Vapour phase Fourier transform infrared spectrometric determination of carbonate in sediments

Amparo Pérez-Ponce, Jose M. Garrigues, Salvador Garrigues and Miguel de la Guardia*

Department of Analytical Chemistry, University of Valencia, 50 Dr. Moliner St., 46100 Burjasot, Valencia, Spain

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A rapid, sensitive and direct procedure for the determination of carbonate in sediments based on vapour-generation Fourier transform infrared spectrometry is described. A 1 ml volume of hydrochloric acid (0.25 M) was injected into a vessel, heated at 40 °C, containing 10 mg of sediment. The CO_2 evolved under these conditions was swept by a stream of nitrogen to an infrared gas cell. The flow injection (FI) recordings were registered as a function of time and the areas of the FI recording obtained in the wavenumber range 2500–2150 cm^{-1} were measured and interpolated in a calibration equation obtained from known amounts of $CaCO_3$ treated in the same way as the samples. The method provided a limit of detection of 0.2 mg of $CaCO_3$, a sampling frequency of 20 h^{-1} and an RSD of 0.7% for three independent analyses of 20 mg of sediment. Results obtained for a series of natural sediment samples compared well with those obtained using a back-titrimetric reference method.

Inorganic carbonate exists in soils mainly as the sparingly soluble alkaline earth metal carbonates calcite ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$). Calcite is commonly the main component. Soluble inorganic carbonates also exist in soils, primarily in highly sodic (alkali metal) soils of arid regions, but their content is generally low compared with the alkaline earth metal carbonates,[1] and for this reason the content of inorganic carbonate in sediments is referred to the percentage of $CaCO_3$.[2]

The determination of carbonate in sediments can be achieved in two ways. The preferred technique is the direct measurement of inorganic carbon.[3–14] However, it is also possible to determine carbonates by the difference between total carbon, in untreated samples, and the organic carbon measured in samples previously acidified in order to remove the inorganic carbon.[15,16]

Methods involving the determination of total inorganic carbonate include (i) dissolution of carbonate in acid and determination of the evolved CO_2 by volume[3] or pressure[4] measurements of CO_2 or by thermal conductivity[5,6] and (ii) dry ashing of the sediment in oxygen at temperatures higher than 1000 °C and thermogravimetric determination of CO_2 by using a thermal conductivity detector[8] or by IR detection[9,10] or possibly continuous titration of CO_2 absorbed in water.[11–14] In general, these techniques involve the use of specific instrumentation devoted to this kind of determination and, additionally, these methods are expensive and time consuming.

In this work, based on the use of common FTIR instrumentation, we developed a simple and rapid procedure for the determination of carbonate in sediments based on previous experience with the flow injection analysis–FTIR determination of carbonate in waters through on-line acid treatment and CO_2 measurement in the vapour phase generated by convective[17] or microwave-assisted[18] heating.

Experimental

Apparatus and reagents

A Magna 750 FTIR spectrometer from Nicolet (Madison, WI, USA), equipped with a temperature-stabilized DGTS detector, a long-lasting Ever-Glo source and a KBr beamsplitter, was employed for spectral measurements obtained by accumulating three scans at a resolution of 16 cm^{-1}, using a laboratory-made gas cell made of PTFE with an internal volume of 490 μl and a bandpass of 39 mm, equipped with ZnSe windows.

Version 2.1 of Omnic software, developed by Nicolet, was employed to control the instrument, for data acquisition and also for processing the analytical results.

The manifold employed for vapour-generation FTIR measurements (Fig. 1) was a single-channel manifold with a nitrogen carrier flow, which included a removable glass sample vessel of 13 ml internal volume with a gas inlet, a gas outlet and a septum. An appropriate acid volume was injected inside the vessel through the septum using Hamilton (Reno, NV, USA) microsyringes of different volumes.

Sample vessels were introduced inside a hot water-bath, the temperature of which was controlled by means of a thermocouple and operated using a laboratory-made electrically controlled heater. The temperature of the N_2 flow was measured with another thermocouple and fixed using an electrically controlled heater from AKO (Barcelona, Spain).

