Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 169 (2016) 7–15

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Raman scattering or fluorescence emission? Raman spectroscopy study on lime-based building and conservation materials

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ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form 2 June 2016
Accepted 4 June 2016
Available online 7 June 2016

Keywords:
Raman spectroscopy
Fluorescence bands
Lime binder
Historical building materials
Conservation materials

ABSTRACT

This work presents an in-depth study on Raman spectra excited with 1064 and 532 nm lasers of lime binders employed in the past as building materials and revealed today as valuable conservation materials. We focus our interest on the bands of strong intensity, which are present in the spectra of all binders acquired with laser excitation at 1064 nm, but absent in the corresponding spectra acquired with laser excitation at 532 nm. We suggest, that the first group of spectra represents fluorescence phenomena of unknown origin and the second true Raman scattering. In our studies, we also include two other phases of lime cycle, i.e. calcium carbonate (a few samples of calcite of various origins) and calcium oxide (quicklime) to assess how structural and chemical transformations of lime phases affect the NIR-Raman spectral profile. Furthermore, we analyse a set of carbonated limewashes and lime binders derived from old plasters to give an insight into their spectral characteristics after excitation with the 1064 nm laser line. NIR-Raman micro-mapping results are also presented to reveal the spatial distribution of building materials and fluorescent species in the cross-section of plaster samples taken from a 15th century chapel. Our study shows that the Raman analysis can help identify lime-based building and conservation materials, however, a caution is advised in the interpretation of the spectra acquired using 1064 nm excitation.

1. Introduction

It is common knowledge that the use of a Nd:YAG laser with wavelength of 1064 nm to excite the Raman effect usually brings improvement in the quality of the Raman spectrum by eliminating strong and broad fluorescence background frequently recorded together with the Raman effect in the visible or ultraviolet range of radiation. However, one can also observe laser-induced fluorescence features of strong intensity when using a near-infrared line, which may be mistakenly identified as Raman scattering. This effect has been observed during collection of NIR-Raman spectra by several groups studying different materials, mostly minerals and inorganic materials [1–14]. Dyer and co-workers have found fluorescence bands in cement materials [1], while others noticed their presence in materials containing calcium phosphate obtained synthetically and in the form of a biomaterial [2–6]. Hadrich et al. have in turn demonstrated the presence of fluorescence bands in stoichiometric fluorapatite, hydroxyapatite and calcium–lead hydroxyapatite compounds [7]. Aminzadeh has not observed fluorescence bands in calcium salts such as oxalates, chlorides, acetates, and sulphates, however, he has found their presence in spectra of calcium hydroxide and calcium carbonate [3]. Other materials for which such bands have been identified, belong to groups of alumina [8], lanthanide salts [9–12] and almandine minerals [13]. Recently, Schmid and Dariz have discussed in detail luminescence features in spectra of lime phases acquired with the laser excitation at 633 and 785 nm [14]. They have concluded that luminescence bands, which interfere with Raman bands depending on excitation wavelength, probably occur due to the presence of rare earth elements, point defects or radical ions and actually their origin must be explained individually for a given material.

There are two straightforward and well-known methods of assessing whether observed bands are true Raman bands or if their origin is different than Raman scattering. The first one involves confirming the presence of corresponding bands in anti-Stokes Raman spectrum. Unfortunately, anti-Stokes bands of many substances are inherently weak in intensity; hence, they can be unrecordable when using less advanced instrumentation. The other way is to confirm the presence of a Raman band in spectra collected using various excitation wavelengths since Raman scattering is independent of excitation wavelength whereas the fluorescence phenomenon demonstrates such correlation.

Our aim is to conduct a systematic study of lime binders and related materials spectra acquired using Raman spectroscopy instrumentation,

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http://dx.doi.org/10.1016/j.saa.2016.06.012
1386-1425/© 2016 Published by Elsevier B.V.

with laser excitation lines of 532 and 1064 nm, in order to distinguish Raman scattering from fluorescence phenomena effects. The work has been motivated by the interest in identifying the chemical composition of works of art by Raman spectroscopy.

The air-hardening lime was in the past the most common and important binder used in the construction of buildings as well as in plaster and renders preparation. Presently, traditional lime has been again employed as the valuable and compatible material for conservation of historical buildings, architectural surfaces and wall paintings. It has replaced cements, which were treated from the end of the 19th century as the remedy for all building problems [16]. The fundamental requirement for any successful conservation is a selection of the most suitable materials and conservation techniques. However, this needs the knowledge of the structure of the preserved object on the one hand and the chemical composition of selected conservation products on the other. Therefore, the results of our research will help prevent data misinterpretation and a false identification of materials, supporting, by that means, the work of conservators.

We analyse a group of materials containing lime commonly used in the conservation of wall paintings and architectural surfaces as well as a group of raw materials used to their preparation. Additionally, we consider spectral characteristics of samples collected from historical buildings. Finally, NIR-Raman mapping is performed to show spatial distribution of Raman and fluorescence signals in a cross-section of the plaster originated from a 15th chapel.

