Original article

Evaluation of vibrational spectroscopic techniques for consolidants' penetration depth determination

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A B S T R A C T

The penetration depth of consolidants applied to cultural heritage objects plays a crucial role in a successful conservation and protection of them. In the frame of HEROMAT FP7 project new consolidants for carbonate and silicate based materials were developed. Among many other investigated properties, the penetration depth was defined by Raman and FTIR spectroscopies, for which their ability was also evaluated. Due to the formation of calcium carbonate in the consolidation process of carbonate forming consolidants, the addition of sodium nitroprusside indicator supported Raman differentiation of treated and non-treated areas in the calcium carbonate based substrate. Furthermore, the combination of the indicator reaction and Raman results gave much more precise penetration depth estimation than the visual assessment alone. For following the penetration depth of modified TEOS based consolidants for silicate based substrates, FTIR spectroscopy turned out to be very successful without any indicator application or pre-treatment of samples. Furthermore, the penetration depth related to different application methods, such as brush, cellulose pulp, airless spray and roller, was also studied. The deepest penetration was achieved by 8 h of application of consolidants in cellulose pulp, while in comparing one application by roller, airless spray and brush within the same substrate, the deepest penetration can be achieved by brush.

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1. Introduction

Since the middle of the last century different synthetic polymers have been used for consolidation of limestone surfaces. Due to their aesthetical alteration, change in the polymers solubility and degradation, which could alter the physico-chemical properties, such as creaking, flaking and glossy effect, their potential application is hindered. In this respect, the use of "compatible" materials is preferable since this way durability and long-term stability is granted [1,2]. In the last decade much of the research has been made in the field of synthesis of macro- and nano-particles of $Ca(OH)_2$ in different alcohols [1]. Dispersions of $Ca(OH)_2$ nanoparticles have been proven to be effective for consolidant treatment due to their small dimensions and ease of the penetration as well as increased

reactivity towards CO_2 [2,3]. However, there still exist important obstacles for their use such as the variable particle size, incomplete carbonization (due to the need of atmospheric CO_2) and the low concentrations (5–25 g/L) [1,3]. In fact, a consequence of the low concentration and volatility of solvents used in consolidants is that multiple applications are needed [1,2].

For effective consolidation of deeper layers of degraded substrates, use of soluble starting materials is desirable. However, since the solubility of calcium carbonate is low, the preparation of such a material is very difficult [4]. In the scope of HEROMAT FP7 project a new solution of calcium acetoacetate for consolidating carbonate based substrates was developed [5]. Since the consolidant is a solution, it can penetrate deeper into the material, where re-cohesion between particles can be established. Additionally, due to higher concentrations (from 5–100 g/L) the number of consolidant applications can be strongly reduced.

On the other hand, for consolidation of silicate substrates consolidants based on alkoxylanes or tetraethoxy silane (TEOS) are used [6,7]. They can have a poor affinity to materials with large pores, for example such as found in some sandstones. Namely, during the hardening phase or under mechanical stress thick and brittle

silica-gel structures of consolidants fill the pores with silica-gel resulting in a material that is less permeable to the water vapour [8,9]. For the silicate based substrates modified formulations of commercial product based on silicate ester was developed in the scope of HEROMAT FP7 project. Due to its balanced combination of polysilicate, dioxalane, mixture of C11-C13 alkanes (liquid paraffin) and diethylethanolamine, the consolidant has a low dry mass and therefore does not reduce the porosity of consolidated material. Furthermore, it has a good retained water vapor permeability, efficient and uniform consolidation through the profile of the substrate without skin forming.

Chemical and/or physical response of the substrate (*i.e.* calcareous and silicate materials) varies strongly due to their heterogeneous properties (*e.g.* different porosity, distribution of components). Therefore, to validate the conservation treatment of the materials composing cultural heritage objects, a careful selection of the application method of the consolidant and the analytical technique for monitoring and assessing the performance of the consolidation should be made. The non-destructive methods, in which a sample is left intact, such as Environmental Scanning Electron Microscopy (ESEM-EDS), spectrophotometry, ultrasound velocity, Nuclear Magnetic Resonance (imaging and relaxometry) and Optical Surface Roughness analysis could offer a platform to determine not only the chemical characteristics, but also the morphological, physical and the hydric properties of the materials before and after consolidation [10]. One of the parameters besides the compatibility, durability, effect on appearance [11] *etc.*, which should be taken under consideration, when evaluating new consolidant formulations is also the depth of consolidant penetration. Regarding compatibility of the consolidant with the material being consolidated, the *in situ* carbonation using the solutions of calcium hydroxide is gaining much attention, as has been previously mentioned. Despite the fact that the formed carbonate could exist in different grain size and different crystal-aggregate texture [11], it is difficult to differentiate them from the original one constituting the cultural heritage object. With the assumption that the magnesium hydroxide particles have the same capability as the calcium hydroxide for the penetration, Dei and Salvadori [12] showed that by using the magnesium hydroxide as the marker, SEM-EDX analysis and superficial area analysis (BET) could be used for following the depth of penetration of the consolidant in addition to water absorption capillarity measurements for evaluation of water-interaction properties. Pinto and Rodriguez [13] quantified the consolidation effect and the role of treatment procedures (*i.e.* by capillary absorption, by immersion and by brushing) for on-site building stones (monuments) in complementation to laboratory studies of different carbonate samples with different intrinsic properties by weighing, micro drilling resistance (DRMS), ultrasonic velocity and flexural strength. In accordance, also the penetration depth could be consequentially correlated with those results. Moreover, Pinto and Rodriguez [14] showed, that DRMS methodology is one of the most promising for the assessment of the consolidation rate in the soft stones, while the depth of the strengthening action could be further successfully determined by other techniques such as by the collection of longitudinal ultrasound velocity profiles. For evaluation of penetration depth of the polymer consolidant within porous stone substrates, several direct analytical methods such as staining test using for example iodine vapor [15] or fluorescent dyes for visualizing the location of the consolidant, Fourier transform infrared spectroscopy (FTIR), SEM-EDX and XPS, and also indirect, which includes measurements of contact angle, bending strength, modulus of elasticity *etc.* could result in gaining valuable information of the interaction between the consolidant and the substrate [16]. μRaman mapping proved to be an effective tool for assessing the penetration depth of consolidant products based on oxalate formation. Consolidation with ammonium oxalate (oxammite) in