A ganged distribution valve from Omnifit (Manchester, UK) was used as a by-pass system when sample vessels were

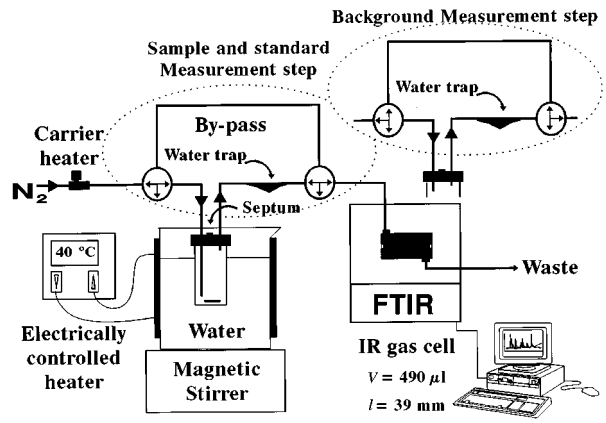

Fig. 1 Manifold employed for vapour-generation FTIR determination of carbonate in sediments.

changed, in order to ensure a permanent N_2 flow through the IR cell. All tubes employed in the manifold were made of PTFE of 1/32 in id and 1/16 in od. To avoid the presence of water drops inside the measurement cell, a 1.6 ml piece of glass was installed at the exit of the glass reactor to act as a water trap in which the excess water vapour condensed before passing inside the gas cell.

Analytical-reagent grade $CaCO_3$ from Panreac (Barcelona, Spain) was employed for the preparation of standard solutions and 37% HCl from Fluka (Buchs, Switzerland) was used for sample and standard solution acidification. Nitrogen C-45 (99.995% purity) from Carburos Metálicos (Barcelona, Spain) was employed as the carrier gas and de-ionized water with a resistance >10 MΩ obtained using a Milli-RX system from Millipore (Molsheim, France) was used throughout.

Vapour phase FTIR analysis

Amounts of 20 mg of samples were accurately weighed into the glass vessels that were employed as sample vessels and incorporated in the manifold depicted in Fig. 1. Prior to any measurement, an N_2 carrier flow was passed through an empty vessel and the corresponding background was obtained. The empty vessel was then removed by by-passing the N_2 flow using the ganged distribution valve, and a new vessel containing sample or standard solution was placed inside the water-bath at 40 °C; the N_2 flow was passed through the vessel again and 1 ml of 0.25 M HCl was injected into the vessel and the CO_2 generated was transported inside the gas cell of the FTIR spectrometer using a nitrogen carrier flow of 50 ml min^{-1}, without the need for an equilibrium time before measurement. The FTIR spectra were continuously recorded, as a function of time, between 3000 and 1000 cm^{-1}, which includes the CO_2 absorption band at 2350 cm^{-1}. From the absorbance data in the 2500–2150 cm^{-1} range, integrated absorbance measurements were obtained, providing transient recordings which correspond to the absorbance of CO_2, in the selected wavenumber range. The areas of the aforementioned peaks, obtained with a baseline correction established between two sequential injections, were interpolated in the calibration line obtained with peaks corresponding to known amounts of $CaCO_3$ treated in the same way as the samples.

Reference back-titrimetric procedure

The method recommended by the American Society of Agronomy[1] is based on the neutralization of carbonates with H_2SO_4 and back-titration of the excess of acid. To 0.1 g of sediment, 9 ml of 1% H_2SO_4 and 40 ml of de-ionized water were added and the mixture was shaken and heated until boiling to eliminate the H_2CO_3 formed. After cooling, a few drops of phenolphthalein were added and the solution was titrated with 0.1M NaOH, adding a drop of titrant every 2–3 s until the appearance of a pink colour. The percentage of $CaCO_3$ in sediment was calculated using the expression

$$CaCO_3\ (\%\ m/m) = \frac{16.9 - 5VM_{NaOH}}{m_{sed}}$$

where V is to the reading volume, M_{NaOH} the NaOH molar concentration and m_{sed} the mass of sediment.

