

# A flexible method of carbonate determination using an automatic gas analyzer equipped with an FTIR photoacoustic measurement chamber

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A Fourier transform infrared spectrometer was employed to determine automatically the total inorganic carbonate (TIC) in solids and waters, based on active photoacoustic absorption of infrared light by carbon dioxide. A 2.0 l reactor, connected to the spectrometer, is immersed in water-bath at 20 °C. After purging with pure N<sub>2</sub>, 5 ml of 0.5 mol l<sup>-1</sup> HClO<sub>4</sub> are injected into 50 ml of solid suspension or solution with continuous stirring. The specific absorption of infrared light by the CO<sub>2</sub> evolved induces corresponding fluctuations of temperature and pressure in a measurement chamber. Accordingly, photoacoustic signals, with frequencies dependent on the absorbed wavelengths, are generated and measured by the chamber microphones in the form of an absorption spectrum and concentration. For solids, the method exhibits a linear response up to 120 mg of CaCO<sub>3</sub> with a detection limit of 0.02 mg; in the case of waters, these figures of merit are 36.4 mmol l<sup>-1</sup> and 3 µmol l<sup>-1</sup> NaHCO<sub>3</sub>, respectively. Since proton consumption by TIC in clay minerals may commonly influence the evaluation of surface acid–base properties, the methodology was applied to determine TIC in three natural illite samples of different origins. In addition, some potential interferences and modifications of this method are discussed.

## Introduction

Total inorganic carbonate (TIC), commonly existing in solids (*e.g.*, rock, soil and sediment) and fluids (*e.g.*, natural and waste waters), may have a notable influence on the regulation of acid buffering capacity in these media. In addition, proton consumption by TIC in natural clay minerals during addition of acid can cause errors in the estimation of surface acid–base characteristics, derived from the results of potentiometric titrations.<sup>1</sup> Furthermore, the measurement of total organic carbon (TOC), an important index of water quality, can be implemented by TIC methods in combination with wet chemical oxidation of samples pre-treated by acidification.<sup>2,3</sup>

On the basis of different mechanisms, numerous methods have been developed for the determination of carbonate in various samples. Most current procedures focus on water samples, some relevant techniques including Fourier transform infrared spectroscopy<sup>4</sup> and passive acoustic emission.<sup>5</sup> In addition, flow injection systems, using acoustic wave impedance sensors<sup>3</sup> and conductimetric detectors,<sup>6,7</sup> have also been applied to practical measurements. However, progress in the direct analysis of geological samples is relatively slow, mainly involving the ‘carbonate bomb’ technique,<sup>8</sup> two routine methods based, respectively, on a pH measurement and a gravimetric procedure,<sup>9</sup> gas chromatography,<sup>10</sup> ion exchange resins,<sup>11</sup> near-infrared reflectance analysis and attenuated total reflectance FTIR spectrometry,<sup>12,13</sup> and also electron microprobe analysis.<sup>14</sup> Nevertheless, some limitations, such as non-linear calibration, low sensitivity and poor reproducibility, still remain.

Photoacoustic spectroscopy (PAS), belonging to the active acoustic emission methods,<sup>5,15</sup> employs the following excitation means to produce the analytical signal. Broadband IR radiation is modulated to generate a time-varying signal by passage through a modified Michelson interferometer. A laser diode and detector constitute a reference system to trigger and

synchronize sampling of the interferograms produced. Subsequently, the IR radiation reflected from the interferometer output mirror enters a measurement chamber. Meanwhile, the pump draws and renews the gas sample through a pair of air filters, then the sample is hermetically sealed in the measurement chamber by closing the inlet and outlet valves. The selective absorption of IR radiation by the gas sample creates internal temperature fluctuations, and therefore alteration of corresponding pressure (*i.e.*, an acoustic signal). This can be detected, by two sensitive microphones mounted on the chamber wall, in the form of electrical signals proportional to the absorption intensities. After filtration, analogue/digital (A/D) conversion and Fourier transformation, both absorption spectra and concentration values based on user-defined filter band(s) can be obtained. The photoacoustic frequencies depend on the wavelengths of the light absorbed by the gas sample, and the variations in IR intensity are recorded by a sensor for energy normalization of all measured spectra. Some photoacoustic analyzers based on this mechanism have been made in practice.<sup>16,17</sup>

In this preliminary work, we further utilized such an instrument to determine directly the TIC existing in solids and waters. Moreover, the reaction kinetics can be monitored by built-in time history records, which are conducive to ascertaining visually the achievement of reaction equilibrium. To our knowledge, there are very few practical studies based on this technique in particular.

