The Use of Portable Raman Spectroscopy to Identify Conservation Treatments Applied to Heritage Stone

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ABSTRACT

Non-destructive in situ analysis of materials is highly desirable in cultural heritage studies, for it precludes the need for intensive sampling. The present study focused on the usability of Raman spectrometers, which can provide such analysis, in the identification of conservation treatments applied to stone materials forming part of the architectural heritage. Two products commonly used to conserve stone monuments, an ethylmethacrylate co-polymer and an ethyl orthosilicate, were analysed with a Raman spectrometer, both as supplied and after application to limestone. The main conclusion drawn was that portable Raman analysers can detect the presence, and in some cases identify the nature, of products on stone substrates. The latter is not always possible due to product-stone substrate interaction. The study clearly showed that a product and substrate database is needed for portable Raman spectroscopy to be usable in the analysis of conservation products, both before and after application to stone substrates.

KEYWORDS: stone, consolidant, micro Raman spectroscopy, portable analysers

INTRODUCTION

Consolidants and water-repellents have been widely used in recent years to halt or retard stone deterioration on buildings and monuments. Consolidants are used to restore cohesion and water-repellents to prevent water ingress, because water is responsible for most of the decay processes in porous materials. The application of such products is seldom documented, even today, and the specific product used is recorded even more rarely. Sometimes these treatments need to be removed or re-applied; or the treated stone develops stains or other forms of decay associated with these products. Two types of consolidants were used in the present study: an acrylic compound and an ethyl orthosilicate. Beginning in the nineteen twenties to date, acrylic and vinyl polymers have been the substances most widely used for this purpose^[1,2]. Despite the adverse effects of this type of polymers, attributable to their age-related physical-chemical instability^[3], their use is very popular among restorers^[4] and they are commonly applied to conserve heritage buildings. Some authors believe that removing these resins is one of the goals of conservation science and that their use should be avoided when not strictly necessary^[5].

Alkoxysilanes such as tetraethoxysilanes (TEOS) are stone consolidants commonly applied in monument restoration to introduce silicon-based compounds (e.g., $\text{Si}(\text{OC}_2\text{H}_5)_4$) into stone pores^[6]. When in contact with atmospheric moisture, these compounds undergo hydrolysis, in which ethoxy groups (OC_2H_5) are gradually replaced by hydroxy groups (OH)^[17,18]. When the latter react, the molecules carrying them condense to form a gel.

Restoration planning entails collecting as much information as possible about the building, its construction and materials. This is not always possible, however, for want of documentation. In such cases chemical, mineralogical and microstructural information must be obtained with analytical techniques. One of the most difficult tasks in this stage is to determine whether or not surface treatments have been applied and to study any detected. Scanning electron microscopy (SEM) and Raman spectroscopy are the two techniques most widely used to identify the treatment applied^[9-13]. Stone samples need to be taken for SEM analysis, with the concomitant

destruction of the materials studied. By contrast, portable Raman spectroscopy is non-destructive and can be used in situ.

Raman spectroscopy has shown to be a useful and reliable technique in conservation research^[14-17]. While laboratory equipment yields more accurate results than portable Raman analysis as a rule, in cultural heritage investigations the in situ study of possible artefacts with non-destructive techniques (NDT) is of utmost importance.

AIM

This study explored the use of a portable non-destructive “Inspector Raman Delta Nu” Raman system to detect the existence of conservation treatments in the architectural heritage as a substitute for intensive sampling, which should be avoided in cultural heritage research.

MATERIALS AND METHODS

Two consolidants were tested: PARALOID B-72 (a high molecular weight ethylmethacrylate co-polymer whose two monomers were a methyl acrylate and an ethyl methacrylate) and FTB SH75 (ethyl orthosilicate, 75 %). These products have been used in a number of recent restorations in Spain: PARALOID B72 in the artistic plasterwork in the women’s section of Tránsito Synagogue (Toledo, Spain)^[18] and FTB SH75 in Leon Cathedral (Leon, Spain)^[19]. PARALOID B72 has been used extensively as a consolidant, protective coating, adhesive and varnish in the conservation and restoration of heritage materials since 1950^[20-22].

De Witte and De Clercq^[23], reporting on tests performed with FTB SH75 on several types of building stone, concluded that the product appeared to be a good consolidating agent for stones with a powdery surface. No crust formation or other adverse effects were observed. The active principle is $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ and the solvent methylethylacetone.

The substrate for the treatments was Colmenar stone, which has been used in heritage buildings for centuries^[24] and characterised by several authors^[25, 26]. Mineralogically it consists primarily of calcite (CaCO_3). Small specimens (3x3x1cm) were impregnated with the conservation

products tested. Analyses were conducted first on the untreated fresh limestone to identify possible spectral effects and thereafter on the impregnated specimens, 3 months after application of the surface treatments. The products were also analysed in their original liquid form.

The portable “Inspector Raman Delta Nu” Raman analyser (Figure 1) used was fitted with a 785-nm diode laser whose maximum output power at the source was 120 mW and a thermoelectrically cooled, charge-coupled detector with a range of 200–2000 cm^{-1} .

