

Calcium carbonate phase analysis using XRD and FT-Raman spectroscopy

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There is a need for the quantitative determination of the ternary mixtures of calcium carbonate polymorphs (calcite, aragonite and vaterite), which are present in a number of materials including limestones, industrial scale formation and several pathological cases. Application of infrared spectroscopy proved to be inadequate, due to band overlapping, while use of Raman spectroscopy and X-ray powder diffraction (XRD) has been reported only for the calcite–aragonite mixture. In order to address the problem, a comprehensive non-destructive methodology for the simultaneous quantitative determination of the calcium carbonate crystal phases in their ternary mixtures based on the use of Fourier transform Raman spectroscopy (FT-RS) was developed. Binary mixtures were used to construct the calibration graphs using the Raman bands at 711 cm^{-1} for calcite, 700 cm^{-1} for aragonite and 750 cm^{-1} for vaterite. Detection limits were found to be 0.13, 0.18 and 1.3 mol.-% for calcite, aragonite and vaterite, respectively, while the relative errors in determining the mol.-% of a known ternary mixture of calcium carbonate polymorphs were 1.6% for calcite, 0.3% for aragonite and 1.1% for vaterite. A similar methodology was developed using XRD. XRD calibration graphs were constructed using the 104 reflection of calcite, the 221 reflection of aragonite and the 110 reflection of vaterite. Detection limits for calcite, aragonite and vaterite were found to be 0.90, 2.90 and 6.90 mol.-%, respectively, while the relative errors in determining the mol.-% of the same ternary mixture used for testing the FT-RS methodology were 2.5, 1.8 and 0.6%, for calcite, aragonite and vaterite, respectively.

Introduction

Three crystal phases of anhydrous calcium carbonate are encountered in nature. The most stable phase thermodynamically is calcite followed by aragonite and vaterite.¹ CaCO_3 polymorphs are present in numerous materials including, but not limited to, industrial scale formation,² limestones³ and several pathological cases^{4–6} (urinary stones, pancreatic calcification, etc.). Physical properties of these specimens depend largely on the percentage of each calcium carbonate phase present and thus a quantitative methodology is needed. Furthermore, vaterite and aragonite are precursor phases for calcite and thus tracking quantitatively their transformation is of paramount importance for elucidating calcium carbonate formation and dissolution mechanisms.

Unfortunately, no reliable methodology is available due to the difficulty in discriminating the different phases. Infrared spectroscopy (IR) has been used^{7–9} but the methodologies developed were restricted to binary mixtures. Application of IR to cases where all three polymorphs were simultaneously present was hindered by the presence of overlapping bands. Other disadvantages of the technique include broadness of inorganic adsorption bands and specimen preparation, involving grinding and pelleting, which can lead to the conversion of vaterite and aragonite to calcite. Furthermore, although no detection limits were reported by the authors, the effective range of each calibration line made it apparent that the proposed methodologies could not be used in cases where one component in the mixture was less than 5 mol.-% while calibration lines starting at 30 mol.-% were also used. Alternative quantitative techniques capable of discriminating among the different crystal phases include application of X-ray powder diffraction (XRD) and Fourier transform Raman spectroscopy (FT-RS). FT-RS¹⁰ and XRD^{10–12} have been used for the quantitative determination of the binary mixture of calcite–aragonite but to

our knowledge no quantitative analysis of specimens containing calcium carbonate polymorphs has been reported.

In the present work, a methodology was developed for the simultaneous quantitative determination of the calcium carbonate phases based on the use of FT-RS and XRD, and their detection limits were determined. The reliability of the proposed method was tested by analyzing a known sample where all phases were present.

Experimental

Preparation of chemicals and samples

Calcite powder was prepared as follows: 1 L of 1 M $(\text{NH}_4)_2\text{CO}_3$ (Ferak, Berlin, Germany) was added dropwise to 1 L of 1 M $\text{Ca}(\text{NO}_3)_2$ (Ferak) and magnetically stirred at ambient temperature. The suspension was incubated in the mother liquor for 15 d. Next, it was filtered through membrane filters and washed with triply distilled water at 70°C . The crystals were dried at 120°C for 2 d and stored in a desiccator. Median particle size, given as diameter of equivalent spheres ($D_{[4,3]}$), was measured to be $18\text{ }\mu\text{m}$ (Mastersizer S, Malvern Instruments, Ltd., Spring Lane South, UK).