## Experimental

### Reagents

All chemicals used in the experiments were of analytical-reagent grade or better. A 0.04 mol l<sup>-1</sup> stock standard solution

of sodium hydrogencarbonate was freshly prepared using boiled, de-ionized water prior to the actual measurements, and sealed during use to decrease the influence of atmospheric  $\text{CO}_2$ . Perchloric acid ( $0.5$  or  $1.0 \text{ mol l}^{-1}$ ) was utilized to generate carbon dioxide. The purity of  $\text{N}_2$  for purging was  $>99.995\%$ . Powders of calcite and sodium hydrogencarbonate were dried at  $105$  and  $110^\circ\text{C}$  overnight, respectively, and stored in a desiccator.

## Apparatus

The configuration of the manifold reactor is illustrated in Fig. 1. The gas analyzer (Brüel and Kjær, Type 1301), coupled with a patented photoacoustic measurement chamber, is employed to determine the amount of carbon dioxide automatically. This versatile instrument is suitable for on-site determination or continuous monitoring of various gases within the detection wavenumber region  $4000\text{--}650 \text{ cm}^{-1}$ . The detection thresholds are gas dependent (typical values  $0.1\text{--}10 \text{ ppm}$ ). Additionally, the analyzer is characterized by high selectivity, which users can define up to three filter bands for each gas, and the filter bands with different weighted contributions are used as the integration limits of the measured absorption spectrum for determining the gas concentration. The extensive data handling capabilities allow the results to be displayed as either absorption spectra or concentration curves on the graphics screen. Furthermore, the device can store all the results on floppy disk and retrieve them later by a built-in disk drive. In this study, the set-up options for  $\text{CO}_2$  determinations were as given in Table 1.

## General procedure

The equipment first undergoes a zero-spectrum measurement, to compensate for the background signal in the chamber using pure nitrogen gas; then an indirect span calibration is conducted, by loading a reference spectrum from the data disk supplied by

the manufacturer, in order to evaluate the conversion factor for carbon dioxide with the filter band(s) specified in Table 1.

For solid standards, an exact amount of calcite (ranging from  $0.25$  to  $120.18 \text{ mg}$ ) was added to a  $2.0 \text{ l}$  flask containing  $50 \text{ ml}$  of de-ionized water. Water standards were prepared by serial dilution of the  $0.04 \text{ mol l}^{-1} \text{ NaHCO}_3$  solution ( $0.05\text{--}50.00 \text{ ml}$ ), then de-ionized water was added to bring the total initial volume to  $50 \text{ ml}$ . Subsequently, we started to purge the circuit with pure  $\text{N}_2$ , and the air was displaced through the bubbling pipe. The criterion of residual  $\text{CO}_2$  below  $4 \text{ ppm}$  (linear value) for  $15 \text{ min}$  was adopted as representing a stable baseline. Thereafter, we turned off the  $\text{N}_2$  input and fastened the bubbling tube immediately. A  $5 \text{ ml}$  volume  $0.5 \text{ mol l}^{-1} \text{ HClO}_4$  was then injected into the flask. The gas analyzer recorded the  $\text{CO}_2$  level in the circuit until the reactions were completed.

In the present study,  $50 \text{ ml}$  of de-ionized water were considered as the blank, its analysis being performed identically with the procedure described above. All final results were represented as linear concentration values of carbon dioxide (ppm, equivalent to partial pressure) *versus* amount of  $\text{CaCO}_3$  (mg) or concentration of  $\text{NaHCO}_3$  ( $\text{mmol l}^{-1}$ ).