Results and discussion

FTIR spectra of sediments in solid and vapour phase

It is known that carbonate provides two sensitive and well defined bands corresponding to the C–O vibration, one at 1400 cm^{-1}, with strong intensity, and another at 870 cm^{-1}, with medium intensity. Both bands suffer small shifts depending on the cation present in carbonate and large shifts when CO_3^{2-} changes to HCO_3^- as a function of pH [Fig. 2(A)]. Furthermore, natural soil and sediment samples contain a mixture of carbonates and hydrogencarbonates with different cations, and other inorganic anions that show absorption in this spectral

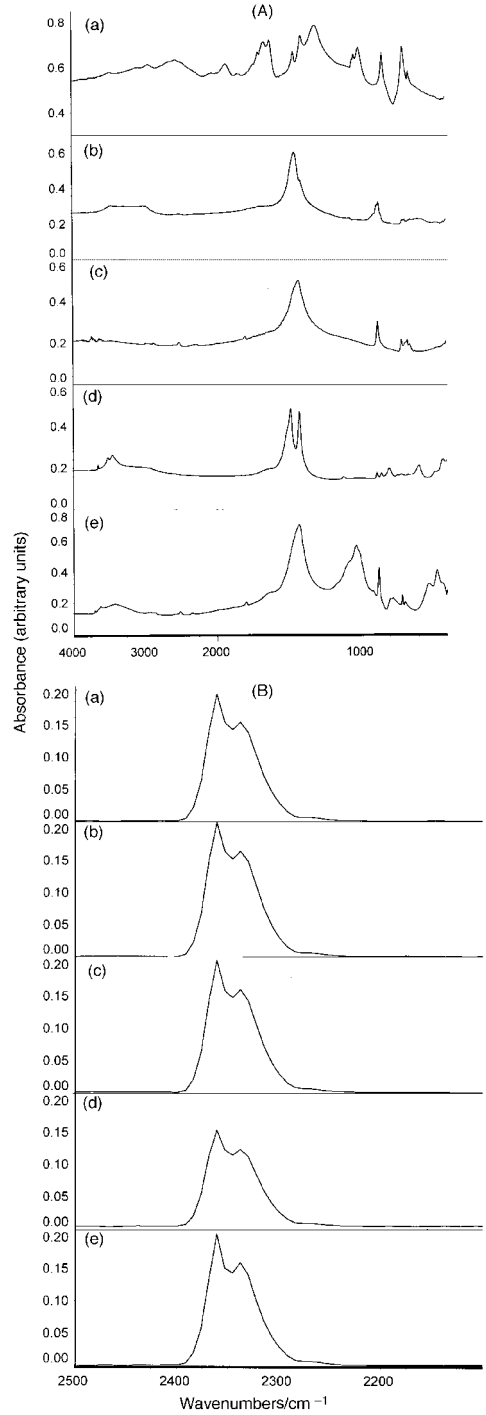

Fig. 2 Solid and vapour phase FTIR spectra of carbonate and hydrogencarbonate. (A) Solid phase spectra obtained from KBr pellets of (a) sodium hydrogencarbonate, (b) sodium carbonate, (c) calcium carbonate, (d) magnesium carbonate and (e) a sediment sample. Experimental conditions: spectra obtained from 50 accumulated scans at a resolution of 16 cm^{-1} establishing the background with air. (B) Vapour phase co-added spectra obtained from 2 min recording obtained for (a) sodium hydrogencarbonate, (b) sodium carbonate, (c) calcium carbonate, (d) magnesium carbonate and (e) a sediment sample. Experimental conditions: spectra obtained from three accumulated scans at a resolution of 16 cm^{-1}, using a gas cell of 39 mm pathlength with ZnSe windows, for a solid mass equivalent to 4 mg of $CaCO_3$, an injection volume of 1 ml of 0.25 M HCl using 13 ml reactors heated at 40 °C and a 50 ml min^{-1} N_2 carrier gas flow rate. The spectral background was obtained from an N_2 flow passed through an empty vessel. The co-added spectra were obtained during 2 min from the starting point of the transient signals obtained after the injection of HCl into the sample reactors installed in the manifold.

region, such as silicates. All this makes it difficult to determine the total carbonate content by direct measurement of IR absorbance in solids. Additionally, quantitative analysis using alkali metal halide pellets needs the use of internal references or rigorous control of the bandpass.