different plasters made of lime and carbonate aggregate was studied by Conti et al. [17]. It was shown that during consolidation process, oxammite induces the transformation of calcium carbonate to calcium oxalate (whewellite), which gives a better resistance to decay phenomena. Strong and characteristic bands at 1462 cm^{-1} (whewellite) and at 1085 cm^{-1} (calcite) have been considered for following the penetration depth by μRaman mapping. Furthermore, neutron radiography and tomography allow the visualization of polymerized as well as non-polymerized conservation materials inside the porous materials. With these methods Cnudde et al. [18], Dierick et al. [19] and Masschaele et al. [20] successfully defined the impregnation depth of silicate-based materials inside the natural building stones and resulting effects on the uptake water. Alternative technique for the investigation of depth profile, which also allows the visualization of the presence and distribution of different hydrophobic product in stone material, is magnetic resonance imaging (MRI) [10,21]. The structure of natural building stones as well as the visualization of consolidants and/or water repellents within the stones could be investigated using non-destructive X-ray radiography computed with micro-tomography [22]. As the resolution of micro-tomography depends on the amount of treatment materials inside the investigated sample, the addition of contrast agent (*e.g.* 3-bromopropyltrimethoxysilane) is often needed [22]. Another non-destructive method for observation of penetration depth is the tabletop high-resolution X-ray radiography, which became useful after the integration of pixel detectors of Medipix type. This technique has proved to be an optimal tool for observation of penetration depth of organosilicon consolidants in the Opuka stone [23].

When using Raman and FTIR spectroscopy, which are usually available in conservation laboratories, the difficulties may arise due to the overlapping of modes of consolidants and the matrix. For that reason our study was focused on exploring the abilities of vibrational spectroscopic techniques for penetration depth evaluation, where the same composition is formed in the consolidation process as it is present in the matrix of the material that is consolidated.

2. Research aims

In this work, in the framework of HEROMAT FP7 project, spectroscopic techniques, Raman and FTIR, were evaluated for following the penetration depth of developed carbonate and silicate forming consolidants for carbonate and silicate substrates, respectively. This, however, was specifically challenging since the same composition is formed in the consolidation process as it is present in the matrix of the material that is consolidated that can result in overlapping of specific vibrational modes. To overcome the difficulties, in the case of carbonate consolidants an indicator sodium nitroprusside is proposed, while in the case of the silicate consolidant, the new formulation itself, consisting also paraffin, offers the solution. Furthermore, different application methods, usually applied in restoration or in buildings refurbishment were tested. The work was done on prepared model substrates that mimic the composition of outside materials at Dornava Manor, one of the selected test sites of the HEROMAT project, in order to provide results relevant for later on-site application of, within the project, developed consolidants.

3. Experimental

3.1. Consolidants

For carbonate substrates new consolidant formulations, thoroughly described in the patent PCT/SI2014/000028 [5] and based on soluble calcium compound calcium acetoacetate Ca(OAcAc)$_2$ were

developed in three different solvents: methanol (CF1), mixture of ethanol and methanol (CF2) and water (CFW). Additionally catalyst (0.05 wt.% ethylenediamine, 99+%, Acros Chemicals) was added into consolidant before the application.

For silicate substrates new consolidant formulation HERO-MAT CF4 was prepared by mixing ethyl polysilicate (WACKER TES 40 WN, Wacker Silicones), solvent (1,3-dioxolan – DOX, 99%, Sigma Aldrich), catalyst (diethylethanolamine – DEEA, 99.5%, Sigma Aldrich) and the mixture of C11-C13 alkanes (paraffin, Samson Kamnik, CAS: 64742-48-9). Catalysts were always mixed into ethanol and added last to the rest of the mixture. Mixture of C11–C13 alkanes (liquid paraffine) were used to reduce the solubility of catalyst and various hydrolysed species of ethyl polysilicate after the evaporation of 1,3-dioxolane. This would prevent formation of the gel in the whole volume of the pore. Mixture of C11–C13 alkanes (liquid paraffine) has low volatility, but will evaporate from the substrate.