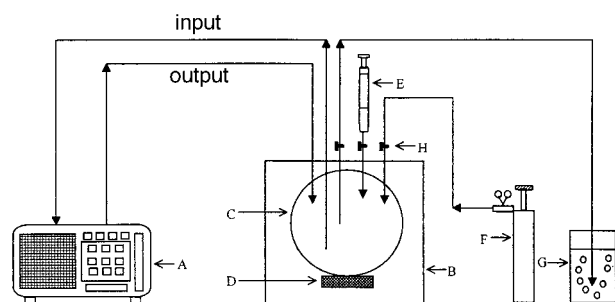
## Results and discussion

### Interferogram and final adsorption spectrum

Generally, the final measurement results can be shown by means of a spectrum (transmission or absorption), time history (instantaneous or time-average) and table (an overview of concentration values). In addition, the PAS interferogram represents the photoacoustic signal in the time domain, and provides the raw data for processing to produce the absorption spectra. This critical intermediate result, together with the corresponding absorption spectrum, is illustrated in Fig. 2.

### Monitoring of kinetics—time history records

One advantage of this method is that the user can watch the dynamic progress of  $\text{CO}_2$  generation. Time history records of some standard samples for solids and waters are shown in Fig. 3. All concentration values are normalized to the field temperature and ambient pressure, both of which are imported as parameters. It should be noted that each data point displayed on the time history curve is the average value over the period given in the 'averaging' field. In our case, a 'long average' of  $15 \text{ min}$  is selected for derivation of time history curves. In effect, this option can decrease some random fluctuations by applying a moving-average smoothing function.<sup>16</sup> Evidently, these approximately S-shaped curves include three stages: (1) the initial baseline representing the background absorption, namely residual  $\text{CO}_2$  in the circuit; (2) the rapid increase in the response, indicating the occurrence of strong carbonate decomposition; and (3) the curve gradually leveling off to a plateau, where the reactions tend to reach equilibrium.



**Fig. 1** Schematic diagram of the circuit devices for photoacoustic determination of carbonate. A, Gas analyzer; B, automatic thermostated water-bath; C, flask reactor ( $2.0 \text{ l}$ ); D, magnetic stirring devices; E, plastic syringe; F, purge gas (pure  $\text{N}_2$ ); G, beaker for bubbling; and H, taps. Input and output connection pipes (each  $0.5 \text{ m}$  long) are made of Teflon (PTFE). Other circuit routes are composed of silicone rubber tubing.

**Table 1** Multiple set-ups for the determination of carbon dioxide

Gas set-up	Measurement set-up	System set-up
Filter limits <sup>a</sup> : $2320\text{--}2305 \text{ cm}^{-1}$ Filter mass factor: 1.000 Molecular mass: 44.01 Conversion factor: 50.1 Reference level of $\text{CO}_2$ : 408 ppm Reference apodization: Hanning	Number of scans: 4 per sampling Sampling interval: 1 min Tube flush length: $0.5 \text{ m}$ Apodization: Hanning Attenuation: 10-fold Ambient pressure: <i>in situ</i> value <sup>b</sup>	Plot data file: HPGL format Print data file: spreadsheet format Floppy disk connection Normalization temperature: $20^\circ\text{C}$ Autoscaled spectra —

<sup>a</sup> Recommended by manufacturer in reference disk file. <sup>b</sup> The reading of a barometer was used.

## Sources of potential interferences

**Other acid-volatile components.** Since natural samples are usually composed of various constituents, in addition to carbonate, some acid-volatile components can also produce IR absorbing gases during sample acidification, such as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and  $\text{HCN}$ .<sup>6,7</sup> Water vapor may also exert an influence on the measurement. All these interferences can be eliminated effectively by employing appropriate specific filter band(s) for IR absorption. The range of filter bands for carbon dioxide used in this work (see Table 1) was proposed by the manufacturer, based on direct span calibration with pure  $\text{CO}_2$ .<sup>16</sup>

**Ambient pressure, relative humidity and temperature.** Since all concentration values are derived from the absorption spectra, which are, in turn, dependent on a single internal reference pressure, an incorrectly specified ambient pressure will result in spectral deviation. Therefore, we actually utilize an *in situ* barometer reading to establish this parameter. The system can maintain normal status up to 90% relative humidity at 30 °C (non-condensing), and automatically compensate for interferences due to fluctuations in temperature and IR intensity in the chamber.<sup>16</sup> Furthermore, all measurements were performed under conditions controlled by a water-bath thermostated at 20 °C, consistent with the normalization temperature