The integration time for recording the spectra was 5 s at a resolution of 8 cm^{-1} . For purposes of comparability with the results obtained by some of the co-authors in a prior study^[15], spectra were also recorded for limestone treated with a TEOS consolidant and a polysiloxane-based water-repellent with a Bruker RFS 100 FT-Raman analyser (using a 1064-nm Nd:YAG laser as the excitation source) and a Renishaw RM2000 micro-Raman spectrometer excited with a 785-nm laser.

RESULTS

Although stone fluorescence posed a problem in the Raman analyses, spectra could be obtained that may contribute to the in situ identification of conservation products. The results showed that when the product was applied to limestone the substrate could be identified from the band observed at 1085 cm^{-1} .

Figure 2 contains the Raman analysis of fresh untreated limestone. The most intense signal (at 990 cm^{-1}) on the spectrum for liquid Paraloid B72, depicted in Figure 3, was attributed to the CH groups in $\text{CH}_2=\text{CHCOOR}$, while the band at 730 cm^{-1} was assigned to the C-H groups in polyethylene. This PB72 spectrum exhibited certain differences with respect to the pattern reported by Ohlídalová et al.^[27]. The major difference was that, due to the fluorescence effect, the most intense band on the latter spectrum, at about 1450 cm^{-1} (methylene group bonding), was not clearly observed in the present findings. The intensity of the bands attributable to C-O-CH₃ or C-O-CH₂-CH₃ was lower in the present study than observed by Ohlídalová et al.^[27],

probably as a result of polymerisation. Similar behaviour was observed for the ester group band ($500\text{--}600\text{ cm}^{-1}$). All these findings were an indication that the PB72 was partially polymerised.

When PB72 was applied to the limestone substrate, the Paraloid signals observed on the spectrum for the product alone were no longer visible, whereas some of the bands attributable to the CaCO_3 in the stone appeared on the spectrum (1085 cm^{-1} , 210 cm^{-1}). Another low intensity band also appeared at 1280 cm^{-1} which, according to Domingo et al.^[15], may be due to C-Si bonding. A prior study reported that this consolidant polymerised on glass, with a band at 1280 cm^{-1} present during the first 6 days. That signal was not observed 2 years after the product had been applied to the stone substrate, however, when only a broad band at 980 cm^{-1} attributed to ν Si-O was visible. In addition, these authors^[15] identified two regions with which to monitor consolidant polymerisation: the increase in Raman intensity at 500 cm^{-1} and the decline in the C-H stretching band at around 2900 cm^{-1} . In the present study, this second region could not be recorded with the portable Raman spectrometer, while the band in the first was not clear enough to determine whether or not it grew.

The broad band at $1480\text{--}1370\text{ cm}^{-1}$ on the spectrum for the FTB SH75 liquid (Figure 4) was attributed to the CH_2 and CH_3 vibrations in the ethyl groups and Si-OCH_3 . The Raman spectra for different types of silicate glass may be differentiated by their Si-O stretching vibration frequencies. In the present study, absorption at 1092 cm^{-1} indicated that silicates with only one terminal oxygen atom were present in the product. When FTB SH75 was applied to limestone, the broad band at $1480\text{--}1350\text{ cm}^{-1}$ disappeared, an indication of product polymerisation. The stretching of carbonyl groups present in the product appear at 1710 cm^{-1} and two additional bands were observed on the spectrum for the stone sample treated with the TEOS product: one at 1160 cm^{-1} attributed to out-of-plane C-H bending vibrations and the other at 1280 cm^{-1} .

According to Ohlídalová et al.^[27] different consolidants yielded spectra with two similar bands, one at $1297\text{--}1299\text{ cm}^{-1}$ (from C-O-CH₃) and another at $1123\text{--}1112\text{ cm}^{-1}$ (from C-H), which did not concur with the signals observed in the consolidated limestone.

In both cases, when the consolidant was applied to the substrate, new, low intensity bands appeared that were very likely attributable to some minor interaction between the treatment and the limestone.

CONCLUSIONS

The main conclusions on the use of portable Raman spectrometers to identify conservation products are set out below.

- 1.- Portable Raman spectroscopy it is a non-destructive technique that can be used in situ, features that are very important for cultural heritage materials.
- 2.- The portable Raman spectrometer was able to detect the presence of the traditional consolidant (PB72) on the limestone surface, for the spectrum exhibited a low intensity band at 1280 cm^{-1} attributed to C-Si bonding.
- 3.- After application of consolidant FTB SH 75, its presence on the limestone was detected thanks to the formation of two new bands on the Raman spectra at 1280 and 1160 cm^{-1} , respectively reflecting the C-O-CH₃ and out-of-plane C-H bending vibrations.

Portable Raman analysers were also able to identify the stone substrate and detect the existence of a conservation product as well as the interactions between the product and the substrate. This technique can likewise be used in process and quality control for intervention on stone façades to verify whether the treatments are actually applied. Further analysis should be conducted using other conservation products and stone substrates and varying the post-treatment analysis times to build a database as an aid to the identification of product families or perhaps even individual products.

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FIGURES

Figure 1. Portable Raman “Inspector Raman Delta Nu”

Figure 2. Raman spectra of untreated limestone

Figure 3. Raman spectra of liquid Paraloid B72 (black line) and applied on limestone (dash line).

Figure 4. Raman spectra of liquid FTB SH75 (black line) and applied on limestone (dash line).

Figure 1.

Figure 2

Figure 3.

Figure 4