3.2. Samples

3.2.1. Carbonate substrate samples

On the basis of petrographic analysis of a sample taken from the outside carbonate surface of the garden fence at Dornava Manor the most appropriate quarry for aggregates was selected, and characteristics of lime and cement were defined. The silicate gravel fraction 0/4 mm from Hoče quarry was acquired and sieved out to get similar grading curve as the aggregate from the analyzed carbonate sample. For binder clean pucolan cement was used. In order to weaken mechanical properties, a part of the cement was replaced with a special pucolan additive. Also traditionally prepared slaked lime from local producers was used. The substrates were prepared combining coarse and fine carbonate to achieve the appropriate thickness. On approximately 3.5 cm thick coarse layer 3–4 mm thick layer of fine carbonate was applied. Steel moulds of 16 cm × 4 cm × 4 cm and 15 cm × 15 cm × 4 cm dimensions were used for models preparation. The models were then cut out to the required dimensions for testing. Wetting and curing was done for a minimum of 14 days before the cutting was performed. The porosity of the carbonate model substrate was 39.34%, measured by Hg-porosimetry.

3.2.2. Silicate substrate samples

A bulk sample of silicate known as Ptujska Gora sandstone or Vundušek sandstone was taken from the Jelovice quarry, which is located near the town of Majšperk, in the eastern part of Slovenia. This silicate belongs to the Middle Miocene geological period. It is a coarse grained, moderately well sorted sandstone, comprising quartz, dolomite, feldspar, muscovite and unusual minerals such as zircon and apatite. It also contains a fine grained pore filling matrix/cement of a high Fe content, of uncertain mineralogy. Secondary interstitial calcite cement is also present. The porosity of the silicate was 14.20%, measured by Hg-porosimetry.

3.2.3. Preparation of samples for penetration depth investigation

For investigation of the depth of consolidation in carbonate substrates three different consolidants (CF1, CF2, CFW), developed within HEROMAT project, were applied directly on the upper surface of the carbonate model substrates. For the silicate model substrate a silicate forming HEROMAT CF4 consolidant was used. The model substrates were then cut across the depth profile in order to provide a suitable surface for the penetration investigation. Table 1 gathers the description of investigated samples related to different developed consolidants. The penetration depths of consolidants were tested on the carbonate and silicate substrates. In the case of carbonate forming consolidants indicator sodium nitroprusside, $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ (5% water solution; Sigma Aldrich)

Table 1
Investigated samples related to different developed consolidants.

Sample	Consolidant	Consolidant composition
Carbonate	CF1	9.6 wt.% Ca-acetoacetate in methanol
Carbonate	CF2	8.4 wt.% Ca-acetoacetate in ethanol/methanol (9:1)
Carbonate	CFW	9.6 wt.% Ca-acetoacetate in water
Silicate	CF4	Diethylethanolamine (DEEA) 5 wt.%, 1,3-dioxolan (DOX) 20 wt.%, alkanes C11–C13 (P) 25 wt.%, ethyl polysilicate 50 wt.%

was applied over selected area of the penetration depth profile of each substrate after curing period (three days at RT). In the period of few minutes the red colour appeared. All Raman measurements of penetration depth were performed within 1 h (the red colour was visible more than 1 h). The chemical identification of the material components was performed on the penetration depth profile of the carbonate substrates using micro-Raman spectroscopy. In the case of silicate forming consolidant FTIR microscopy was used on the penetration depth profile of the silicate substrates without any indicator application.

3.3. Application methods

One of the developed carbonate forming consolidants (CF1) was applied directly on the upper surface of the carbonate model substrate, and silicate forming consolidant CF4 was applied on the silicate model substrate, using different techniques: roller, airless spray, brush and cellulose pulp.

Table 2 gathers the description of investigated samples related to different application method used. The application of the consolidant in the cellulose pulp was done by the following procedure: 8.6 g of cellulose pulp was mixed with 43 g of consolidant (previously mixed with catalyst) and laid over the substrate which was covered with Japanese paper. Thickness of the pulp containing the consolidant was approximately 1 cm. To investigate the time of the application influence on the depth of penetration, the pulp had been applied over the substrate for 1 and 8 h, and then removed. Samples were then left to dry for three days. In the case of the carbonate model substrate also different numbers of applications by the same method were tested.

3.4. Instrumentation

3.4.1. Raman spectroscopy

Raman analysis of consolidated carbonate model substrates was performed using 633 and 785 nm laser excitation lines with a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer

Table 2
Description of investigated samples related to different application method used.

Sample description	Application technique	Number of applications/time of application	Consolidant
Carbonate R1	Roller	1	CF1
Carbonate R2	Roller	2	CF1
Carbonate R3	Roller	3	CF1
Carbonate A1	Airless spray	1	CF1
Carbonate A2	Airless spray	2	CF1
Silicate A3	Airless spray	1	CF4
Carbonate B1	Brush	1	CF1
Silicate B2	Brush	1	CF4
Carbonate P1	Cellulose pulp	1 h	CF1
Carbonate P2	Cellulose pulp	8 h	CF1
Silicate P3	Cellulose pulp	1 h	CF4
Silicate P4	Cellulose pulp	8 h	CF4

coupled to an Olympus BXFM optical microscope. The spectra were recorded using ×50 lwd (long work distance) objective lens and 600 grooves/mm grating, which gave the spectral resolution of 1.3 cm^{-1}/pixel and 0.83 cm^{-1}/pixel, respectively. The power at the samples was set between 0.1 and 35.8 mW using neutral density filters. A multi-channel, air cooled CCD detector was used, with integration times between 5 and 20 s, and the spectral range was set between 50 and 4000 cm^{-1}. The wave number calibration was performed using a silicon wafer. Spectra obtained on samples treated with CF1 and CF2 are translated upon vertical axis for ease of comparison, and the spectra obtained on substrates treated with CFW are baseline corrected (LabSpec, polynom 8 degrees) and translated upon vertical axis for ease of comparison.

