

Localized quantification of anhydrous calcium carbonate polymorphs using micro-Raman spectroscopy

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ABSTRACT

Micro-Raman spectroscopy is a powerful technique for qualitative and quantitative analysis of different mineral mixtures. In this paper, micro-Raman spectroscopy was used for quantification in local regions ($180 \times 180 \mu\text{m}$ area) of ternary mixtures of the synthetic calcium carbonate (CaCO_3) polymorphs (vaterite, aragonite, calcite) as well as CaCO_3 formed during the carbonation of nanolime suspension. The obtained results of localized quantification were in agreement with the detected concentrations obtained from bulk quantitative phase analysis of X-ray powder diffraction patterns. The detection limits were found to be below 0.5 wt.% for each CaCO_3 polymorphs. Through the use of 2D mapping, localized quantification of CaCO_3 polymorphs can be achieved. This information could be potentially useful for conservation of valuable Cultural Heritage objects, as it might influence the consolidation treatment chosen.

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1. Introduction

Calcium carbonate (CaCO_3) is one of the most abundant minerals in the Earth's crust. It can be present in three anhydrous polymorphs – vaterite, aragonite, calcite and three hydrated phases – amorphous CaCO_3 (ACC), monohydrate ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) [1,2]. CaCO_3 is of high importance in natural systems as in the process of biomineralization [3,4], and in many industrial sectors where it is used as filler, extender and pigment, including the production of paper, rubber, plastic, pharmaceuticals, food, paint, textiles and numerous other different materials [5–8]. From ancient times, lime produced from CaCO_3 (using limestone rocks) was the key component of mortars hardened through the carbonation reaction [7]. More recently, novel nanolime suspensions were introduced on the market for the consolidation of Cultural Heritage objects, like wall paintings and stones or for the conservation of paper, canvas and wood [9,10]. As in the case of lime mortars, the consolidation effect is based on the carbonation reaction of $\text{Ca}(\text{OH})_2$ resulting in the formation of CaCO_3 phases [11]. It was found that different CaCO_3 phases could be formed during nanolime carbonation and their formation is highly dependent on the climate conditions, such as relative humidity [12–14].

Raman spectroscopy is extensively used for qualitative analysis and its effectiveness has been demonstrated in the quantitative phase analysis of pharmaceuticals [15,16], lignin [17] and geological samples [18–21]. The main advantage of the using of micro-Raman spectroscopy (μ -RS) is the ability to focus the laser beam onto the specific sites of the samples and thus perform localized quantifications. Depending on the microscope parameters used, a spatial resolution on the order of $1 \mu\text{m}$ can be potentially achieved. Another advantage is the relatively small amount of the sample needed, especially when compared with bulk techniques like X-ray powder diffraction (XRPD). In this respect, μ -RS is very appealing for localized quantification and/or the analysis of samples that cannot be collected in large quantity, as in the case of the samples originated from Cultural Heritage objects.

In the present paper, the methodology for the localized quantitative determination of the anhydrous calcium carbonate polymorphs – vaterite, aragonite and calcite – using μ -RS is described. The validity of this method was tested on synthesized CaCO_3 samples as well as on sample of carbonated nanolime. The results were compared with those obtained from quantitative phase analysis of the measured XRPD patterns, using Rietveld refinement, an established technique for quantification of components in different powder mixtures [22].

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2. Experimental

2.1. Samples preparation

Vaterite was synthesized following a procedures described elsewhere [23] from two supersaturated solutions of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (p.a.) and K_2CO_3 (p.a.) without use of additives. The reagents were purchased from Lach-Ner (Czech Republic) and used as received. Aqueous solutions ($c = 2 \text{ mol l}^{-1}$, $V = 50 \text{ ml}$) of these reactants were prepared using deionized water (Barhstead Smart2pure, Thermo Scientific) of the following characteristics: $\lambda = 0.055 \mu\text{s cm}^{-1}$; $R = 18.2 \text{ M}\Omega\text{cm}$; $\text{pH} = 8.2$. The synthesis of aragonite was performed from the vaterite precursor refluxed for the 150 min [24]. The synthesis of calcite was previously described elsewhere [23]. Six mixtures containing various concentrations of CaCO_3 polymorphs were prepared and the phase composition of each sample was verified using XRPD measurements. Each final powder mixture was homogenized in a zirconia ball mill (Pulverisette 23, Fritch) at 30 oscillations s^{-1} for 30 s. The suspension of nanolime (CaLoSil E25 , (IBZ-Salzchemie, Germany), $c = 25 \text{ g l}^{-1}$, $V = 5 \text{ ml}$) was cured in a climate chamber for the 4 weeks at constant relative humidity ($\text{RH} = 65(5) \%$) and temperature ($t = 20(1) \text{ }^\circ\text{C}$).

2.2. Analytical techniques

A micro-Raman spectrometer (DXR, Thermo Scientific) equipped with high resolution grating ($1800 \text{ lines mm}^{-1}$) was used. The laser beam ($\lambda = 532 \text{ nm}$) was focused with a $20\times$ objective ($\text{N.A.} = 0.40$), and laser power of 10 mW was used. Maps were collected over an area of $180 \times 180 \mu\text{m}$ using a $20 \mu\text{m}$ step size (100 points). Raman spectra were collected over a spectral range of $1300\text{--}50 \text{ cm}^{-1}$. Twenty exposures for each spectrum were recorded with exposure time 2 s. The Raman bands at 701 , 711 , 750 cm^{-1} were used for quantitative analysis of aragonite, calcite and vaterite, respectively.

