussite or hydrocerussite) or both [24].

In light of our evidence, if lead white is composed solely of cerussite or hydrocerussite, the outcome will be different even after hundred years of aging, and it will show mostly lead azelate if lead white is made only by cerussite, and mostly lead palmitate/lead stearate if it is made only by hydrocerussite. In all those cases in which a mixture of cerussite and hydrocerussite was used, the presence of lead azelate will appear to a variable extent depending most on the cerussite amount, and this is the subject of current studies.

Moving to reality: *in situ* detection of lead carboxylates by portable FT-MIR

In this section are presented two example of *in situ* individuation and identification of lead carboxylates by Mid-FTIR concerns two oil paintings: *Presentazione al Tempio* by Giuseppe Velasco realized on XVIII century (fig. 7 left) and *Santa Rita e Sant'Antonio* (fig. 7 right) by an unknown author ascribable at the XVII century.

The painting by Giuseppe Velasco dates back to the 18th century and is located in the Saint Biagio Church of Nicosia, in Sicily (Italy). The analyses were carried out during the cleaning process of the painting when the presence of a whitish surface *patina* was found.

The mid-FTIR measurements detected calcium carbonate and lead white by the presence of the combination band ($\nu_1+\nu_3$) at 2512 and 2420 cm^{-1} respectively, and by the presence of the band $\nu(\text{CO})$ at 1320 cm^{-1} (Figure 9 top).

Sulfates and oxalates were found everywhere and identified by the ($\nu_1+\nu_3$) combination band around 2200 cm^{-1} , the inverted $\nu_3(\text{SO}_4)$ at 1150 cm^{-1} [25], and the $\nu(\text{CO})$ at 1320 cm^{-1} [26].

The presence of lead carboxylates in the painting film was ubiquitary. Figure 9 top shows some of the collected spectra. The broad inverted band at 1506 cm^{-1} with two shoulders at 1514 cm^{-1} and 1540 cm^{-1} easily reveals the presence of lead carboxylates in all investigated regions and in particular, the predominance of lead azelate together with lead stearate and lead palmitate, as seen all spectra at 1470 cm^{-1} and 1450 cm^{-1} , belong to the fatty acid CH_3 asymmetric bending [19], and to the lead carboxylate symmetric stretching, respectively.

Moreover, the joint presence of the three types of lead carboxylates also indicates that the aging process is in an advanced state. The other two signals appearing in almost all spectra at 1470 cm^{-1} and 1450 cm^{-1} , belong to the fatty acid CH_3 asymmetric bending [19], and to the lead carboxylate symmetric stretching, respectively.

The painting *Santa Rita e Sant'Antonio* is by an unknown author of the XVII century and is temporarily under restoration. The painting showed some regions affected by protrusions, indicating a very advanced state of degradation. FT-MIR analyses revealed the presence of lead white, calcium oxalates, and lead carboxylates identified by the $(\nu_1+\nu_3)$ at 2420 cm^{-1} , the inverted band $\nu(\text{CO})$ at 1320 cm^{-1} , and the inverted band centered at 1504 cm^{-1} with two shoulders at 1520 and 1540 cm^{-1} . In this case, a pronounced shoulder at 1490 cm^{-1} has been found, in addition to the signal at 1450 cm^{-1} ascribable to lead carboxylate symmetric stretching (Figure 9bottom). Also for this painting, the aging process is in a far-gone state, and from FT-MIR results, it is possible to assert that a mixture of lead azelate, lead stearate, and/or palmitate is present. Furthermore, an infrared signal at 1490 cm^{-1} combined with the inverted band at 1504 cm^{-1} allowed the identification of lead oleate too [6, 16].

Conclusions

In this paper, we demonstrated that portable FT-MIR is a suitable technique for non-invasive individuation and discrimination of lead carboxylates *in situ*, without sampling.

By comparing the results obtained with benchtop and portable MIR spectrometers on artificially aged samples it was possible to assess the accordance between the two modes of data acquisition and thus to establish the suitability of portable FT-MIR as a diagnostic, non-invasive tool, for lead carboxylates. Furthermore, the comparison of the aged samples with synthesized lead carboxylates chosen from the most abundant fatty acids contained in linseed oil, allowed us not only to individuate the presence of lead carboxylates but also to discriminate their type, as confirmed by XRD spectroscopy on the analyzed samples.

