



Quantitative analysis of synthetic calcium carbonate polymorphs using FT-IR spectroscopy

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Received 28 October 2002; received in revised form 28 November 2002; accepted 17 December 2002

Abstract

Fourier Transform Infrared Spectroscopy (FT-IR) was used successfully for the simultaneous quantitative analysis of calcium carbonate phases (calcite, aragonite, vaterite) in ternary mixtures. From the FT-IR spectra of pure calcite, aragonite and vaterite powders with KBr, the absorptivities, α , of the absorption bands at 713 cm^{-1} for calcite, 745 cm^{-1} for vaterite, 713 and 700 cm^{-1} for aragonite, were determined. In order to overcome the absorption band overlapping a set of equations based on Beer's law was developed. The detection limits were also established and found to be 1.1×10^{-4} mg calcite per mm^2 of pellet at 713 cm^{-1} , 3.6×10^{-4} mg aragonite per mm^2 of pellet at 700 cm^{-1} , 1.8×10^{-4} mg aragonite per mm^2 of pellet at 713 cm^{-1} and 3.1×10^{-4} mg vaterite per mm^2 of pellet at 745 cm^{-1} . Analysis of a known ternary mixture of calcium carbonate polymorphs tested the validity of the method.

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Keywords: FT-IR; Calcite; Aragonite; Vaterite; Quantitative analysis; Synthetic calcium carbonate

1. Introduction

Calcium carbonates are often present as persistent, insoluble hard scale formations in boilers, cooling towers, heat exchangers, geothermal processing equipment [1] as well as in several pathological cases (stone formation, pancreatic calcification) and in minerals (marble, limestones). The various calcium carbonate polymorphs en-

countered in aqueous media include vaterite, aragonite and calcite, in the order of decreasing solubility [2]. The less stable phases can be transformed to calcite [3,4], the thermodynamically most stable phase. Successful intervention to prevent or retard calcium carbonate formation requires careful investigation of the kinetics of formation of the different polymorphs as well as their transformation to the more stable phase. For this reason an analytical tool capable of discriminating among the different phases that coexist during the kinetic studies is needed. Furthermore, such methodology can be applied also for the quantitative determination of the calcium carbon-

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ate polymorphs, which are present in numerous cases.

Because of their different crystal structure the three phases can be discriminated by using a vibrational technique i.e. infrared spectroscopy (IR) and/or Raman spectroscopy (RS). X-ray powder diffraction (XRD) can be also used although the capability of XRD for quantitative analysis is limited to the minerals having good crystal structure. A successful application of RS and XRD on mixture of the calcium carbonate polymorphs was published recently [5]. Unfortunately, due to inherent difficulties in the application of RS only molar ratios were determined. Similarly, molar ratios, instead of the concentrations, were determined also in cases where IR was applied as analytical tool for the determination of the CaCO_3 crystal phases [3,6–11]. Also, the IR methodologies developed were restricted only to binary mixtures of the calcium carbonate phases probably due to strong overlapping of the bands. Furthermore, although no detection limits were reported by the authors, the effective range of each calibration line made 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 that started at 30 mol% were also used.

The relative disadvantages of the FT-IR involve: (a) mixing with KBr and pelleting; and (b) the need of having particles with size less than 2 μm in order to avoid light scattering [12–14]. Despite these problems the widespread availability of the FT-IR instrumentation in several laboratories is a compelling reason for developing a methodology for the quantitative determination of these polymorphs using infrared spectroscopy. Furthermore, Beer's law permits the determination of the respective absorptivities and consequently the concentration of the species in a mixture. But even in very recent articles where FT-IR was applied for quantifying the presence of calcite in minerals the constant ratio method was used instead [15]. In the present work, FT-IR was used for the determination of the absorptivities of all three calcium carbonate crystal phases that in turn were used in order to quantitatively discriminate among the three calcium carbonate

polymorphs in a ternary mixture. The detection limits were also determined.

2. Experimental

2.1. Instrumentation

All spectra were recorded from 4000–400 cm^{-1} , using the EQUINOX 55 (Bruker) FT-IR spectrometer. Each spectrum was the average of 200 scans using a spectral resolution of 2 cm^{-1} . The IR spectra were recorded and stored using a spectroscopic software (OPUS, Version 2.0). For the deconvolution of the IR absorption bands the PeakFit v4.0 software from Jandel Scientific was used. In addition to the use of FT-IR spectroscopy all solids (calcite, aragonite and vaterite) were also characterized prior to their use by FT-Raman spectroscopy (FRA-106/S FT-Raman, Bruker, Karlsruhe, Germany) and X-ray Diffraction (1830/40 Philips, Eindhoven, the Netherlands). The crystal size was measured by using the Mastersizer S (Malvern Instruments, England).