3.4.2. FTIR spectroscopy

FTIR analysis of consolidated silicate model substrates was carried out with a Perkin Elmer Spectrum 100 FTIR spectrophotometer coupled to a Spotlight FTIR microscope equipped with nitrogen cooled MCT detector. Spectra were recorded in reflection mode over a 4100–500 cm^{-1} wavenumber range at 4 cm^{-1} spectral resolution over 64 scans. The spatial resolution was about 50 μm^2. After applying the CF4 consolidant FTIR analyses were performed on the penetration depth profiles of silicate substrates.

4. Results and discussion

4.1. Evaluation of the usefulness of Raman spectroscopy in carbonate substrates

The principle of consolidation with new consolidant is the spontaneously decarboxylation of calcium acetoacetate in the presence of water what leads to calcium carbonate, carbon dioxide and acetone [5]. Decarboxylation of calcium acetoacetate is greatly influenced by the treatment conditions, such as temperature and relative humidity. On the other hand by varying treatment conditions, a range of different crystalline polymorphs can be obtained. Xu et al. [24] reported that amorphous CaCO$_3$ has been stable more than three months under room temperature and dry conditions, while Spanos et al. [25] mentioned a long time (several months) solid-state vaterite transformation into further polymorphs. For this reason, we assumed that in presented experiments, all three developed consolidant variations, designated as CF1, CF2 and CFW, form unstable amorphous CaCO$_3$, which transform into vaterite form.

Another polymorph of calcium carbonate, calcite, is the most common form present in cultural heritage objects, and is a constituent of the prepared model substrates. Vaterite exhibits Raman bands at 305, 671, 1078, 1089 cm^{-1} [26], while calcite bands can be found at 156, 283, 713, 1087 cm^{-1} [27].

The strongest bands assigned to non-degenerate symmetric stretching vibrations of vaterite carbonate ion (v_1) which appear at 1078 and at 1089 cm^{-1} could potentially be selected to follow the penetration depth of consolidants. The other bands typical for vaterite have weak intensity using the chosen excitation line and in addition could be hindered by the fluorescence emission and/or by the interfering signal belonging to other components of the heterogeneous substrate. Moreover, the non-degenerate symmetric stretch of calcite carbonate ion (v_1) at 1086 cm^{-1} causes difficulties in the interpretation due to the possible overlapping with the signal of vaterite.

It is worth to emphasize that transformation of amorphous CaCO$_3$ to vaterite phase is slow and transformation may not be uniform through the depth of the substrate, therefore following the vibrations of vaterite carbonate ion to determine penetration depth is questionable. The evaluation of penetration depth only through the vaterite Raman analysis suffers of a limitation, not only for the vaterite/calcite bands overlapping, but also because we cannot exclude a calcite crystallization induced by the reaction, which
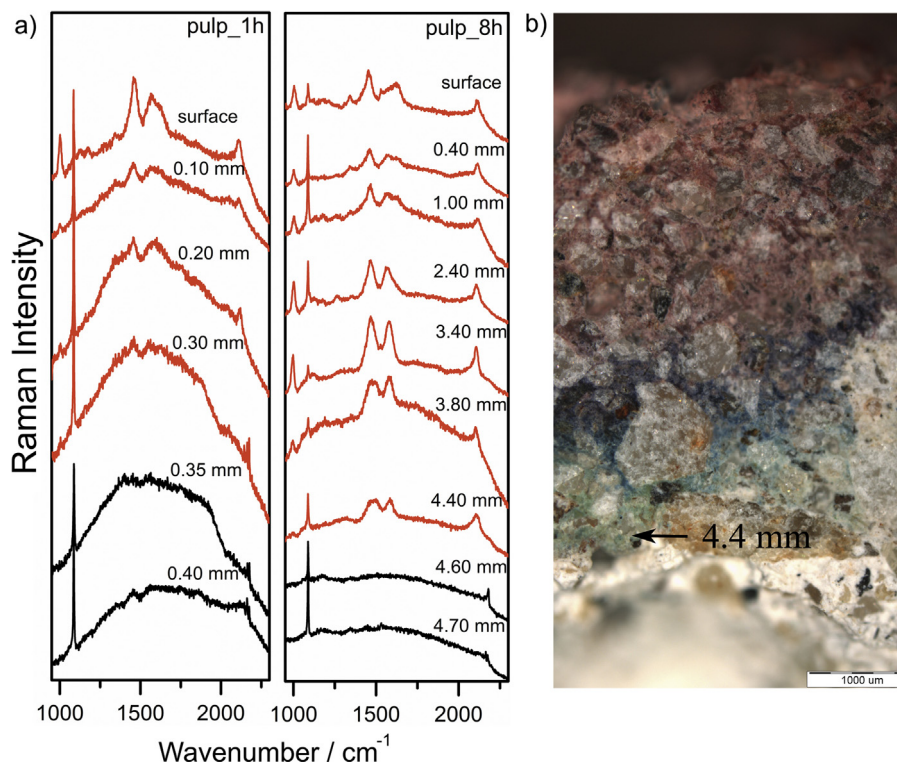