By studying the aging processes of the two main components of lead white, i.e. hydrocerussite and cerussite, a peculiar behavior never reported before emerged for each one.

The use of very different aging conditions termed “mild aging” and “harsh aging” made it possible to understand that under “mild aging” different degradation products occur, depending on the starting substance, whilst under “harsh aging” the same mixture is obtained for both the components.

Such a difference, which emerged also with portable FT-MIR, may be useful for establishing any early stage of degradation and clarifying the composition of employed lead white, as well.

The very clear accordance obtained for 140 days of aging in both the mixtures -100 of which under harsh conditions- let us hypothesize that for a very long period of aging an equilibrium occurs, which is mostly shifted towards the formation of azelate, being stearate, and/or palmitate only by-products. In light of the data presented in this paper is thus evident that in real artworks the composition of the employed lead white is then crucial –even more than temperature and humidity- in determining which kind of lead carboxylate will form.

The campaign of measurement carried out *in situ* by portable FT-MIR definitively demonstrated that the presence and type of lead carboxylates in oil paintings can be detected in a fully non-destructive and non-invasive way without any sampling.

Finally, the proven efficacy of portable FT-MIR for individuating and discriminating lead carboxylates needs to be flanked by a previous screening on purposely prepared standards to verify, from time to time, not only the efficacy of this non-invasive technique but also to individuate any difference in carboxylates formation due to the starting pigment, to better understand the behavior of other metal carboxylates.

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Conflict of interest

The Authors declare no conflict of interest.

Captions

Figure 1. Infrared spectra in ATR mode at different times of: a) lead azelate, lead palmitate, and lead stearate standards; b) zoomed view of 700-1800 cm^{-1} range; c) pure linseed oil.

Figure 2: XRD patterns of lead palmitate, lead stearate, and lead azelate.

Figure 3. *Left:* Infrared spectra in ATR mode of A) linseed oil/hydrocerussite 1:1; B) linseed oil/cerussite. *Right:* zoomed view of the corresponding mixtures in the range 1200-1700 cm^{-1} .

Figure 4. XRD patterns of: a) cerussite: linseed oil=1:1 mixture, and b) hydrocerussite: linseed oil=1:1 mixture. Both the mixtures were analyzed before and after aging (H=hydrocerussite, C=cerussite, S=lead stearate, P=lead palmitate, A=lead azelate).

Figure 5. FT-MIR reflectance spectra of 1:1 linseed oil/hydrocerussite mixture. *Left:* spectra collected at different time intervals; *right:* zoomed view of the 1500 cm^{-1} signal.

Figure 6. FT-MIR reflectance spectra of 1:1 linseed oil/cerussite mixture. *Left:* spectra collected at different time intervals; *right:* zoomed view of the 1500 cm^{-1} signal.

Figure 7: *Left:* *Presentazione al Tempio* by Giuseppe Velasco. *Top right:* reflectance mid-FTIR spectra recorded on *Presentazione al Tempio*. *Bottom right:* zoomed view.

Figure 8. *Left:* Santa Rita e Sant'Antonio. *Top right:* reflectance mid-FTIR spectra recorded on Santa Rita e Sant'Antonio. *Bottom right:* zoomed view.