2.2. Reagents

The reagents used and their suppliers were: ammonium carbonate and calcium nitrate from Ferak (Berlin, Germany) sodium carbonate (GR for analysis), potassium nitrate (GR for analysis), sodium hydrogen carbonate (GR for analysis), 2-propanol (GR for analysis), potassium bromide (IR spectroscopy, Uvasol) and standard sodium hydroxide (Tritisol, 0.1 M) from Merck (Darmstadt, Germany). The 0.22 μm membrane filters used for filtering the precipitating solids were from Millipore (Bedford, MA, USA). For the preparation of the calcium carbonate crystals the water used was supplied by a Milli-Q RG water purification system.

2.3. Procedures

Calcite powder was prepared using the methodology described by Reddy et al. [16]. The precipitated crystals were dried at 120 $^\circ\text{C}$ for 2 days and stored in a desiccator. The medium

particle size, given as diameter of equivalent sphere ($D_{[4,3]}$) was measured to be 13 μm .

Pure aragonite crystals were prepared according to [17]. The crystals, in the form of slurry, were filtered 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 29 μm .

Pure vaterite was prepared using the constant composition method as described by Spanos and Koutsoukos [18]. At the end of the precipitation process the suspension was filtered through membrane filters. The solid collected was then dried for 2 h at 80 °C. $D_{[4,3]}$ for vaterite particles was measured to be in the order of 5 μm .

It's generally accepted that particle size plays a considerable role at the shape of the infrared spectra. Previous reports have demonstrated the inverse relation between particle size and the intensity of the absorption peaks [12,13]. For reliable infrared studies the grain size of solid powders should be below than 2 μm . In order to obtain crystals with size below than 2 μm and to avoid disorder effects at their structure, the following procedure was employed: Each crystal phase was suspended at an organic solvent (2-propanol). The suspension was transferred into a cylinder and allowed to stand undisturbed for several hours. At the end of this time aliquots were withdrawn from the upper part of the cylinder and the crystals were sized. If the size of the suspended particles was less than 2 μm the crystals were dried and stored in a desiccator.

Prior to use the FT-IR FT-Raman and XRD spectra of calcite, aragonite and vaterite were recorded and found to match those reported by others researchers [10,11,19–23].

FT-IR pellets were prepared as follows: potassium bromide and the calcium carbonates were dried overnight at 110 °C and were stored in a desiccator. Various quantities, of the small size fraction, from the desired phase was thoroughly mixed with 1 mg of KBr in an agate mortar. An additional quantity of 2 mg of KBr was added and was again thoroughly mixed. In the resulted solid 3 mg KBr was added and the same procedure was applied. The pattern of adding a quantity of KBr

was repeated several times until the total added KBr was 100 mg. The mixture then was pressed into a pellet die for 5 min using a force of 5 tons. The measured thickness of the pellets was $0.30 \pm 4 \times 10^{-3}$ mm while the diameter was 13 mm. No transformation of the less favored thermodynamic phases to calcite was observed as it was verified from the FT-IR spectra recorded from the vaterite and aragonite pellets.

3. Results and discussion

3.1. Determination of absorptivities

The selection of the appropriate bands for the quantitative analysis was a difficult task since there is a strong overlapping. The absorption bands chosen for the quantitative analysis of a ternary mixture were the 713 cm^{-1} for calcite, the 700 and 713 cm^{-1} for aragonite, and the 745 cm^{-1} for vaterite (Fig. 1). Even with these

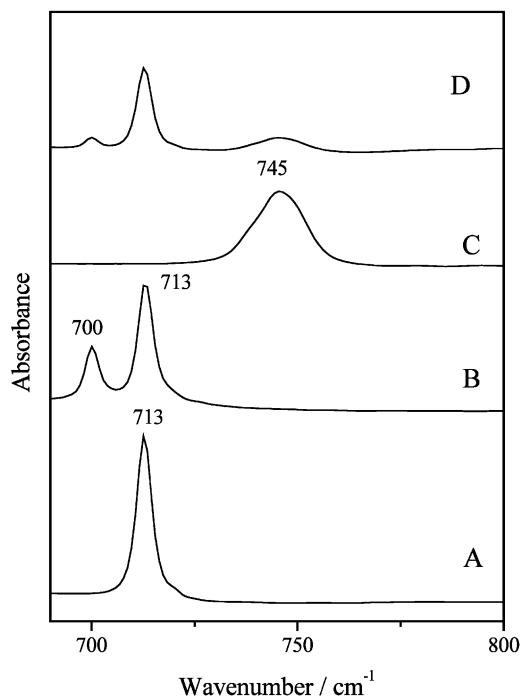


Fig. 1. Absorption FT-IR spectra of: (A) calcite; (B) aragonite; (C) vaterite; (D) ternary mixture of 0.2 mg calcite, 0.1 mg aragonite and 0.15 mg vaterite.