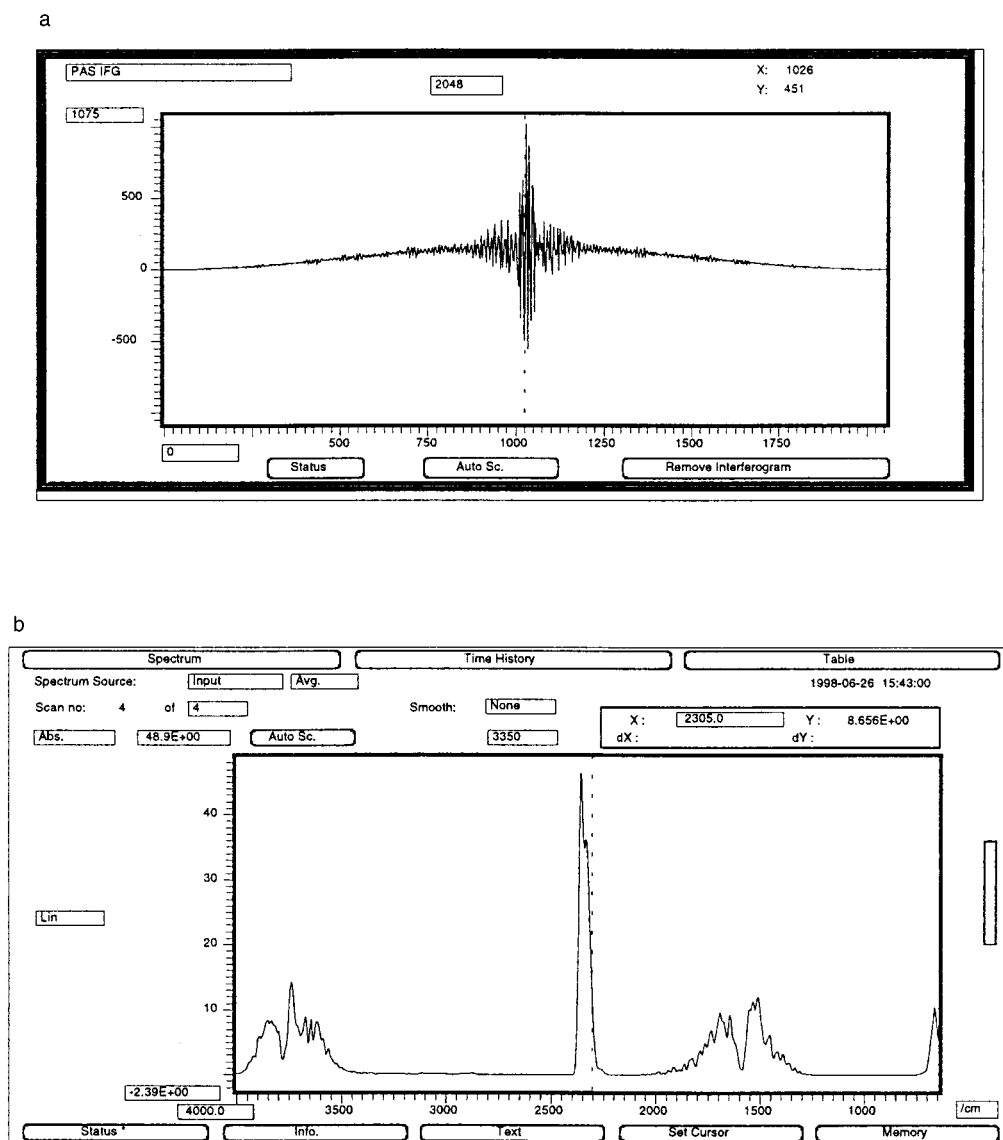
used for the system set-up (see Table 1); thereby, these influences can be neglected during general operation.

**Completeness of carbonate decomposition.** Two circumstances should be considered: one is when the reaction equilibrium is achieved; the other is whether the dosage of acid is sufficient to complete the conversion of carbonate to  $\text{CO}_2$ . The former can be determined by monitoring the variations in the amount of  $\text{CO}_2$  generated (*i.e.*, the time history records). We can ensure the latter by calculating the stoichiometric relationships or examining the final pH (usually lower than 3).