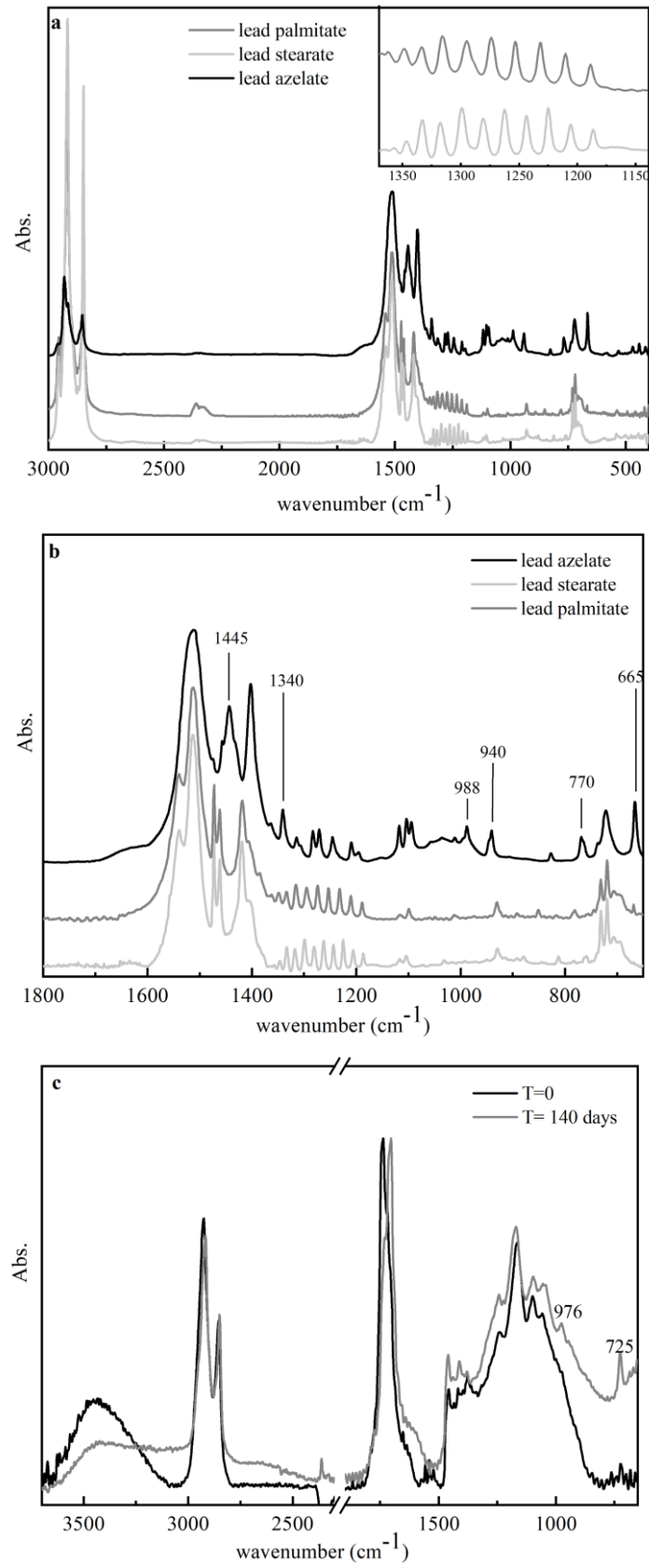


Figure 1

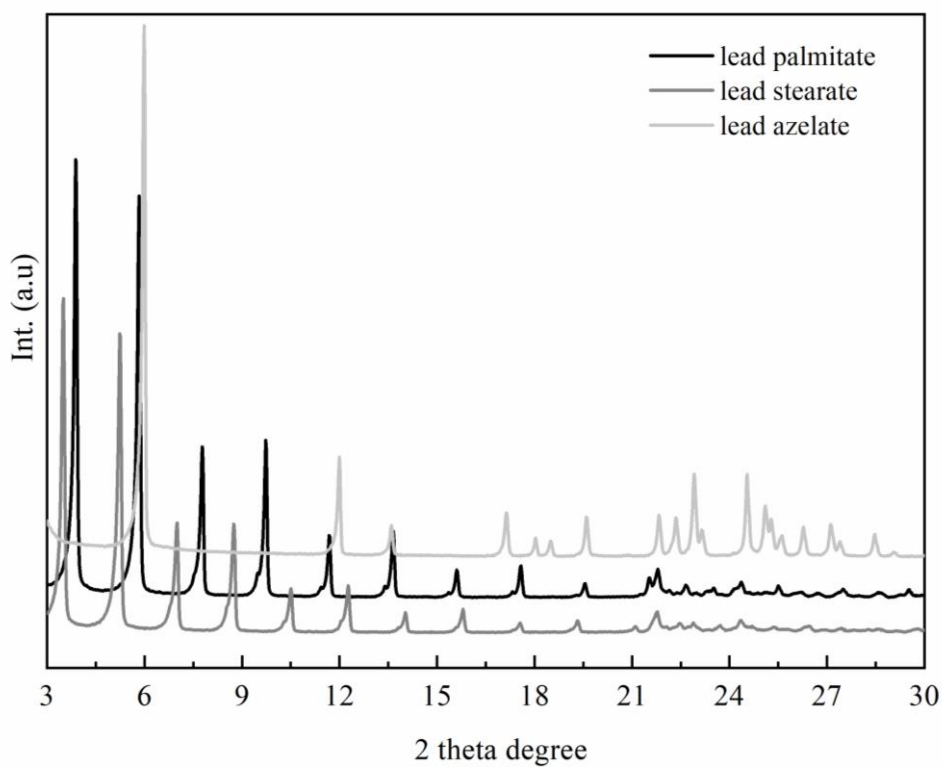


Figure 2