When carbonate standards and natural sediment samples were treated with acid and the spectra of CO_2 generated by decomposition of carbonates were recordered in the range 3000–1000 cm^{-1}, a sensitive double band was obtained between 2400 and 2300 cm^{-1} that corresponds to the asymmetric vibration of CO_2 [Fig. 2(B)]. In this spectral range, water shows a very low absorption and for this reason the use of vapour phase generation of CO_2 from carbonate in soils and sediments provides a simple and sensitive approach for the determination of carbonate in natural samples.

Effect of HCl on CO_2 generation

The most important step in the determination of carbonate by vapour phase FTIR spectrometry is the acidification of sediments in order to generate CO_2, so the concentration and volume of HCl necessary for a complete generation of CO_2 from $CaCO_3$ was evaluated.

Table 1 shows the effect of HCl concentration and volume on the area of the integrated absorbance signals obtained for 10 mg of $CaCO_3$, analysis being carried out in a monoparametric mode with a volume of 1 ml and a concentration of 0.25 M for natural sample analysis.

In theory, 10 mg of $CaCO_3$ needs 2×10^{-4} mol of HCl, *i.e.*,1 ml of 0.2 M HCl or 0.8 ml of 0.25 M HCl, to be converted quantitatively into CO_2. The results in Table 1 demonstrate that, in this method, rapid and complete CO_2 formation only needs a stoichiometric amount of HCl. Therefore, 1 ml of 0.25 M HCl was selected for the treatment of 10 mg of $CaCO_3$ or a natural sediment, although for sediment a slight excess was used. However the aforementioned amount of acid was taken as a general criterion without observing deleterious effects on the analytical signals due to the presence of a small excess of acid.

Effect of reactor temperature

The reaction between carbonate and HCl and the release of CO_2 are very efficient and rapid processes and the effect of temperature is not a decisive factor with regard to thermodynamic aspects, but it affects the kinetics of the reaction. As can be seen in the inset in Fig. 3, the peak width decreases and the peak height increases when the reactor temperature increases, thus improving the reaction speed. However, from the experimental point of view, the extremely fast measurement of CO_2 creates problems with respect to monitoring absorption spectra and the peak area decreases at reactor temperatures higher than 60 °C; therefore a temperature of 40 °C was selected in order to obtain a compromise between speed, sensitivity and reproducibility of the analytical signals.

Effect of reactor volume

As can be seen in Table 2, an increase in the sample reactor volume, which increases the CO_2 dispersion by increasing the total volume of the system, has a very small influence on the analytical signals obtained from the areas of the transient peaks. A reactor volume of 13 ml, which corresponds to standard glass vials, can be recommended for the determination of carbonate in sediments. The only problem created by the use of small reactors is the transport of water vapour inside the measurement cell, but this can be solved easily by incorporating a water trap consisting of a 1.6 ml glass cell which helps to condense the water before the measurement cell.

Effect of volume of water added to samples

To prevent acid splashing and to improve the homogeneous mixture between solid samples and acid, different volumes of water, from 1 to 5 ml, were added to the solid samples before acidification. As can be seen in Table 3, the volume of water used does not seriously affect the peak areas corresponding to 10 mg of $CaCO_3$ or those of a sediment treated following the general procedure. However, the addition of water decreases the reaction speed and consequently the frequency of analysis.

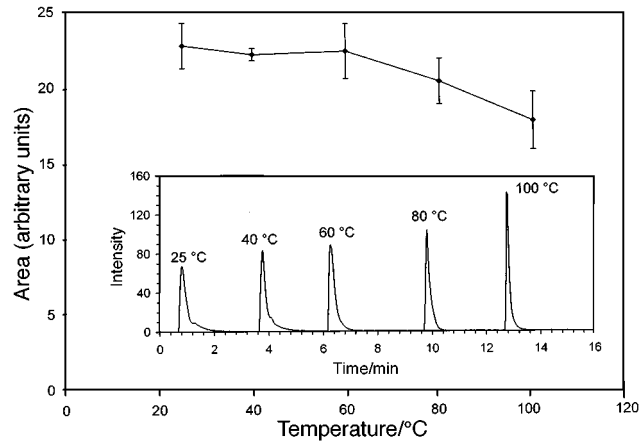

Fig. 3 Effect of the reactor temperature on vapour-generation FTIR determination of carbonate in sediments. Inset: peaks corresponding to the wavenumber range 2500–2150 cm^{-1}, obtained for 10 mg of $CaCO_3$ at different reactor temperatures. Experimental conditions: 10 mg of $CaCO_3$, 1 ml of 0.25 M HCl, 13 ml reactor volume and 120 ml min^{-1} N_2 flow rate. Areas, expressed in arbitrary units, were measured from the absorbance in the range 2500–2150 cm^{-1}. Error bars indicate the interval of the average value ± the corresponding standard deviation of three independent measurements.