Pure aragonite crystals were prepared by using the simultaneous dropwise addition of 5 mL of a solution of 1 M $\text{Ca}(\text{NO}_3)_2$ at 90°C and 5 mL of 1 M $(\text{NH}_4)_2\text{CO}_3$ at 45°C into 200 mL of triply distilled water at 95°C . The solution, during precipitation, was saturated with CO_2 by bubbling the gas through the slurry. The crystals, in the form of a slurry, were filtered (Millipore, Bedford, MA, USA; $0.22\text{ }\mu\text{m}$), and washed with triply distilled water at 90°C and with absolute ethanol at room temperature. The powder was dried at 80°C for 1 h and stored in a desiccator. $D_{[4,3]}$ for aragonite crystals was found to be $49\text{ }\mu\text{m}$.

Pure vaterite was prepared by using the constant composition method.¹³ Stock solutions of 0.1 M calcium nitrate and 1 M potassium nitrate were prepared from the respective crystalline reagents (Merck, Darmstadt, Germany) using triply distilled water. Sodium carbonate (Merck) and sodium hydrogencarbonate (Merck) solutions were freshly prepared before each experiment by dissolving the corresponding solid reagents in triply distilled water. Equal volumes of calcium nitrate, sodium hydrogencarbonate and potassium nitrate solutions were simultaneously added at 25 °C into the thermostated reactor vessel under vigorous stirring. The pH of the supersaturated solutions was adjusted to 9.0 through the addition of standard sodium hydroxide (0.1 M) (Merck). The CaCO₃ precipitation reaction resulted in the release of protons in the supersaturated solution. Lowering of the solution pH triggered the addition of titrant solutions (calcium nitrate and a mixture of calcium carbonate and calcium hydrogencarbonate) at the molar stoichiometry dictated by the precipitating calcium carbonate. At the end of the precipitation process the suspension was filtered through membrane filters (Millipore; 0.22 µm). The solid collected was then dried for 2 h at 80 °C. $D_{[4,3]}$ for vaterite particles was measured to be of the order of 5 µm.

All the solids were characterized prior to use by FT-RS (FRA-106/S FT-Raman, Bruker, Karlsruhe, Germany), XRD (1830/40 Philips, Eindhoven, The Netherlands), and FTIR spectroscopy (EQUINOX 55, Bruker) and their spectra found to match those reported by others researchers.^{14–21}

In order to avoid preferred orientation of sample crystallites the powders were pulverized to a particle size of lower than 1 µm prior to use. Aragonite and vaterite were characterized again after pulverization and no conversion to calcite was detected. Calibration graphs were constructed by preparing weighed mixtures of calcite–vaterite and calcite–aragonite, ranging from 0 to 100 mol.-% purity, from the respective solids. The solid mixtures were thoroughly mixed mechanically. The homogeneity of the mixed powders was verified by obtaining several Raman spectra for each mixture, focusing the laser beam at randomly selected parts of the surface.

Instrumentation

Raman spectroscopy. Raman spectra were recorded using a Bruker FRA-106/S FT-Raman spectrometer. The exciting source was a Nd:YAG laser operating at 1064 nm with a power of about 400 mW. A secondary filter was used to remove the Rayleigh line. The scattered light was collected at an angle of 180° (back-scattering). The system was equipped with a liquid N₂ cooled Ge detector (D 418). Typical spectral resolution was 1 cm⁻¹.

X-ray diffractometry. X-ray powder diffraction analysis was performed with a Philips 1830/40 X-ray powder diffractometer on finely powdered samples using Cu Kα radiation (40 kV and 30 mA) and an Ni filter with a scanning speed of 0.005° 2θ s⁻¹. The time constant was set at 2 s.

Results and discussion

Theory for construction of Raman calibration graph

The Raman spectra of calcite, aragonite and vaterite were in good agreement with previous reports^{15–20} and are shown in Fig. 1. Unfortunately, the strongest bands of the calcium carbonate phases, 1089 cm⁻¹ for vaterite and 1084 cm⁻¹ for calcite and aragonite, overlap and cannot be used for analytical purposes. The Raman active bands at 711, 700 and 750 cm⁻¹ for calcite, aragonite and vaterite, respectively, were used for

quantitative analysis. Since the purpose was to find an easy and reliable method to calculate each ingredient's percentage, peak heights were used instead of the integrated intensities.