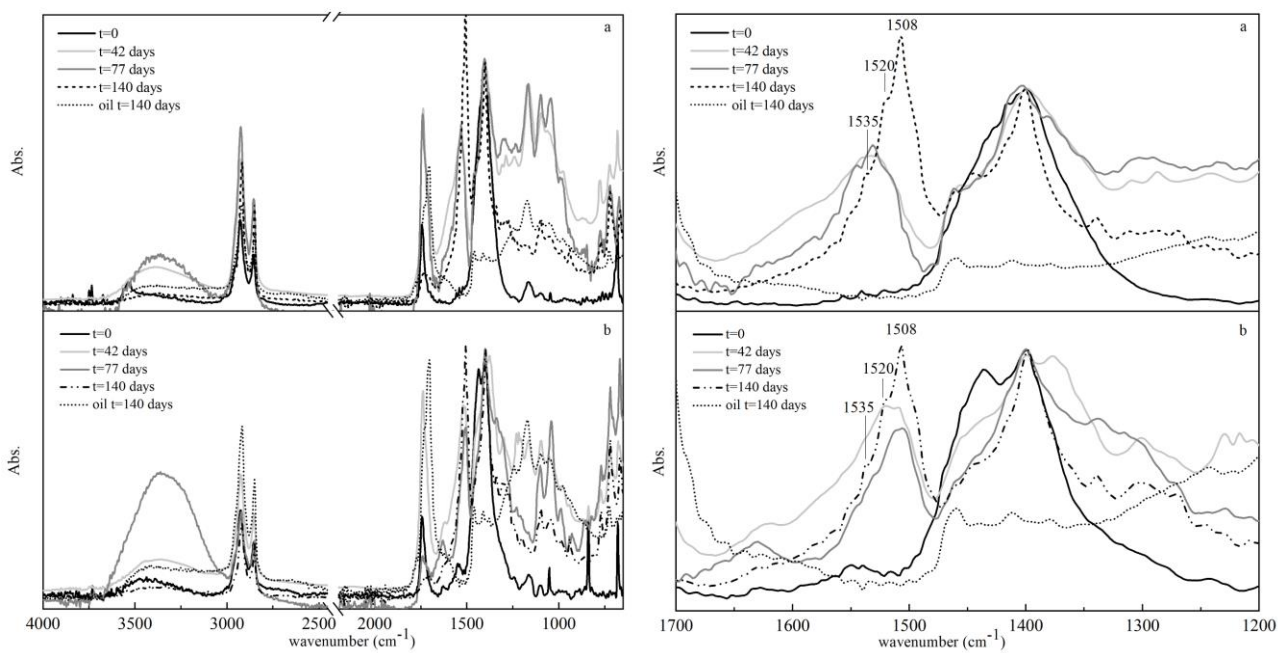


Figure 3

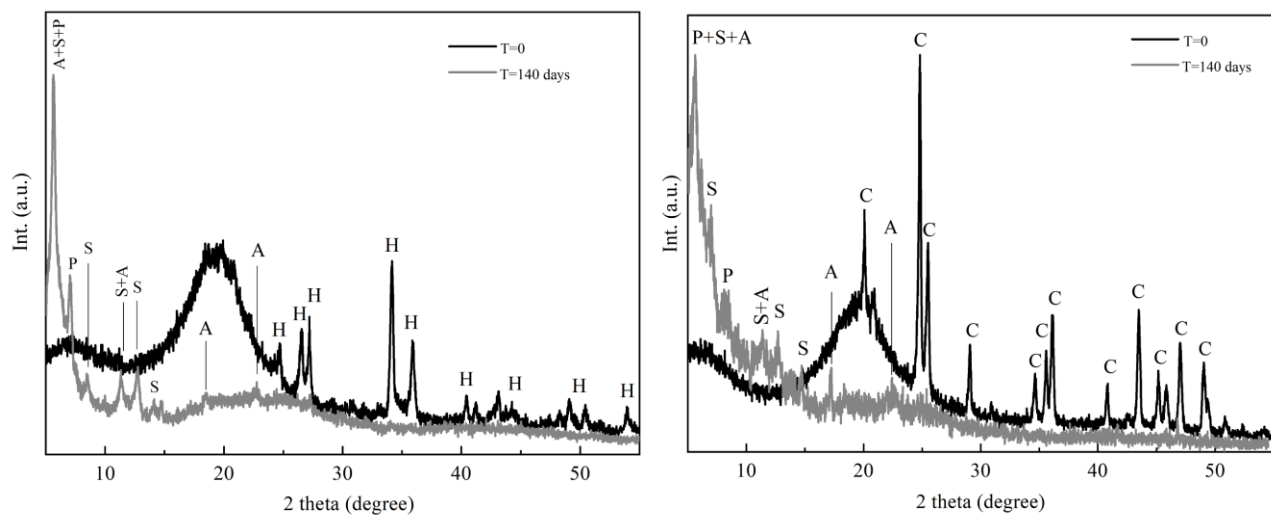


Figure 4