Fig. 1. Penetration depth of carbonate consolidant applied in cellulose pulp for 1 and 8 h: (a) Raman spectra after consolidant and indicator application related to different penetration depth; (b) cross section of the treated carbonate model substrate (8 h of consolidant in cellulose pulp) after the indicator application ($\lambda_0 = 633$ nm). Obtained blue colour is a result of reaction between indicator, calcium acetoacetate and calcium hydroxide due to not fully carbonized substrate.

cannot be distinguished from the calcite of the substrate. For this reason, following the penetration depth with tracing calcium acetoacetate seems a better solution. It turns out that sufficient amount of calcium acetoacetate is unreacted under used conditions. For fast and simple identification of penetration depth of consolidants CF1, CF2 and CFW we introduce the combination of indicator method and Raman mapping of acetoacetate. Before Raman analysis indicator sodium nitroprusside was applied on consolidated sample. In the consolidation process, calcium acetoacetate decomposes into calcium carbonate, carbon dioxide and acetone. It is known from the literature, that the sodium nitroprusside could be used as the analytical reagent for the detection of methyl ketones and it can also detect acetoacetate [28]. Actually sodium nitroprusside mainly reacts with acetoacetate ion and is practically not reactive to acetone, if latter it is in low concentrations [29]. It is communicated by Swinehart [30] that during the reaction of acetoacetate with nitroprusside red colouration takes place. Consequently, as the solution of the indicator gives different colour reactions only with ground carbonate than with ground carbonate mixed with the consolidant, it can be applied to detect the calcium acetoacetate in the substrate. Therefore it can be used for the determination of the penetration depth of the consolidant within the carbonate substrate. The results indicate that the consolidated carbonate substrates impregnated with sodium nitroprusside mostly give red colour or sometimes blue colour (as it is visible in Fig. 1b) in the case of calcium hydroxide presence in the substrate. On the other hand, the impregnation of not-consolidated carbonate substrates with sodium nitroprusside has usually no effect on colour or only in the case of the presence of calcium hydroxide slightly yellow hue can be observed. The combination technique of visual determination together with Raman spectroscopy was established as the method which can offer a more precise evaluation of the penetration. Fig. 2 shows Raman spectra of ground carbonate mixed with indicator, with and without consolidant, and Fig. 3 shows the change of the indicator colour from yellow to red-violet in the presence of consolidant.

In the absence of consolidant, the strongest bands, typical of the indicator sodium nitroprusside appear at 2096 and 2122 cm^{-1} (Fig. 2b). When adding the consolidant, the CN stretch [31] of the indicator shifts to 2101 and 2178 cm^{-1}, and bands at 563, 647, 901, 996, 1465 and 1569 cm^{-1} appear (Fig. 2a). The characteristic Raman modes at 2178, 2101, 1569, 1465 and 996 cm^{-1} can therefore be used for following the penetration depth of carbonate forming consolidants.

Fig. 4 shows the comparison of the developed consolidants and their penetration depth in the same substrate. As evident in Fig. 4,
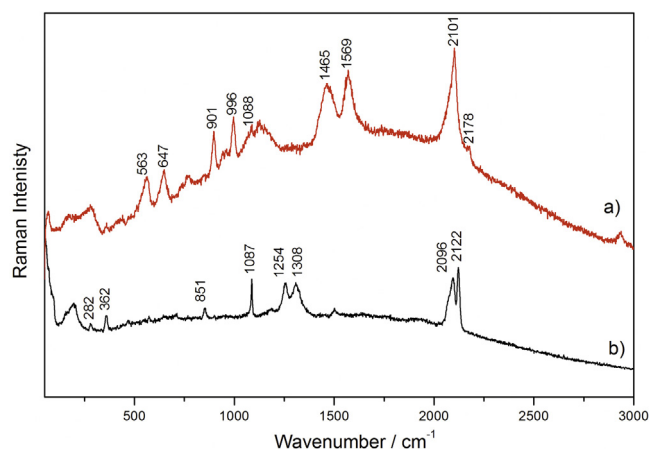

Fig. 2. Raman spectra of (a) ground carbonate substrate with consolidant and indicator and (b) ground carbonate substrate and indicator. $\lambda_0 = 633$ nm.

CF2 showed the highest penetration of 2.8 mm into the carbonate model substrate, while the lowest penetration of 0.8 mm was identified for the CF1 consolidant.

4.2. Evaluation of the usefulness of FTIR in silicate substrates

Several FTIR techniques (*e.g.* ATR, diamond cell, *etc.*) were tested for monitoring the penetration depth of silicate forming consolidant CF4. The best results were achieved with the micro-reflection FTIR spectroscopy. Indeed, the spectra obtained with this technique, in the particular spectral area (3000–2800 cm^{-1}) most clearly revealed characteristic CH stretching bands of silicate forming consolidant CF4 among all other FTIR techniques. The penetration depth for HEROMAT promising improved TEOS-based formulation, CF4, may be therefore evaluated on CH groups' vibration bands from both, TEOS and paraffin.