Table 1 Effect of HCl concentration and volume on the vapour phase FTIR determination of carbonate in sediments. Experimental conditions: in both series of measurements we employed 10 mg of $CaCO_3$, 13 ml reactor volume and 60 °C reactor temperature, using 120 and 100 ml min^{-1} N_2 flow rates for HCl concentration effect and HCl volume effect, respectively. Area values, expressed in arbitrary units, were measured from the absorbance in the wavenumber range 2500–2150 cm^{-1} and the standard deviation values correspond to three independent measurements

HCl concentration/M (V = 1 ml)	Area ± s_{n-1}*	HCl volume/ml (C = 0.25 M)	Area ± s_{n-1}*
0.125	17.2 ± 0.8	0.5	20.63 ± 0.10
0.25	22.35 ± 0.21	0.75	26.9 ± 0.7
0.5	21.8 ± 0.7	1	26.7 ± 0.8
1	22.6 ± 1.6	1.5	26.9 ± 0.7
1.5	23.7 ± 1.4	2	27.6 ± 0.4
2	23.6 ± 0.9		
5	22.7 ± 1.2		

* S_{n-1}: Standard deviation for $n - 1$ degrees of freedom.

Table 2 Effect of reactor volume on vapour phase FTIR determination of carbonate in sediments. Experimental conditions: 10 mg of $CaCO_3$, 1 ml of 0.25 M HCl, 40 °C reactor temperature and 120 ml min^{-1} N_2 flow rate. Areas, expressed in arbitrary units, were measured from the absorbance in the wavenumber range 2500–2150 cm^{-1} and standard deviation values correspond to three independent measurements

Reactor volume/ml	Area ± s_{n-1}
5.3	17.8 ± 0.9
6.7	16.8 ± 2.0
12.8	19.4 ± 1.1
13.2	19.4 ± 1.1
21.5	19.3 ± 1.6
28	20.5 ± 1.2

Because of this, it is preferable to add HCl directly to the solid in order to improve the sampling frequency.

Effect of sample mass

The effect of sediment mass on the peak areas of the transient signals of evolved CO_2 was evaluated in order to ensure the appropriate sensitivity and precision of analysis by vapour phase FTIR spectrometry. For these experiments, a 3 ml volume of 0.4 M HCl was fixed, which provides a stoichiometric amount of acid to provide the total neutralization of 60 mg of pure $CaCO_3$.

The results Table 4 indicate that on increasing the sediment mass, the peak area also increases without changing the sampling frequency, but the reproducibility of the signals corresponding to a high sample mass decreases. A typical regression line, $A = (3.1 \pm 1.0) + (2.44 \pm 0.03)m$, where A is peak area and m the sample mass (mg), with a regression coefficient $r = 0.9998$, was obtained for increasing sediment mass. This indicates that the system works correctly for different sediment masses, thus providing a good means of improving the analytical sensitivity in the analysis of samples containing a very low carbonate concentration.

Effect of N_2 carrier flow rate

The carrier gas flow rate is a critical parameter in vapour phase FTIR spectrometric analyses[17–20] which affects the analytical sensitivity and the sampling frequency. This parameter affects the volatility of the analytes and controls the speed of vapour introduction into the measurement cell. An increase in the carrier flow rate causes a decrease in sensitivity (Fig. 4), but increases the sampling frequency, as can be seen in the inset, from 10.9 h^{-1} for 11 ml min^{-1} to 30 h^{-1} for 100 ml min^{-1}. Hence a nitrogen flow rate of 50 ml min^{-1}, which allows a 20 h^{-1} sampling frequency, was selected in order to achieve a compromise between analytical sensitivity and sample throughput.

Use of a fixed reaction time

A series of additional experiments were carried out by isolating the reaction vessel from the N_2 carrier flow, after the addition of HCl and introducing the CO_2 into the carrier stream after a fixed reaction time.