The intensity of a Raman line depends on a number of factors including incident laser power, frequency of scattered radiation, absorptivity of the materials involved in the scattering and the response of the detection system. Thus, the measured Raman intensity, $I(\nu)$, can be represented as:²²

$$I(\nu) = I_0 K(\nu) C \quad (1)$$

where I_0 is the intensity of the excitation laser line, ν is the Raman shift, and $K(\nu)$ is a factor which includes the frequency-dependent terms: the overall spectrophotometer response, the self-absorption of the medium and the molecular scattering properties. C is the concentration of the Raman active species.

Raman calibration lines

For a calcite–aragonite mixture, eqn. (1) can be rewritten for the 711 cm⁻¹ peak of calcite and the 700 cm⁻¹ peak of aragonite as follows:

$$\frac{I_C^{711}}{I_A^{700}} = \frac{K_C^{711}}{K_A^{700}} \times \frac{X_C}{X_A} \quad (2)$$

A plot of the ratios I_C^{711}/I_A^{700} vs. X_C/X_A , as expected, yielded a straight line, eqn. (3), shown in Fig. 2.

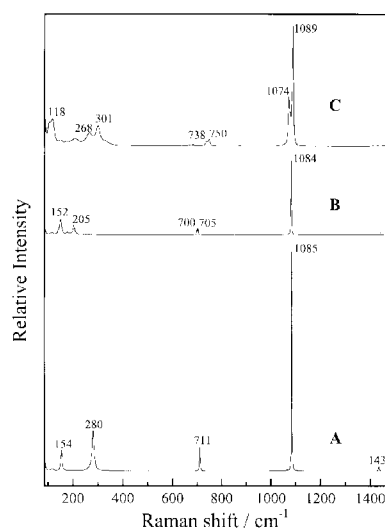


Fig. 1 Raman spectra of the synthetically prepared calcite (A), aragonite (B) and vaterite (C).

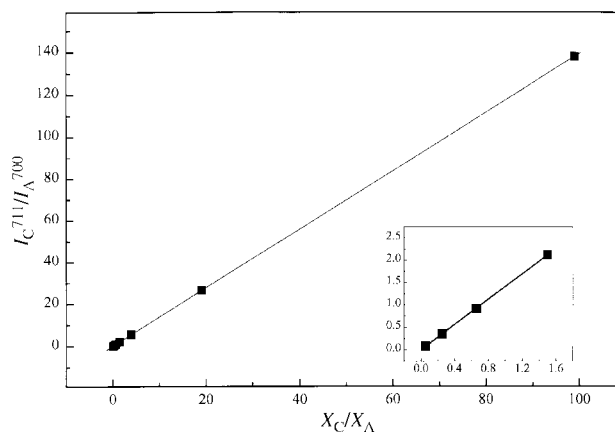


Fig. 2 Raman calibration line for calcite–aragonite mixtures.

$$\frac{I_C^{711}}{I_A^{700}} = 1.395 \times \frac{X_C}{X_A} \quad (3)$$

The correlation coefficient, r , was 0.9999 while the standard deviation of the slope was found to be 8.9×10^{-4} . The detection limits (DL), at the 99.9% confidence level, were calculated to be 0.13 mol.-% for calcite and 0.18 mol.-% for aragonite. DL is defined as:²³

$$DL = t \times s_b \times \sqrt{\frac{N+1}{N}}$$

where t is the statistical parameter t , which is often called the Student's t -value defined as: $t = (x - \mu)/s$, where s is the standard deviation of the measurements and $(x - \mu)$ represents the absolute deviation from the mean value; s_b is the standard deviation of the blank measurements; N is the number of blank measurements.