absorption bands a small overlap of the 700 and the 713 cm^{-1} bands can be observed (Fig. 1B and D). In order to avoid complications arising from the overlap the bands were deconvoluted prior to the determination of respected absorptivities, in the case of the aragonite pellets, or the calculation of the aragonite and calcite crystal phase concentration in the case of ternary mixtures. A typical deconvoluted spectrum can be seen in Fig. 2.

Beer's Law describes the relationship between the absorbance and the concentration of an analyte in a solid sample:

$$A = \alpha \times c, \quad (1)$$

where, A indicates the absorbance of the electromagnetic radiation, α is the absorptivity in $\text{mm}^2 \text{mg}^{-1} \text{CaCO}_3$, and c the concentration of the respective calcium carbonate phase in mg per mm^2 of the FT-IR pellet.

For the 745 cm^{-1} vaterite band the Eq. (1) can be rewritten as follows:

$$A_V^{745} = \alpha_V^{745} \times c_V, \quad (2)$$

where the subscript V represents the vaterite crystal phase, and the superscript is the wavenumber of the respective absorption band. The spectra

of five vaterite pellets, with each pellet having different quantity of vaterite dispersed in 100 mg KBr, were recorded and from their respective absorption at 745 cm^{-1} the absorptivity, α_V^{745} , was determined by plotting the measured absorption against the added amount of vaterite in each pellet. The absorptivity i.e. the slope of the resulted line which was drawn using linear regression, found to be $21.8 \text{ mm}^2 \text{mg}^{-1} \text{CaCO}_3$.

Similarly, the absorptivities for aragonite and calcite were calculated using the deconvoluted absorption bands at 700 and 713 cm^{-1} for aragonite, and the 713 cm^{-1} band for calcite. The cumulative information for the absorptivities and the respected standard deviations is in Table 1.

Using the calculated absorptivities and spectra of 100 mg KBr calcium carbonate-free pellets the detection limits (DL) resulting from the application of Eq. (1), were calculated. Where DL is defined as [24]:

$$\text{DL} = ts \sqrt{\frac{N_1 + N_2}{N_1 N_2}}, \quad (3)$$

where t is Student's t -test; s is the standard deviation of N_2 blank calculations of the respected calcium carbonate phase concentration; N_1 is the

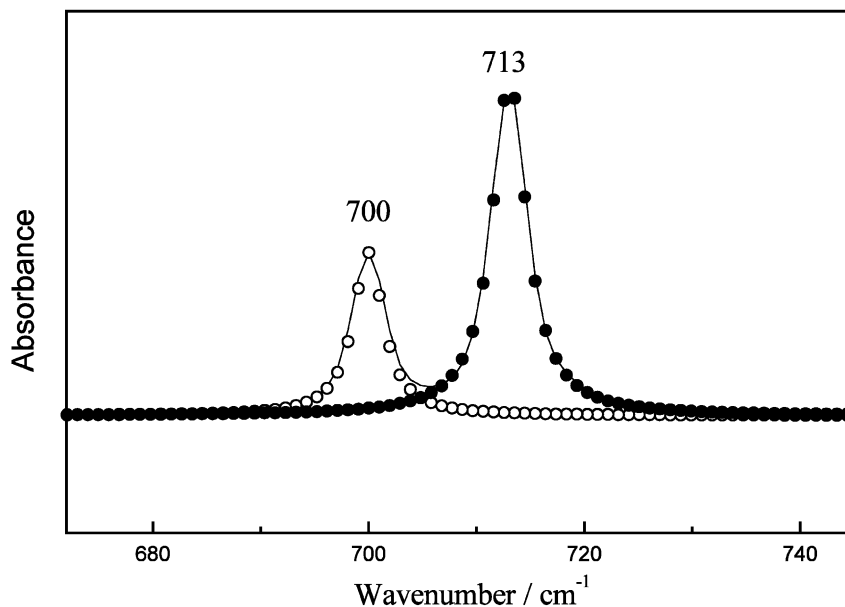


Fig. 2. Typical deconvolution of the 700 (○) and the 713 cm^{-1} (●) absorption bands of an FT-IR aragonite spectrum (solid line).