Times between 0.6 and 2 min were tried and, as can be seen in the inset in Fig. 5, an increase in the reaction time leads to an increase in the peak height and a decrease in the peak width. However, there is no variation of the peak area, hence the analytical sensitivity remains constant or is slightly lowered, probably owing to small leaks of CO_2 through the manifold connections. Therefore, in order to obtain as reproducible data as possible, it is recommended to work in the continuous flow mode after the injection of HCl using a constant flow of N_2 to introduce the evolved CO_2 continuously into the measurement cell.

Table 3. Effect of water volume added to samples, before acidification, on vapour phase FTIR determination of carbonate in sediments. Experimental conditions: 10 mg of $CaCO_3$ or sediment, 1 ml of 0.25 M HCl, 13 ml reactor volume, 40 °C reactor temperature and 120 ml min^{-1} N_2 flow rate. Areas, expressed in arbitrary units, were measured from the absorbance in the wavenumber range 2500–2150 cm^{-1} and the standard deviation values correspond to three independent measurements. Sampling frequency was established from the peak width

	$CaCO_3$		Sediment	
Water volume/ml	Area ± s_{n-1}	Sampling frequency/ h^{-1}	Area ± s_{n-1}	Sampling frequency/ h^{-1}
0	19.3 ± 0.7	40	8.1 ± 0.3	46
5	19.6 ± 0.3	20	7.7 ± 0.4	30
1	20.9 ± 0.3	20	8.5 ± 0.3	24
2	21.4 ± 0.3	20	7.8 ± 0.1	20
3	20.9 ± 0.4	20	8.2 ± 0.3	20

Table 4 Effect of sample mass on vapour phase FTIR determination of carbonate in sediments. Experimental conditions: 3 ml 0.4 M HCl, 13 ml reactor volume, 40 °C reactor temperature and 40 ml min^{-1} N_2 flow rate. Areas, expressed in arbitrary units, were measured from the absorbance in the wavenumber range 2500–2150 cm^{-1} and the standard deviation values correspond to three independent measurements

Sample mass/mg	Area ± s_{n-1}	Sampling frequency/h^{-1}
5	15.7 ± 0.8	20
10	27.8 ± 0.5	20
20	52.3 ± 0.7	20
40	99.0 ± 1.3	20
60	151 ± 4	20

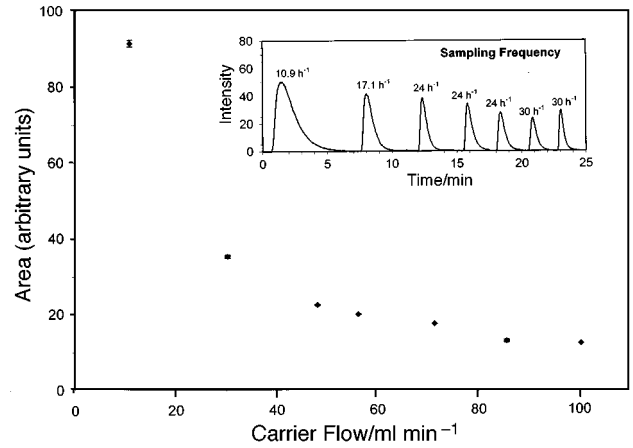

Fig. 4 Effect of the N_2 carrier flow rate on vapour phase FTIR carbonate determination. Inset: peaks corresponding to the wavenumber range 2500–2150 cm^{-1} obtained for 10 mg of sediment using different carrier gas flow rates. Experimental conditions: 10 mg of sediment sample, 1 ml of 0.25 M HCl, 13 ml reactor volume and 40 °C reactor temperature. Areas, expressed in arbitrary units, were measured from the absorbance in the range 2500–2150 cm^{-1} and the standard deviation values were obtained from three independent measurements.