The calibration line for calcite–vaterite was constructed by using the Raman bands at 711 cm^{-1} for calcite and 750 cm^{-1} for vaterite. A plot of the ratios I_C^{711}/I_V^{750} vs. X_C/X_V , as expected, yielded a straight line, eqn. (4).

$$\frac{I_C^{711}}{I_V^{750}} = 9.30 \times \frac{X_C}{X_V} \quad (4)$$

The correlation coefficient, r , was 0.9999 while the standard deviation of the slope was found to be 9.0×10^{-3} . DL, at the 99.9% confidence level, were calculated to be 0.13 mol.-% for calcite and 1.30 mol.-% for vaterite.

Some typical spectra of the various mixtures are shown in Fig. 3.

Calculation of the molar fraction of calcite, aragonite and vaterite in a specimen using the Raman calibration graphs

By using eqn. (3) and (4) and assuming that $X_C + X_A + X_V = 1$, the molar fractions in a calcium carbonate specimen may be determined from the following relationships:

$$X_A = \frac{1.395 \times I_A^{700}}{I_C^{711} + 1.395 \times I_A^{700} + 9.30 \times I_V^{750}} \quad (5)$$

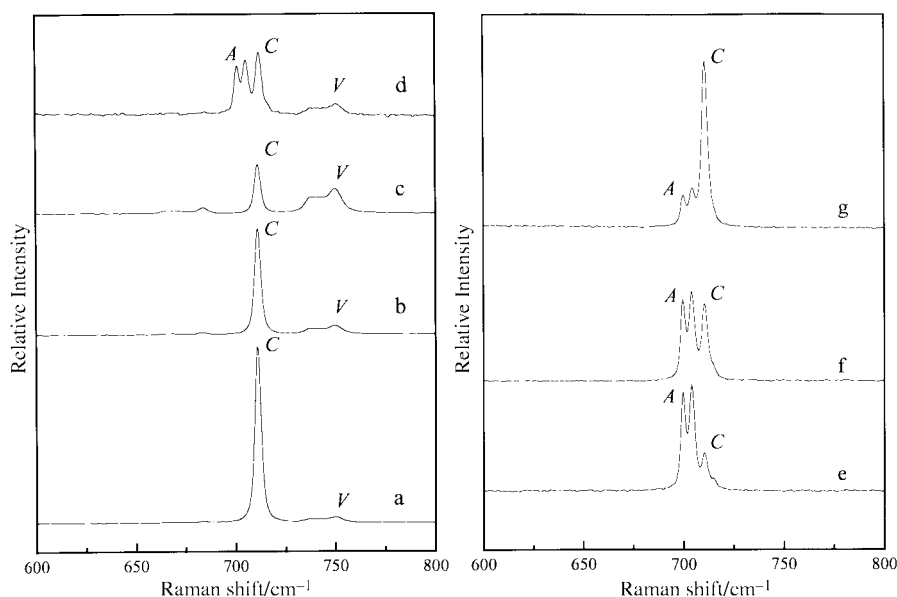


Fig. 3 Raman spectra of: (a) 20 mol.-% vaterite–80 mol.-% calcite; (b) 40 mol.-% vaterite–60 mol.-% calcite; (c) 80 mol.-% vaterite–20 mol.-% calcite; (d) 32 mol.-% calcite–33 mol.-% aragonite–35 mol.-% vaterite; (e) 20 mol.-% calcite–80 mol.-% aragonite; (f) 40 mol.-% calcite–60 mol.-% aragonite; (g) 80 mol.-% calcite–20 mol.-% aragonite.

$$X_C = \frac{I_C^{711} \times X_A}{1.395 \times I_A^{700}} \quad (6)$$

$$X_V = 1.0 - X_A - X_C \quad (7)$$

The validity of these expressions was tested on a spectrum recorded from a powder mixture consisting of 32 mol.-% calcite, 33 mol.-% aragonite and 35 mol.-% vaterite. The following results were obtained: 31.5 mol.-% calcite, 33.1 mol.-% aragonite and 35.4 mol.-% vaterite, a relative error of 1.6, 0.3 and 1.1%, respectively.

It should be noted that the analytical methodology presented here does not depend on the simultaneous existence of the calcium carbonate phases, since there is neither chemical interaction between these species nor overlap of the corresponding bands in the Raman spectra. As a result, the relative intensities used in the analysis are not affected. Moreover, as may be seen from eqn. (1), the intensity of the Raman bands depends solely on the concentration of the investigated species.