Table 1
Absorptivities for pure calcium carbonate polymorphs dispersed in 100 mg KBr pellets

CaCO ₃ phase	Absorption bands (cm ⁻¹)	a ^a (mm ² mg ⁻¹ CaCO ₃)	S.D. ^b	r
Calcite	713	63.4	0.09	0.9993
Aragonite	713	40.5	0.11	0.9996
Aragonite	700	19.3	0.18	0.9995
Vaterite	745	21.8	0.13	0.9991

^a The calculated absorptivities are for pellets with 0.30 mm thickness.

^b S.D. is standard deviation.

number of replicate analyses. For the 745 cm⁻¹ vaterite band, for single analysis, 10 blank determinations of vaterite concentrations in 100 mg vaterite-free KBr pellets and confidence level 99%, DL was found to be 3.1 × 10⁻⁴ mg CaCO₃ per mm² of pellet. All calculated DLs are in Table 2.

3.2. Methodology for determining the calcium carbonate crystal phases in a ternary mixture

In a ternary system, in which all calcium carbonates phases are present, for the absorption peaks at 745, 700 and 713 cm⁻¹ the following relations apply:

$$c_V = \frac{A^{745}}{\alpha_V^{745}}, \quad (4)$$

$$c_A = \frac{A^{700}}{\alpha_A^{700}}, \quad (5)$$

$$c_C = \frac{A^{713} - \alpha_A^{713} \times c_A}{\alpha_C^{713}}. \quad (6)$$

The subscripts C, A and V in all equations denote the calcite, aragonite and vaterite phases, respectively.

The concentrations of the crystal phases in an unknown ternary mixture can be calculated using Eqs. (4)–(6) provided that deconvolution of the

absorption bands of 700 and 713 cm⁻¹ precede the measurement of the respective absorptions.

When one of the CaCO₃ polymorphs is not present, Eqs. (4)–(6) are still valid.

If vaterite is not present then c_V = 0. Eqs. (5) and (6) can be used without modification.

If aragonite is absent, then c_A = 0. Eq. (4) can be applied without change while Eq. (6) transforms to:

$$c_C = \frac{A^{713}}{\alpha_C^{713}}. \quad (7)$$

In the absence of calcite then Eqs. (4) and (5) can be used without any modification.

3.3. Testing the validity of the methodology

The validity of these expressions was tested on a spectrum recorded from a powder mixture consisting of 0.2 mg calcite, 0.1 mg aragonite and 0.15 mg vaterite that were dispersed in 100 mg KBr (Fig. 1D). Using the absorptivities of Table 1, the measured deconvoluted absorptions of the 700 and 713 cm⁻¹ bands as well as the 745 cm⁻¹ absorption band and Eqs. (4)–(6) the concentrations of the crystal phases per mm² of the pellet were calculated. Multiplication with the area of the pellet yielded the total quantity of each phase. The

Table 2
Detection limits for CaCO₃ crystal phases and different absorption bands

Crystal phase	Calcite	Vaterite	Aragonite	Aragonite
Absorption band (cm ⁻¹)	713	745	713	700
DL ^a (mg CaCO ₃ mm ⁻² pellet)	1.1 × 10 ⁻⁴	3.1 × 10 ⁻⁴	1.8 × 10 ⁻⁴	3.6 × 10 ⁻⁴

^a DL is detection limit.

results were: calcite $0.202 \pm 9.8 \times 10^{-3}$ mg, aragonite $0.108 \pm 7.7 \times 10^{-3}$ mg and vaterite $0.146 \pm 5.9 \times 10^{-3}$ mg. The standard deviations were calculated using the error propagation theory. The relative errors were 1, 8 and 2.7%, respectively.

It may be also possible to apply the described methodology in any sample with calcium carbonate phases provided that: (a) the sample is carefully grinded to sizes below 2 μm ; (b) the absorption bands arising from the possible presence of other constituents do not overlap with the chosen absorption bands i.e. 700, 713 and 745 cm^{-1} .

4. Conclusions

A new methodology, based on the use of FT-IR, was used successfully for the simultaneous quantitative determination of anhydrous calcium carbonates crystal phases. The absorptivities for the absorption bands of the polymorphs used in the analytical technique were established and the respected detection limits were determined. The proposed methodology allows a direct simultaneous quantitative determination of calcium carbonates phases as opposed to Raman spectroscopy where only relative ratios can be determined.

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