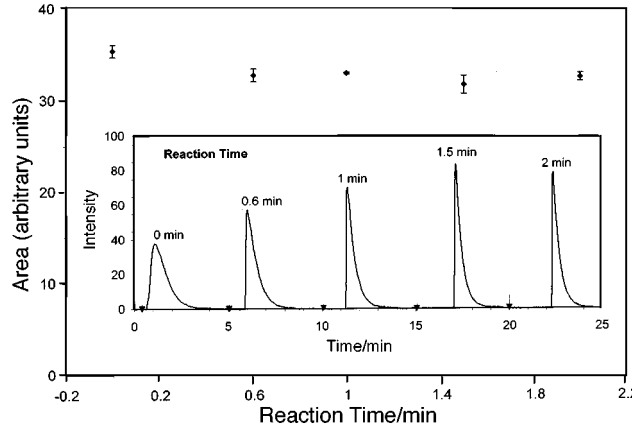

Fig. 5 Effect of the reaction time on vapour phase FTIR determination of carbonate. Inset: each peak corresponds to the measurement of CO_2 evolved from a separate sample of 10 mg of $CaCO_3$. Arrows indicate the injection of HCl. The assays were carried out on different $CaCO_3$ portions weighed in different glass vials, which were installed separately in the manifold. Experimental conditions: 10 mg of $CaCO_3$, 1 ml of 0.25 M HCl, 13 ml reactor volume, 40 °C reactor temperature and 32 ml min^{-1} N_2 flow rate. Areas, expressed in arbitrary units, were measured from the absorbance in the range 2500–2150 cm^{-1} and the standard deviation values correspond to three independent measurements.

Determination of carbonate in natural samples

The developed vapour-generation FTIR procedure was employed to analyse six natural sediments and two sewage sludge samples, containing different carbonate concentrations from 23 to 78% m/m (expressed as calcium carbonate). The values obtained were compared with those found by a back-titrimetric reference method,[1] and results are summarized in Table 5, which gives the average values ± the standard deviation corresponding to three independent analyses of each sample.

The regression between values found by the developed procedure (y) and those obtained by the reference method (x) provided the regression equation $y = (-2.6 \pm 1.9) + (1.01 \pm 0.04)x$, with a regression coefficient $r = 0.996$. This regression clearly indicates that the developed procedure does not require any blank correction, because the intercept of this line is statistically comparable to zero,[21] and it does not have constant relative errors, the slope being statistically equal to unity.

Analytical figures of merit

The main analytical characteristics of the method were established from typical calibration lines, obtained under the optimum experimental conditions and from the analysis of natural samples.

A typical expression for a calibration obtained up to 16 mg of $CaCO_3$ is $A = (-1.4 \pm 1.4) + (5.95 \pm 0.14)\ m$, with $r = 0.996$, where A is the area of the transient peaks and m the mass of $CaCO_3$ (mg), and from this, and taking into consideration the repeatability of blank measurements, a limit of detection of 0.2 mg of $CaCO_3$ can be established for a probability level of 99.6%.

The precision of carbonate determination in natural samples of sediments can be established from the relative standard deviation (RSD) of three independent analyses and, as can be seen from the data in Table 5, an average RSD of $< 2\%$ was obtained. The sampling frequency of the method is 15 h^{-1}, including the time required for the installation of glass sample vials in the manifold.

Table 5 Results obtained for the determination of carbonate in sediment samples by vapour phase FTIR spectrometry and by a reference titrimetric method.[1] Experimental conditions: 20 mg of sample, 1 ml of 0.4 M HCl, 40 °C reactor temperature, 13 ml reactor volume and 50 ml min^{-1} N_2 flow rate.

	Carbonate (% m/m $CaCO_3$)	
Sample	Found ± s_{n-1}	Reference ± s_{n-1}
Sediment 1	34.4 ± 0.5	38.6 ± 1.0
Sediment 2	33.8 ± 1.3	36.0 ± 1.9
Sediment 3	50.9 ± 0.5	50.6 ± 1.2
Sediment 4	76.1 ± 3.0	78.0 ± 1.2
Sediment 5	22.7 ± 0.4	23.4 ± 0.6
Sediment 6	33.6 ± 0.3	37.5 ± 0.7
Sewage sludge 1	52.2 ± 1.0	53.1 ± 1.4
Sewage sludge 2	48.9 ± 0.8	51.4 ± 0.9

Conclusion

This work confirmes the applicability of the vapour phase generation methodology for the FTIR analysis of solid samples without the need for a preliminary treatment of samples and offers a good alternative for the direct determination of total carbonate in sediment samples.

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