If an additional compound is also present and provided that this does not contribute to the FT-RS signal at the chosen frequencies and that there is no chemical interaction among the species present, eqn. (3) and eqn. (4) are still valid and the ratio of the calcium carbonate phases can be determined.

Theory for construction of X-ray calibration graph

The X-ray spectra of calcite, aragonite and vaterite are shown in Fig. 4. These spectra are in good agreement with those reported in the literature.¹⁵ Assuming that the specimen is a uniform mixture of two components and extinction and micro-absorption effects are neglected, it can be shown that:²⁴

$$\frac{I_A}{I_B} = \Lambda \times \frac{X_A}{X_B} \quad (8)$$

where Λ is a proportionality constant, which depends on the component, the diffraction line and the mass absorption coefficient of the species present. I_A/I_B represents the ratio of the intensities of two selected diffraction lines in a mixture of two substances, and X_A/X_B is the molar fraction ratio of the two substances. A plot of I_A/I_B should yield a straight line with an intercept of zero.

X-ray calibration lines

The calibration lines for calcite–aragonite and calcite–vaterite mixtures were constructed. For the calcite–aragonite mixture the equation for the calibration line was obtained by linear regression of the experimental data, using the reflection peaks at 104 for calcite and 221 for aragonite (Fig. 5):

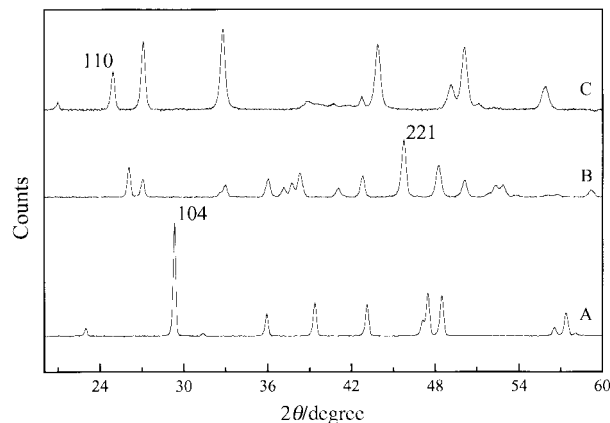


Fig. 4 XRD spectra of the synthetically prepared calcite (A), aragonite (B) and vaterite (C).

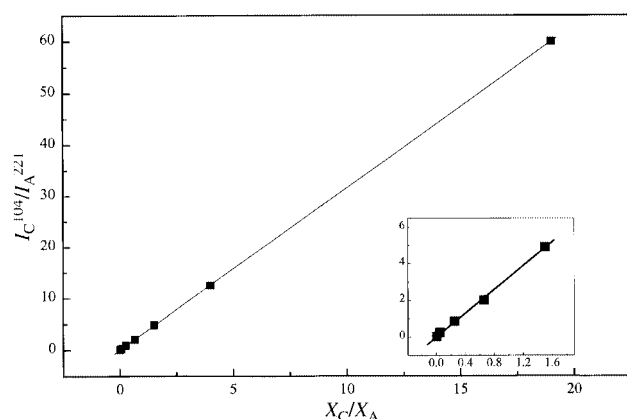


Fig. 5 XRD calibration line for calcite–aragonite mixtures.

$$\frac{I_C^{104}}{I_A^{221}} = 3.157 \times \frac{X_C}{X_A} \quad (9)$$

The correlation coefficient, r , was 0.9999 while the standard deviation of the slope was found to be 5.5×10^{-4} . DL, at the 99.9% confidence level, were calculated to be 0.85 mol.-% for calcite and 2.90 mol.-% for aragonite.

The calibration graph of the mixture calcite–vaterite was constructed by choosing the reflection peaks at 104 for calcite and 110 for vaterite. The calibration line can be described by the following relationship:

$$\frac{I_C^{104}}{I_V^{110}} = 7.691 \times \frac{X_C}{X_V} \quad (10)$$

The correlation coefficient, r , was 0.9999 while the standard deviation of the slope was found to be 1.0×10^{-3} . DL, at the 99.9% confidence level, were calculated to be 0.85 mol.-% for calcite and 6.90 mol.-% for vaterite.

Some typical X-ray diffractograms of the various mixtures are shown in Fig. 6.