Fig. 5 shows FTIR spectra of silicate consolidant mixed to silicate substrate (Fig. 5a), pure consolidant (Fig. 5b), and silicate substrate (Fig. 5c). Immediately, after mixing the consolidant to the silicate substrate only the bands of the TEOS are visible in the CH stretching region at 2978, 2930, 2894 cm^{-1} (Fig. 5a and b). However, the hydrolysis reaction is very fast after application and the signals from paraffin at 2959, 2925 and 2855 cm^{-1} become more visible and may become more intense that those of TEOS after the very first days. Paraffin has low volatility and therefore gradually evaporates
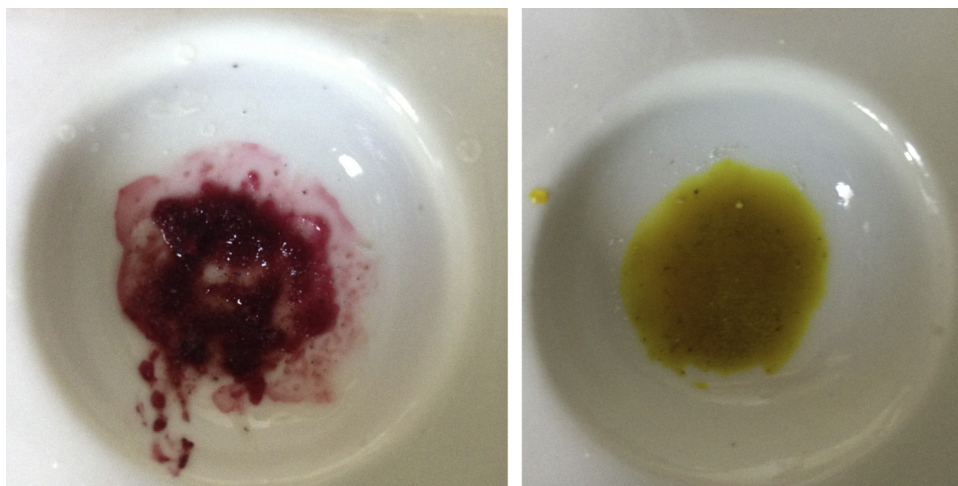

Fig. 3. Left: ground carbonate substrate mixed with consolidant CF1 and indicator giving red–violet colour. Right: ground carbonate substrate mixed with indicator giving yellow colour.
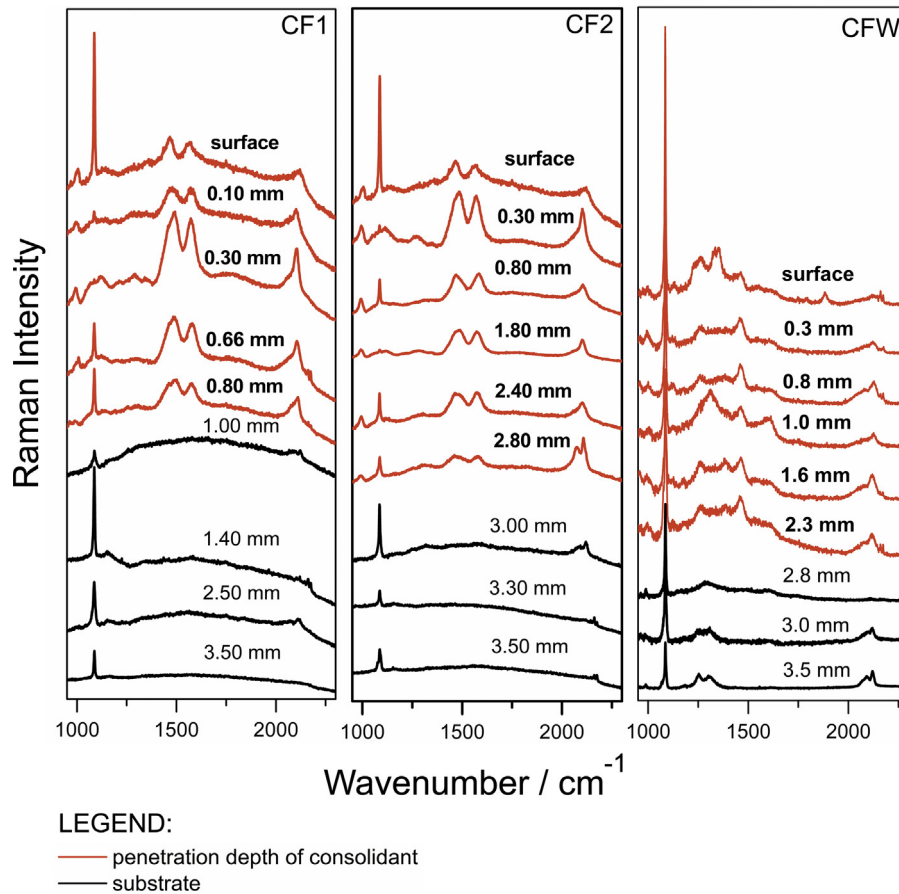
Fig. 4. Raman spectra of CF1 ($\lambda_0 = 633$ nm), CF2 ($\lambda_0 = 633$ nm) and CFW ($\lambda_0 = 785$ nm) consolidants after indicator application, applied to carbonate model substrate related to different penetration depth.

from the surface. The strongest signal at 2925 cm^{-1} from paraffin overlaps the diagnostic TEOS-assigned band at 2930 cm^{-1}. Nevertheless, this does not lead to problems since both signals are related to consolidant itself and may be used as diagnostic bands for determining the penetration depth. The fingerprint region in the spectra in Fig. 5 reveals also other characteristic bands of silicate forming consolidant, CF4, as well as bands belonging to silicate substrate.