In our study, two exceptional cases occurred after we injected 5 ml of  $0.5 \text{ mol l}^{-1} \text{ HClO}_4$ : one was the  $36.4 \text{ mmol l}^{-1} \text{ NaHCO}_3$  standard solution (*i.e.*, the upper limit of the calibration range for waters), the final pH being above 4; the other was the illite sample gathered from Williams Town, its final pH lying between 5 and 6, which was probably due to the protons consumed by intensive dissolution and ion exchange of the illite.<sup>18</sup> Alternatively, 5 ml of  $1.0 \text{ mol l}^{-1} \text{ HClO}_4$  were used to satisfy the required pH.

## Calibration curves

Regression analysis reveals the linearity over the entire working range. The relevant equations are expressed as followed:



**Fig. 2** (a) PAS interferogram and (b) corresponding absorption spectrum of carbon dioxide. The abscissa represents the number of data points and the ordinate the signal level.

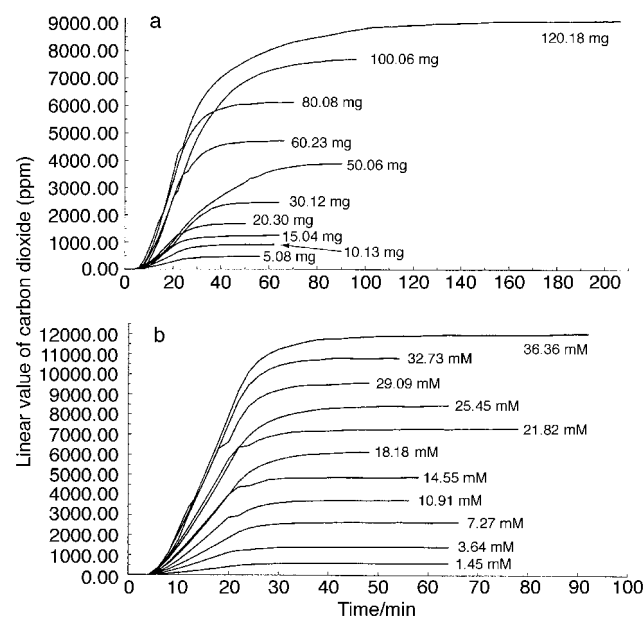
$$y = 75.8789x + 60.7182 \quad (r = 0.9998, n = 17) \text{ for solids} \quad (1)$$

$$y = 328.5818x + 85.7286 \quad (r = 0.9998, n = 17) \text{ for waters} \quad (2)$$

where  $y$  is the linear value of  $\text{CO}_2$  concentration (ppm),  $x$  denotes the corresponding amount of calcite in mg (0.25–120.18 mg) or concentration of sodium hydrogencarbonate in  $\text{mmol l}^{-1}$  (0.04–36.36  $\text{mmol l}^{-1}$ ) and  $r$  is the regression coefficient. Based on the standard deviation of the determinations of the system blank (*i.e.*, 50 ml of de-ionized water) and the slope of the calibration curve, we can derive the detection limits of 0.02 mg ( $3\sigma$ )  $\text{CaCO}_3$  for solids and 3  $\mu\text{mol l}^{-1}$  ( $3\sigma$ )  $\text{NaHCO}_3$  for waters. Although averaging a large number of scans can improve the signal-to-noise ratio with the square root of time, the accuracy of the results may deteriorate significantly, ascribable to the diffusion and release of the gas sample. Accordingly, we adopted four scans for each sampling as a compromise, and the actual effect was satisfactory.

### Application to real samples

Carbonate is commonly an important source of proton consumption during the acid treatment of natural clay minerals, and consequently this situation may produce some errors in the evaluation of corresponding surface acid–base properties, such as total surface site concentration, based on the results of potentiometric titrations.<sup>1,18</sup> In order to estimate the influence quantitatively, three illite samples collected from different origins were analyzed as model compounds. Duplicate time