Calculation of the molar fraction of calcite, aragonite and vaterite in a sample using the XRD calibration graphs

By using eqn. (9) and (10) and assuming that $X_C + X_A + X_V = 1$, the molar fractions in a sample may be determined from the following relationships:

$$X_A = \frac{3.157 \times I_A^{221}}{I_C^{104} + 3.157 \times I_A^{221} + 7.691 \times I_V^{110}} \quad (11)$$

$$X_C = \frac{I_C^{104} \times X_A}{3.157 \times I_A^{221}} \quad (12)$$

$$X_V = 1.0 - X_A - X_C \quad (13)$$

The validity of this expression was tested on an XRD spectrum recorded from a powder mixture consisting of 32 mol.-% calcite, 33 mol.-% aragonite and 35 mol.-% vaterite. This ternary mixture was the same as that used for testing the Raman calibration graphs. The results obtained were: calcite 31.2 mol.-%, aragonite 33.6 mol.-% and vaterite 35.2 mol.-%, yielding a relative error of 2.5, 1.8 and 0.6%, respectively.

As mentioned for the FT-RS method, the presence of a fourth compound does not affect the validity of the derived equations provided that there is no chemical interaction among the species

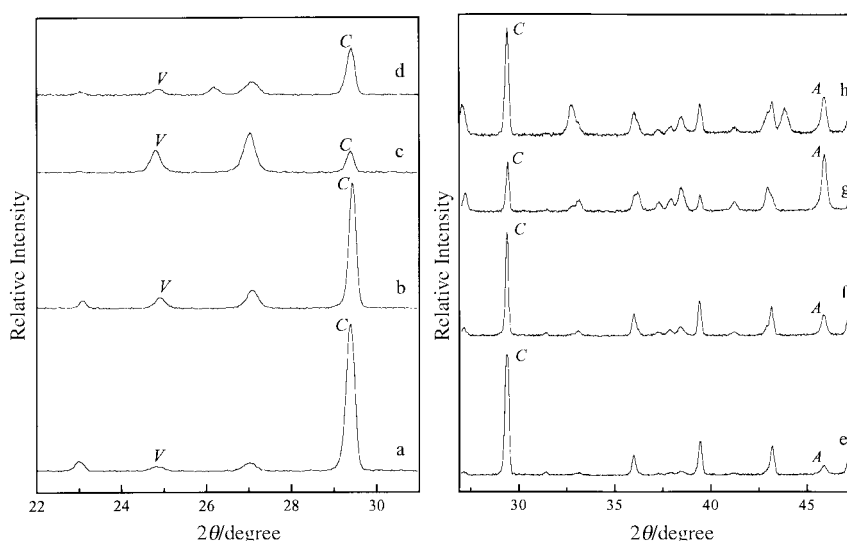


Fig. 6 XRD spectra of: (a) 80 mol.-% calcite–20 mol.-% vaterite; (b) 60 mol.-% calcite–40 mol.-% vaterite; (c) 20 mol.-% calcite–80 mol.-% vaterite; (d) 32 mol.-% calcite–33 mol.-% aragonite–35 mol.-% vaterite; (e) 20 mol.-% aragonite–80 mol.-% calcite; (f) 40 mol.-% aragonite–60 mol.-% calcite; (g) 20 mol.-% aragonite–80 mol.-% calcite; (h) 32 mol.-% calcite–33 mol.-% aragonite–35 mol.-% vaterite.

present or overlap of the XRD peaks used for the analysis with the XRD lines of the additional species.

Comparison between RS and XRD

Both techniques were used successfully for the estimation of the relative percentage of the calcium carbonate phases in a ternary mixture, but FT-RS exhibits certain advantages over the XRD method: (a) FT-RS yielded much lower *DL* and lower relative errors; (b) FT-RS can be used for a non-destructive point-by-point *in situ* analysis ('mapping') of the specimen surface while XRD yields only the average percentage of the bulk, grounded powder sample.

Conclusions

Two methodologies, based on FT-RS and XRD, respectively, were developed for the simultaneous quantitative determination of calcium carbonate crystal phases. Calibration graphs from mixtures of calcite, aragonite and vaterite were constructed. The lower detection limits given by FT-RS and the potential use of the technique for *in situ* mapping of specimen surfaces are among the major advantages of FT-RS over powder XRD.

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