Spectrum of pure consolidant (Fig. 5b) shows strong and sharp signals in the region between 1500–1300 cm^{-1} [32]. These characteristic bands are assigned to TEOS bending vibration of CH group and are present also in the spectrum of mixture of silicate substrate and consolidant (Fig. 5a). Additional broadened TEOS signals in the region below 1200 cm^{-1} correspond to different combination bands of stretching vibrations of Si–O–Si, Si–OH, Si–O$^-$ as well
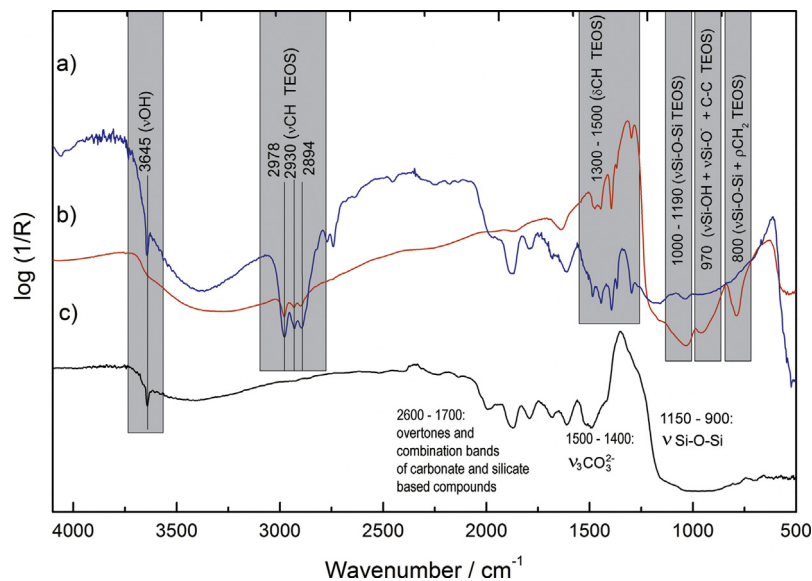

Fig. 5. FTIR spectra of (a) silicate consolidant mixed to silicate substrate, (b) pure consolidant, and (c) silicate substrate.

as bending vibration of CH group (Fig. 5b) [32]. Mentioned strips are in lesser extent visible also in the spectrum of mixture of silicate consolidant and silicate substrate (Fig. 5a).

Silicate substrate is mostly comprised of clay minerals. Accordingly, a strong and broaden band in the region of 1150–900 cm^{-1} corresponds to Si–O stretching vibration [33]. Another broaden band of asymmetric stretching vibration of carbonate ion (ν_3) in the range between 1500 and 1400 cm^{-1} can be ascribed to calcium carbonate. Spectral features in the region from 2600 to 1700 cm^{-1} are correlated to overtone and combination bands of carbonate and silicate based compounds [34,35]. Another mineralogical compound found in the silicate substrate is calcium hydroxide ($Ca(OH)_2$). Its characteristic sharp signal in the OH stretching region is sited at 3645 cm^{-1} (Fig. 5a and c) [36].

4.3. Penetration depth of consolidants applied by different methods

Different methods of application of consolidants are used in the conservation practice, depending on the nature of objects treated, and the scope of treatment. Therefore several techniques, in different combinations of application "runs" were tested in this work, to ascertain the penetration depth of the said combinations. Results on penetration depth of CF1 and CF4 consolidants, related to different application method are gathered in Table 3. In the case of CF1 penetration into the carbonate model substrate 0, 0.4 and 0.5 mm depth was achieved for 1, 2 and 3 applications by roller, respectively. One or two applications by airless spray showed the same penetration of 0.1 mm, while one application by brush showed 0.2 mm penetration. In the case of CF1 consolidant application in cellulose pulp for 1 and 8 h 0.3 mm and 4.4 mm penetration depth was achieved, respectively. Fig. 1a shows Raman spectra of CF1 consolidant applied by cellulose pulp technique at different penetration depths into the carbonate substrate. Following

Table 3
Penetration depth of CF1 and CF4 consolidants applied by different methods on the surface of carbonate and silicate model substrates, respectively.

Sample description	Application technique	Number of applications/time of application	Depth of penetration/ mm
Carbonate R1	Roller	1	0
Carbonate R2	Roller	2	0.40
Carbonate R3	Roller	3	0.50
Carbonate A1	Airless spray	1	0.10
Carbonate A2	Airless spray	2	0.10
Silicate A3	Airless spray	1	3.65
Carbonate B1	Brush	1	0.20
Silicate B2	Brush	1	4.35
Carbonate P1	Cellulose pulp	1 h	0.30
Carbonate P2	Cellulose pulp	8 h	4.40
Silicate P3	Cellulose pulp	1 h	19.10
Silicate P4	Cellulose pulp	8 h	Bottom-through

the above-mentioned Raman modes at 2178, 2101, 1569, 1465 and 996 cm^{-1} after the reaction of consolidant with sodium nitroprusside (Fig. 1a) the penetration depth was defined. Interestingly, when comparing the red colour of the indicator spread over the depth profile of the treated carbonate model substrate (Fig. 1b) with the Raman results it was evident that the positive identification of the consolidant was possible even on the bluish areas below. Therefore, the visual penetration depth assessment on the basis of the red colour was supported by Raman results, which gave even more precise penetration estimation.