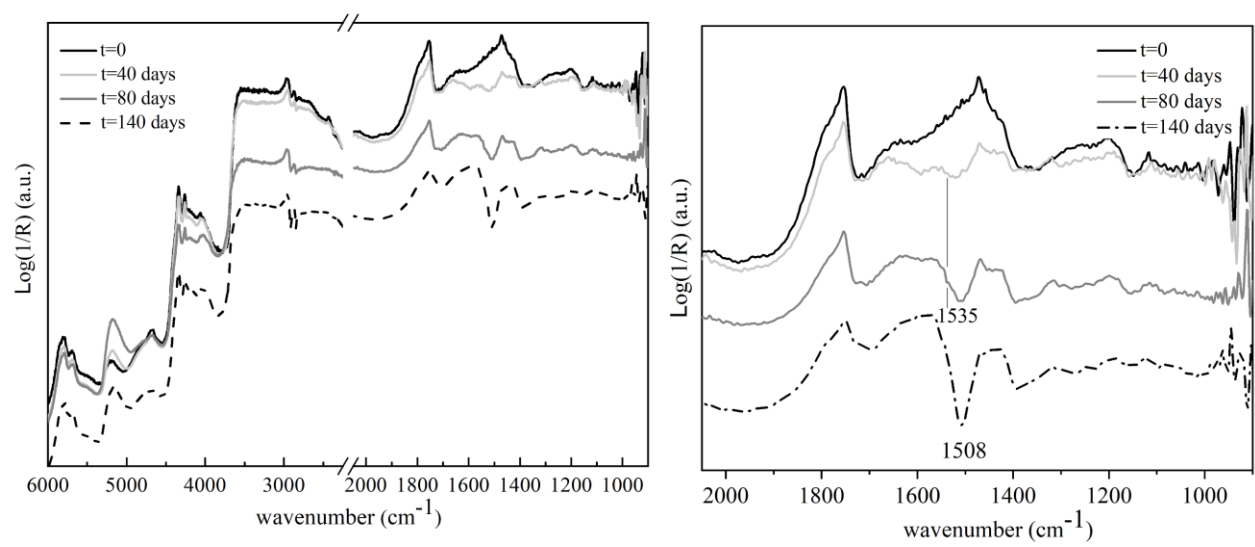


Figure 5

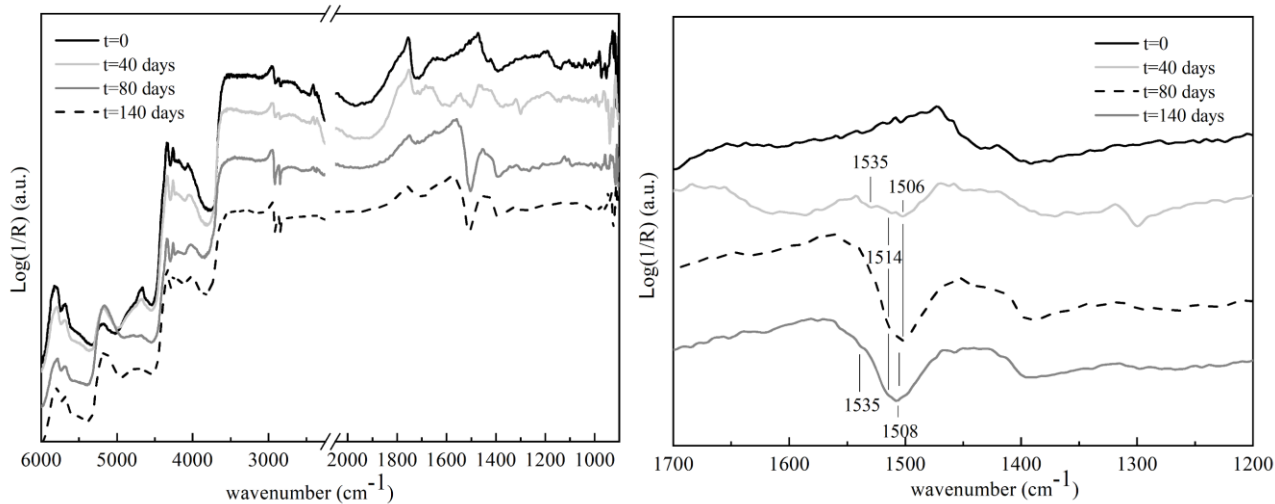