The phase composition of the prepared CaCO_3 polymorph mixtures and of the sample of the carbonated nanolime was investigated with X-ray powder diffraction (XRPD), employing a Bragg-Brentano D8 advance diffractometer (Bruker) equipped with a LynxEye 1-D silicon strip detector, using $\text{CuK}\alpha$ radiation and Ni filter. Patterns were collected at 40 kV and 40 mA at ambient temperature in the angular range $15\text{--}90^\circ 2\theta$ with a virtual step scan of 0.01° and counting time 0.4 s per step. The samples were allowed to spin at 15 rpm to increase the particle statistics. Quantitative phase analysis (QPA) was performed by the Rietveld method [25] using the Topas 4.2 software from Bruker AXS.

Selected samples were examined with a high-resolution scanning electron microscope (SEM) Quanta 450 FEG (FEI) using a secondary electron detector. Analyses were performed at accelerating voltage between 5 and 20 kV. All samples were gold coated with a 5 nm thick layer.

2.3. Quantification methodology

The baseline correction implemented in the software OMNIC for Dispersive Raman 9.1.24 was applied on the collected spectra. The values of the intensities at 701 , 711 , 750 cm^{-1} (for aragonite, calcite and vaterite, respectively) were extracted using the software SpectraGryph vs. 1.2 and the outliers were identified using software Statistica vs. 10. The average values for the specific wavenumbers of each sample were used to plot calibration curves. The calibration method used is described in [19] using the two binary calibrations (calcite/aragonite and calcite/vaterite) for the ternary mixtures. The calibration curves were plotted as the ratios of I_C^{711}/I_A^{701} vs. X_C/X_A and I_C^{711}/I_V^{750} vs. X_C/X_V , where X_A , X_C , X_V are

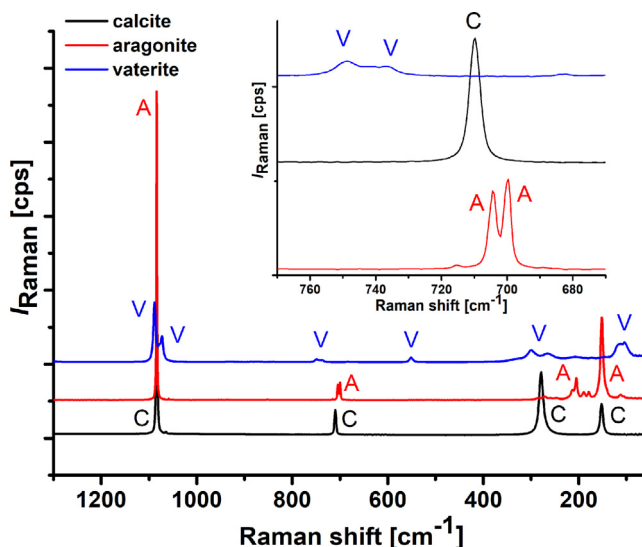


Fig. 1. Raman spectra of the pure anhydrous CaCO_3 polymorphs – vaterite, aragonite and calcite – in the spectral range $1300\text{--}50 \text{ cm}^{-1}$. Main peaks of polymorphs are indicated (V = vaterite, C = calcite, A = aragonite).

the weight concentrations of aragonite, calcite and vaterite, respectively and I_A , I_C , I_V are their intensities of Raman signal at selected wavelengths. Then, the following equations were used for calculating the concentration of CaCO_3 anhydrous polymorphs:

$$X_A = \frac{a_{CA} \times I_A^{701}}{I_C^{711} + a_{CA} \times I_A^{701} + a_{CV} \times I_V^{750}} \quad (1)$$

$$X_C = \frac{I_C^{711} \times X_A}{a_{CV} \times I_A^{701}} \quad (2)$$

$$X_V = \frac{a_{CV} \times I_V^{750} \times I_C^{711} \times X_A}{a_{CA} \times I_A^{701} \times I_C^{711}} \quad (3)$$

where a_{CA} , a_{CV} are the slopes of the calibration curves.

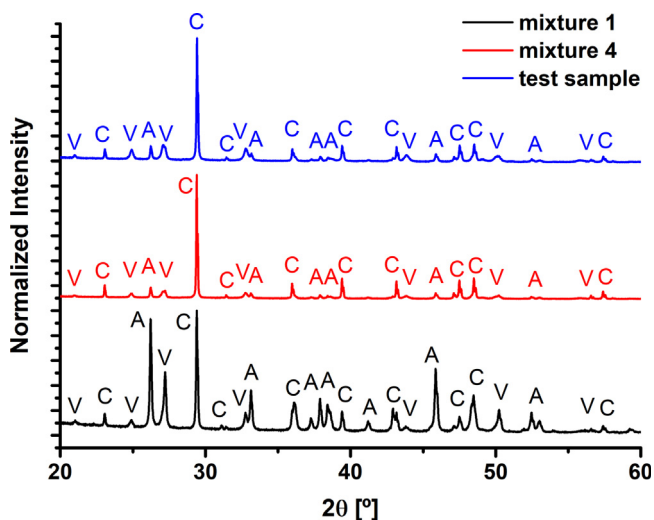


Fig. 2. Selected region of measured XRD spectra of synthesized mixtures and testing sample. Main peaks of polymorphs are indicated (V = vaterite, C = calcite, A = aragonite).

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