Fig. 6 shows FTIR spectra in CH stretching region (between 3250 and 2750 cm^{-1}) where bands of both, paraffin and TEOS are visible, for CF4 applied by different application methods, related to different penetration depth. As evident in Fig. 6, CF4 was detected at 3.65 and 4.35 mm depth when applied in one application by spray and brush, respectively. The application in cellulose pulp for 1 h
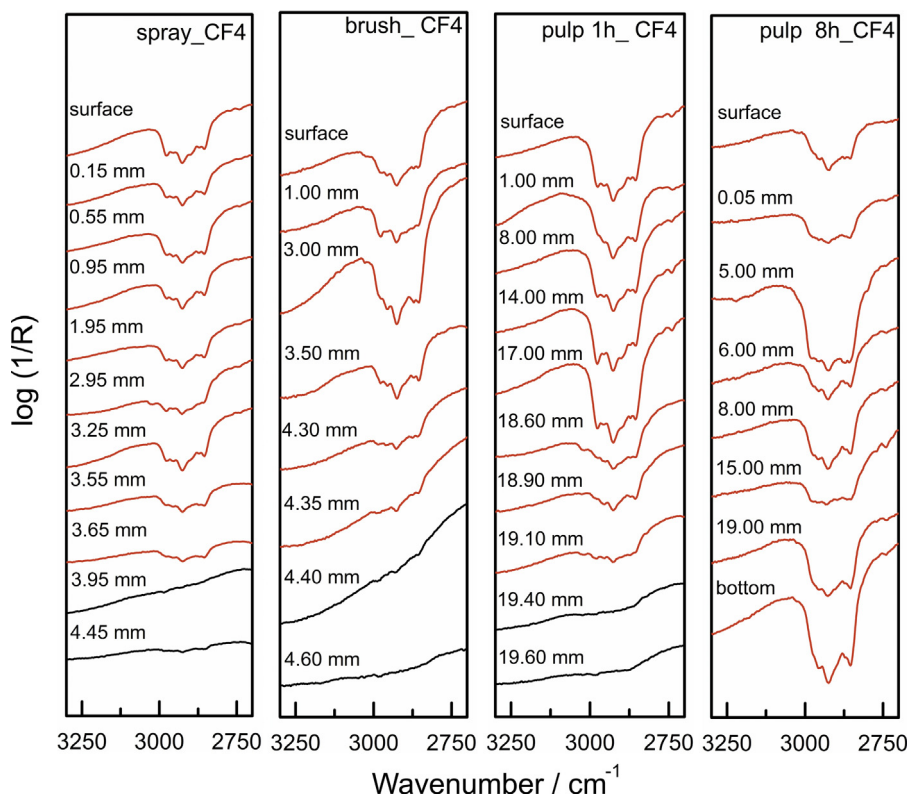

Fig. 6. FTIR spectra in the spectral range between 3250 and 2750 cm^{-1} of CF4 consolidant applied to silicate model substrate by spray, brush and cellulose pulp (1 and 8 h) techniques, related to different penetration depth.

gave 19.1 mm penetration, while in 8 h the consolidant penetrated through the whole silicate model substrate.

5. Conclusions

Vibrational spectroscopic techniques turned out to be useful in the determination of penetration depth of consolidants, which composition is similar to the substrate matrix. Raman microscopy in combination with indicator application, such as sodium nitroprusside, can be used to follow the penetration depth of calcium carbonate forming consolidant within calcium carbonate based substrates. The three, slightly different, developed consolidants also showed some differences related to the penetration depth within the same substrate.

Furthermore, different application methods were tested for one of the selected consolidant. It was shown that increasing the number of consolidant applications, a deeper penetration can be achieved by roller technique. In the case of application by airless spray the number of applications does not seem to influence the depth of penetration.

The depth of penetration also greatly depends on the selected method of application. Comparing one application by roller, airless spray and brush techniques, the deepest penetration can be achieved by brush (of about $200\,\mu m$). Furthermore, it was shown that by 8 h of application of carbonate consolidant in cellulose pulp the depth of 4.4 mm can be achieved, the highest determined depth of carbonate forming consolidant to the selected carbonate substrate in this investigation. However, these trials are not enough to make the final decision of which application is the best without a more detailed study, which would include a higher number of different substrates, different consolidants to be tested and statistically high enough number of applications by different methods.

In the case of silicate forming consolidant FTIR spectroscopy turned out to be very useful. Again, a deeper penetration was achieved by brush technique when comparing to airless spray, while 1 h of consolidant application in cellulose pulp already showed 19.1 mm of penetration, and 8 h were already enough for consolidant to penetrate through the whole selected silicate substrate.

This preliminary study showed that the penetration depth using cellulose pulp can be controlled by the time of the application, while for other application techniques the depth of penetration can be controlled by the number of applications. Controlling the depth of penetration by the time or the number of applications gives the opportunity to adjust the application method for a wide range of substrates of versatile composition and/or physical properties, and can be adjusted according to the damage of the object. Successive applications are not always favourable. In the case of surface damage only, a careful application of consolidant by brush could be sufficient, while in the case a deeper penetration is needed, several successive applications by roller can be used or longer time using the cellulose pulp. Therefore, according to the damage of an object, a careful decision of conservators needs to be made.

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