2. Experimental

2.1. Investigated substances

Investigated materials with a brief description of their properties are presented in Table 1.

2.2. Raman spectroscopy

For NIR-Raman measurements, a few milligrams of the solid samples were directly measured on metal discs in the 90° configuration. 16–128 scans were collected with a spectral resolution of 4 cm^{-1}. Spectra were recorded on a FT-Raman spectrometer Bruker Ramanscope III equipped with a Nd:YAG laser, emitting at 1064 nm, and a germanium detector, cooled with liquid nitrogen. The output power of the laser was 10–100 mW with a spot diameter of ca. 30 μm. To collect Raman maps, back illumination and collection in the backscattering geometry were made through an Olympus microscope equipped with a 10× objective and a motorized x–y stage. An area of 67 μm × 527 μm was mapped with a step 11.2 and 12.1 μm along the *x* and *y* axes, respectively. Spectral measurements were performed with continuous scans in the range of 4000–50 cm^{-1} (a spectral resolution of 4 cm^{-1}), 32 scans per point and an output laser power ca. 350 mW. For the univariate analysis, NIR-Raman spectra were firstly smoothed (7 points) and the maps were constructed by plotting integrated band intensities as a function

Table 1
Studied materials and their features.

Materials based on Ca(OH)2		
1.	Hydrated lime *Manufacturer*: *Hydrat Olkusz*	Dry powder of calcium hydroxide (Ca(OH)2) obtained in a slaking (hydration) process of quicklime (CaO) with a stoichiometric amount of water.
2.	Lime slurry	Thick and fluid suspension of hydrated lime (*Hydrat Olkusz*) in water.
3.	Lime paste *Kremer Pigmente Nr. 31800*	An aqueous suspension of Ca(OH)2 crystals obtained by slaking of quicklime (CaO) with an excess of water and keeping them to age for six years.
4	Calix blanca NHL 3.5 *Kremer Pigmente Nr. 31840*	Natural hydraulic lime with moderate hydraulic properties, produced by calcining limestone containing 12–18% clay (according to EN 459-1).
5	PLM-A *Kremer Pigmente Nr. 31100*	Lime-based injection grout, recommended for fresco and wall painting conservation as free of soluble salts, with an increased depth of penetration and increased stability against sedimentation.
6	PLM-AL *Kremer Pigmente Nr. 31102*	Injection grout with properties like PLM-A, recommended for strengthening of frescos and wall paintings in which weight is a significant factor.
CaCO3 from different sources		
7	Limestone	The most popular source of calcite. Our sample comes from local source in the Krakow-Czestochowa Jura (town: Ogrodzieniec).
8	Marble dust *Kremer Pigmente Nr. 58580*	Marble as the metamorphosed (recrystallized) limestone is the source of the fairly coarse calcite crystals.
9	Chalk *Kremer Pigmente Nr. 58005*	Soft, porous and friable rock, as derived from marine ooze composed of fossil remains (mainly disklike forms called coccoliths). High quality chalk or the finest grade of chalk was called Paris white.
10	Eggshells	Nearly pure calcium carbonate.
Lime family		
11.	Limestone *Wap-Bud*	Products of the *Wap-Bud* manufacture prepared from one type of limestone as a raw material. This series represents two stages of lime cycle. Firstly limestone was calcined to produce quicklime, then quicklime was slaked with an excess of water giving lime paste.
12.	Quicklime *Wap-Bud*	
13.	Lime paste *Wap-Bud*	
Carbonated lime		
14.	Limewash after short-time carbonation	Limewash from hydrated lime (*Hydrat Olkusz*) after 1-year of carbonation.
15.	Whitish nodules (lumps) [15] from the historical mortar 1	From a black-colour plaster layer of a Renaissance sgraffito in a form of rustication in the Branice Castel (Poland, 17th c.). The sample comes from the archives of the Faculty of Conservation and Restoration of Works of Art, Jan. Matejko Academy of Fine Arts in Krakow and was taken in 1954.
16.	Whitish nodules (lumps) from the historical mortar 2	A mortar sample of unknown origin from the archives of the Faculty of Conservation and Restoration of Works of Art, Jan. Matejko Academy of Fine Arts in Krakow, No. 56.
17.	Historical limewash 1	From a black-and-white sgraffito frieze in the castle of Krasiczyn (Poland, 17th c.). The sample comes from the archives of the Faculty of Conservation and Restoration of Works of Art, Jan. Matejko Academy of Fine Arts in Krakow and was taken in 1953.
18.	Historical limewash 2	A coating from the cathedral in Tarnow (Poland, 17th c.). The sample comes from the archives of the Faculty of Conservation and Restoration of Works of Art, Jan. Matejko Academy of Fine Arts in Krakow and was taken in 1959.
19.	Cross-section of old plaster	From an interior of a 15th-century chapel in Katy Bystrzyckie (Poland).