**Fig. 3** Time history records of carbon dioxide produced by (a) solid and (b) water standards.

**Table 2** Information on different illite solids analyzed in this study

Property	WeiChang illite (WC)	LiuPanShui illite (LPS)	William Town illite (WT)
Origin	HeBei Province, North China	GuiZhou Province, South China	Mount Lofty, Adelaide, South Australia
Geologic time-scale	Permian period	Cretaceous period	Late Proterozoic period
Particle size after grinding	< 53 $\mu\text{m}$	< 53 $\mu\text{m}$	< 53 $\mu\text{m}$
Sample preparation	50 ml of 20 g $\text{l}^{-1}$ stock suspension with vigorous stirring	50 ml of 20 g $\text{l}^{-1}$ stock suspension with vigorous stirring	50 ml of 20 g $\text{l}^{-1}$ stock suspension with vigorous stirring
Acid solution added	5 ml of 0.5 $\text{mol l}^{-1}$ $\text{HClO}_4$	5 ml of 0.5 $\text{mol l}^{-1}$ $\text{HClO}_4$	5 ml of 1.0 $\text{mol l}^{-1}$ $\text{HClO}_4^a$
Total inorganic carbonate measured in duplicate	5.74/5.72 mg $\text{CaCO}_3$ in 1 g dry sample	0.82/0.88 mg $\text{CaCO}_3$ in 1 g dry sample	3.66/3.73 mg $\text{CaCO}_3$ in 1 g dry sample

<sup>a</sup> Since some hydrogen ions were consumed by dissolution and ion exchange, the final pH was about pH 6 using 5 ml of 0.5  $\text{mol l}^{-1}$   $\text{HClO}_4$ , so we used 5 ml of 1.0  $\text{mol l}^{-1}$   $\text{HClO}_4$  instead.

history records of TIC determination for each of the samples are illustrated in Fig. 4. Other details, concerning sample preparation and analytical data, are summarized in Table 2.

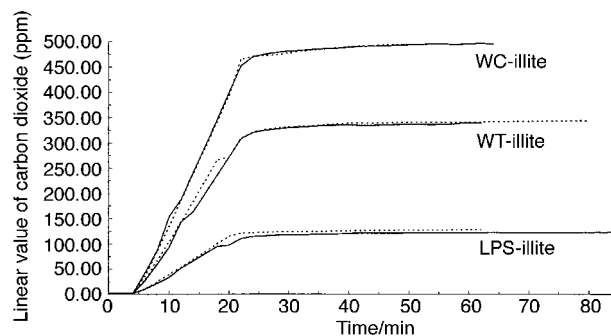
One disadvantage of this method is the relatively long time necessary to purge out the residual  $\text{CO}_2$  inside the circuit and the chamber, before commencing the analysis of a new sample. Since a high-pressure stream of  $\text{N}_2$  will damage the highly sensitive microphones, this limitation restricts the frequency of sample renewal to some extent. As for the gas analyzer, a model measurement cycle may consist of the following time events: pump-time dependent on the length of flushing tube, stabilization time around 10 s, scanning time (16.5 s per scan) and processing time for data updating (9.5 s). Using our conditions (see Table 1), the whole interval is less than 2 min for each sampling, which includes the time for flushing the chamber.

Some possible modifications can be taken into account in future research: (a) changing the size of the flask in order to achieve a more sensitive response to low contents of carbonate in measured samples, by utilizing the 'headspace' effect of the gas volume,<sup>10</sup> (b) since the particle size may significantly affect the reaction rate and the reaction completeness, it is recommended that, to accelerate the procedure, the solid samples should be finely ground to powder and prepared as a slurry prior to measurement. Agitation is needed during the whole procedure.

Finally, it is possible for this method to accomplish the determination of total organic carbon (TOC) or total carbon (TC) in different samples after wet chemical oxidation with or without acidification pre-treatment. The theoretical relationship  $\text{TC} = \text{TIC} + \text{TOC}$  can be used to compare the calculated value of TIC + TOC with the actual determination of TC.<sup>3</sup>

### Conclusions

Based on the results of standard calibration and actual applications, photoacoustic absorption spectroscopy with FTIR



**Fig. 4** Monitoring  $\text{CO}_2$  generated from acidification of natural illites. The solid line corresponds to the first measurement and the dashed line to the duplicate.

spectrometry is a flexible method for reproducible analyses of solid and water samples. A rectilinear calibration relationship is valid over the whole range studied. In addition, the time history records can provide a visual means for monitoring both the reaction kinetics and the achievement of reaction equilibrium.

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