Figure 6

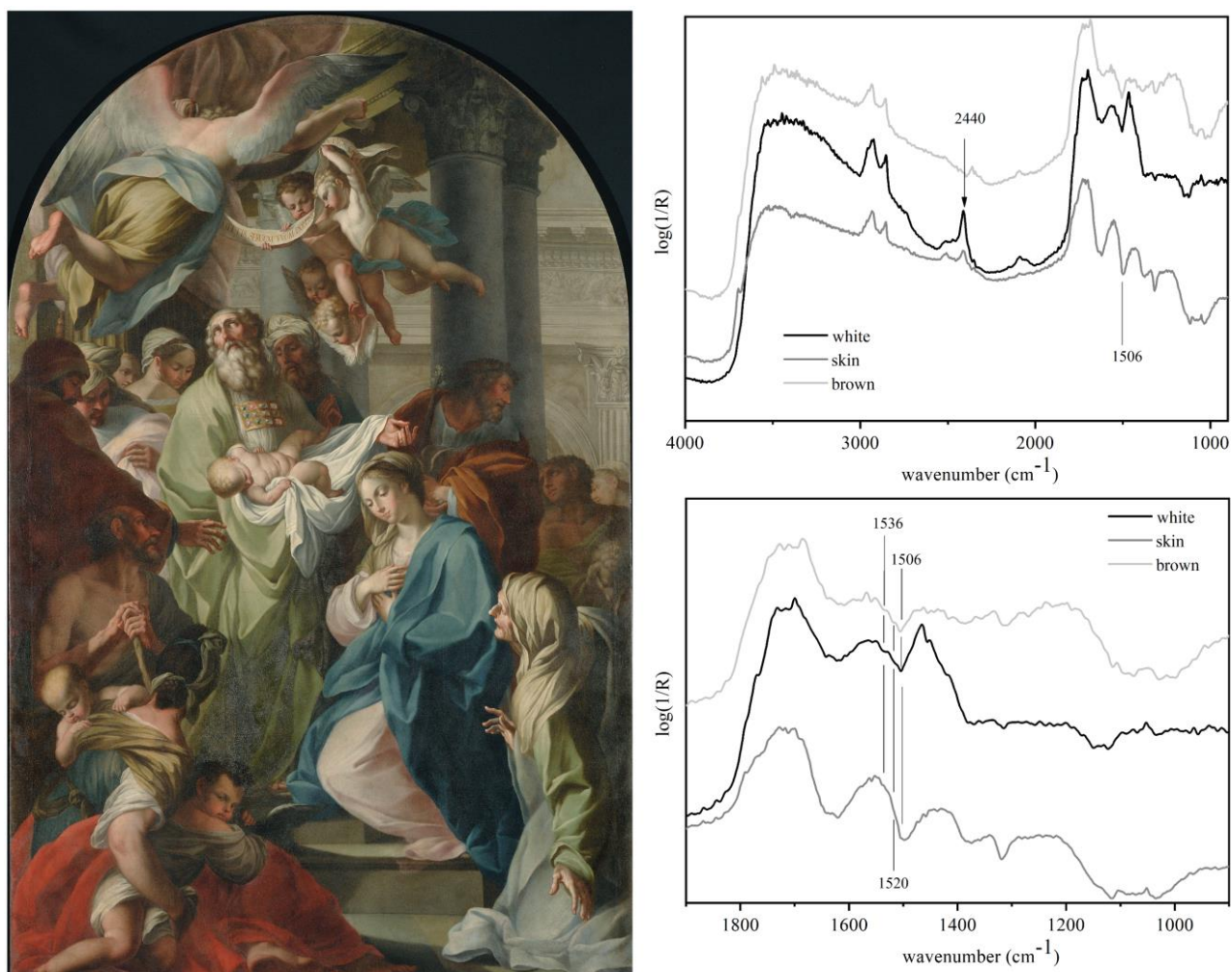


Figure 7

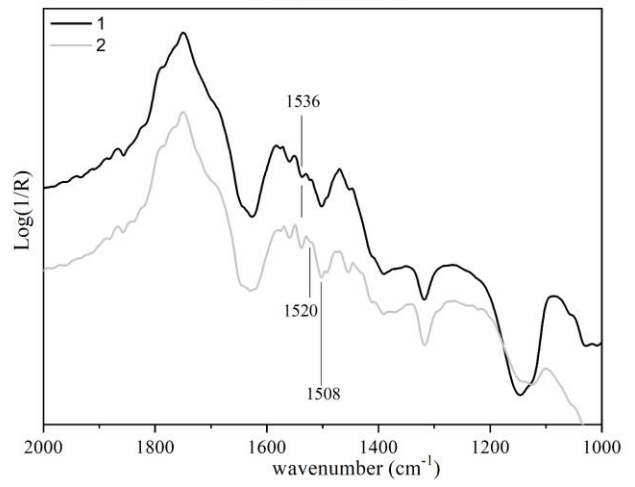
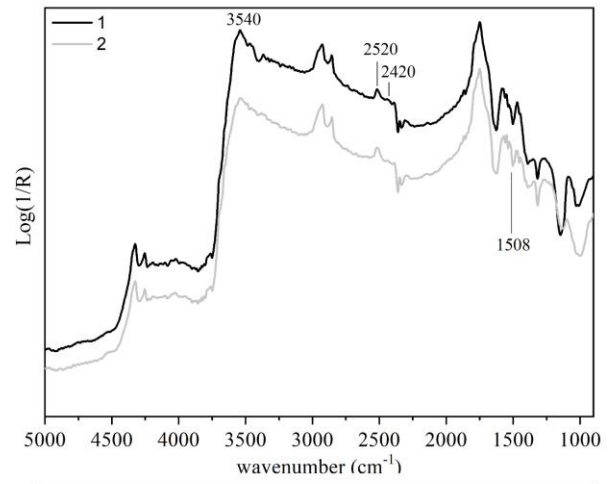


Figure 8

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: