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Direct Measurement of Carbonate Content in Soil Samples by Means of CO Laser Infrared Photoacoustic Spectroscopy

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CO laser infrared (IR) photoacoustic spectroscopy (PAS) at 1801 cm^{-1} was used to determine the content of carbonate in various soils. The PA signal is linearly proportional to the content of carbonate within the 0–30% (w/w) range; the 2% (w/w) limit of detection (LOD) is adequate for the application in practice.

Index Headings: Carbonate content; Soil analysis; Infrared photoacoustic spectroscopy; CO laser.

INTRODUCTION

Inorganic carbonate in soils is found primarily as barely soluble alkaline-earth carbonates of calcite and dolomite; soluble inorganic carbonate occurs in highly sodic (alkali) soils of arid regions. As a dominant metallic component of carbonates in soil, calcium is a nutrient needed for the growth of plants, increases the pH factor of acid soils, and also has a beneficial effect on the development of the physical properties of soil, such as structural stability, hydraulic conductivity, and surface hardness.

Techniques currently available for quantitative determination of inorganic carbonates in soils include both spectroscopic and nonspectroscopic methods.[1] Among the latter category one should mention: (1) the dissolution of carbonate in acid and subsequent determination of evolved CO_2 gas by measuring its volume or pressure; (2) the neutralization of carbonate with acid followed by a back-titration of the excessive acid; (3) determination of Ca and Mg in an acid leachate; (4) determination of sample weight loss; (5) gas chromatography; (6) thermogravimetry; (7) differential thermal analysis; etc. With respect to spectroscopy, diffuse reflectance at near-infrared (NIR) and infrared (IR) wavelengths is often exploited; diffuse X-ray diffraction and atomic absorption spectroscopy are also used. For applications in practice, a method capable of accurately measuring carbonate content between 3% and 50% (w/w) in the soil is preferable.

Spectral features of carbonate in IR are characterized[2,3] by four major absorption peaks centered at 1087 cm^{-1} (v_1), 872 cm^{-1} (v_2), 1400 cm^{-1} (v_3), and 710 cm^{-1} (v_4), along with a weaker[4] peak at 1801 cm^{-1}. Broad bands near 10 000 cm^{-1} observed in reflectance spectra of carbonates are attributed[5] to the iron substituted for appropriate metal ion in the carbonate.

Due to their inhomogeneous character and the effect of light scattering, powders are difficult to study by conventional spectroscopic methods. Before qualitative IR spectra are examined in the transmission mode, the powders are usually pressed into transparent disks. On the other hand, reflectance spectra of diffusely scattering powders depend not only on their molar absorption coefficients but also on parameters such as the size and the shape of the particle, the packing density, the crystalline form, and the refractive index.

Laser-excited photoacoustic spectroscopy (PAS) is a technique suitable for measurement of optical absorbance in powdered samples.[6,7] The quantum yield for the radiationless transition and the transfer of heat by combined conduction through the solid and gas play a role in the generation process of the PA signal [transfer of heat from the sample to the gas (thermal term) and the expansion of interstitial gas (pressure term)]. In general, the PA signal from thermally and optically thick samples depends in a very complex manner on the scattering as well as on the optical and thermal properties of the sample.[8,9] More precisely, the size and the shape of the powder particle, the surface-to-volume ratio, the porosity (packing density, fineness of grain, compactness), a good thermal contact among particles, and other factors all play an important role in generation of the PA signal.

The main objective of the study described here was to evaluate the potential of the CO laser-excited PAS, for a direct, quantitative measurement (by exciting the carbonate band at 1801 cm^{-1}) of carbonate in various soils and to compare the results with those obtained by a more elaborate chemical technique that is frequently used in practice in soil science.

EXPERIMENTAL

The experimental apparatus comprised a step-tunable waveguide CO laser, a mechanical chopper (PTI 4000 Optical Industries), a homemade PA cell, and a lock-in amplifier (Stanford Research SR 850). A 02POA015 rhodium parabolical reflector (clear aperture 50 mm) from Melles Griot collects the laser radiation and focuses (*f* = 66 mm) it into the PA cell (Fig. 1) accommodated within a metal block mounted on the X-Y-Z stage. The diameter of the laser beam at the sample was about 4 mm. The sample holder of the PA cell is a semispherical cup (8 mm in diameter and 2 mm deep) made from a ZnSe flat. Laser radiation enters the PA cell through a 2 mm thick ZnSe top window. O-rings serve to isolate the cell (acoustically) from the environment. The distance between the powder surface and the rear side of the window is 300 μm. A 2 mm diameter channel (consisting of the

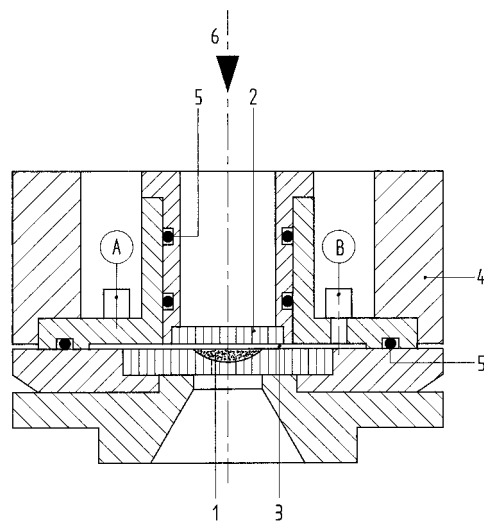* Author to whom correspondence should be sent.

FIG. 1. The transversal cross section of the PA cell showing the sample holder (1); entrance window (2); the air channel (3); housing of the cell (4); and O-ring seals (5). The laser beam (6) is reflected from parabolical reflector before entering the PA cell. Two electret microphones **A** and **B** are used in the differential arrangement.

13 mm long straight tube and 4 mm long bend) connects a miniature electret microphone (Model M32, Microtel, Amsterdam) (**B**) and the sampling volume. The overall sample-to-microphone distance is about 17 mm, which is longer than the thickness (450 μm) of the thermally active gas layer at 35 Hz; consequently the PA signal can fully develop. Another microphone (**A**) mounted in a different channel is used to measure the background signal. Such a differential arrangement allows for automatic subtraction of the background signal.

Soil specimens originating from different depths were collected in the village Mezölak in Hungary where the Transdanubian Mountains and Hungarian Little Plain meet. This region contains soils exhibiting great diversity in their organic, carbonate, and iron oxide content, as well as soil properties. The soils used here (brown forest soil, meadow soil, marsh soil, and Chernozem soil) with their corresponding color, texture, pH factor, carbonate content, amount of organic matter, and corresponding sampling depth are shown in Table I. The samples were first dried and then homogenized before their carbonate content was determined by means of the Scheibler chem-

ical method. Data obtained by chemical analysis were then used to calibrate the PA measurements.

RESULTS AND DISCUSSION

The Scheibler apparatus comprises the container (to mix soil and combine it with 10% hydrochloric acid) and a water-filled, calibrated U-shaped tube to measure the amount of generated CO gas. Depending on the expected content of carbonate, the container is loaded with 1 to 5 g of soil. A $CaCO_3$ weight equivalent to the unit volume of CO_2 found in the literature was corrected for atmospheric pressure and temperature of the laboratory air; the carbonate content was eventually expressed as a percentage of $CaCO_3$ in dry soil.

The only handling required for PA analysis of soil is to hand grind (agate pestle and mortar) a few milligrams of sample until, visually, a fine powder results; the size of the powder grain was not measured. A micro-spatula was used to load the PA cell and to level the soil surface. With the CO laser tuned to 1801 cm^{-1} (power 170 mW), the magnitude of the PA signal was measured at 35 Hz with 1 s for integration time of the lock-in amplifier.

Initially, three soil samples (from Table I) without carbonate were investigated; the PA signals thus obtained served as blank values. Three consecutive measurements were performed with each sample. The PA cell was then emptied and loaded again with soils containing carbonate. The complete series included soil specimens containing 3, 6.8, 7.3, 12.4, 20.1, 27.3, 28.2 and 40.1% (w/w) of carbonate. Since all measurements were performed at a single wavelength (i.e., 1801 cm^{-1}) of the CO laser, it was not necessary to normalize the lock-in signals.

Figure 2 shows the total PA signal (that includes the absorption of the blank) plotted against the content of carbonate in soil; each data point is the arithmetical average of three consecutive measurements. For the concentration range extending from 0 to 30%, the PA signal is a linear function of the carbonate content. The equation for the best linear fit reads: the PA signal (in mV) = $0.248 *$ concentration of carbonate (in % w/w) + 14.543 with $R^2 = 0.984$. The standard deviation for the best fit line is 0.8, which is equivalent to a 3% uncertainty in the carbonate concentration. On the basis of the ratio of a triple standard deviation (0.3 mV) and the slope 0.248 (mV/%) of the best fit in Fig. 2, one obtains 2% (w/w)

TABLE I. Characteristic features of soil specimens investigated in this study.

| Sampling depth (cm)	Color	Texture	pH	Carbonate content (%)	Organic matter (%)	Soil type
0–30	Grayish	Sandy loam	6.2	0	1.2	Brown forest
30–70	Light	Loam	7.2	0	0	Brown forest
0–25	Gray	Loam	8.0	0	2.4	Chernozem
25–50	Light gray	Loam	8.2	3.0	1.6	Chernozem
30–60	Light gray	Loam	8.2	6.8	1.8	Meadow soil
0–25	Black	Silty	7.6	7.3	40.0	Marsh soil
65–130	Reddish	Sandy loam	8.6	12.4	0	Marsh soil
95–150	Pale	Loam	8.5	13.2	0	Meadow soil
20–50	Brownish	Silty	7.2	20.1	55.8	Marsh soil
60–95	Pale	Loam	8.4	27.3	0	Meadow soil
50–80	Light	Loam	8.4	28.2	0	Chernozem
25–65	Blueish	Silty	8.6	28.2	0	Marsh soil
70–130	White	Sandy loam	8.6	40.1	0	Brown forest
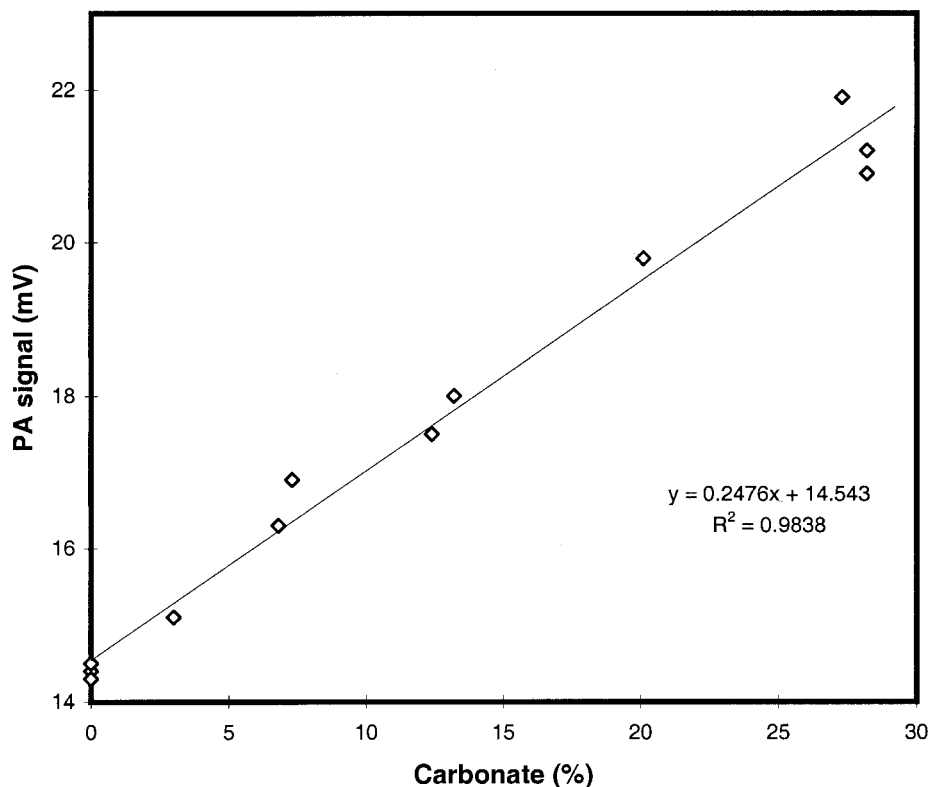
FIG. 2. The total PA signal (including the absorption of the blank) obtained from twelve test soils (Table I) containing varying amounts of carbonate. Data collected from the sample containing maximal (40.1% w/w) content were omitted for the reasons specified above. All measurements were performed at 35 Hz with the CO laser (170 mW) tuned to 1801 cm^{-1}.

carbonate as a limit of detection (LOD) for a given experimental setup. For soils containing more than 28.2% (w/w) carbonate, the PA signal tends to saturate as the optical penetration distance and thermal diffusion length become comparable.

In order to test reproducibility, PA measurements were repeated after three days. The equation of the new best fit line reads: PA signal (in mV) = 0.223 ∗ carbonate concentration (in % w/w) + 11.185 with R^2 = 0.973.

CONCLUSION

On the basis of the linearity of the calibration curve, we conclude that the PA method at 1801 cm^{-1} appears useful for quantization of carbonate levels (0–30% w/w) in selected soils from the Mezölak region. Despite a weak absorption cross section at 1801 cm^{-1}, the LOD of 2% (w/w) carbonate obtained by CO laser-excited PAS is of the same order of magnitude as that of the Scheibler method. An enhanced detection limit is anticipated at a CO_2 laser wavelength of 1087 cm^{-1} characterized by much more favorable absorption cross sections of carbonate. The PA technique offers an advantage in terms of sample handling (easy loading and cleaning of the PA cell), and it substantially reduces (compared to conventional wet techniques) the time needed for analysis. Apparently, grinding of the samples does not significantly affect determination of carbonate.

However, before we assert the general applicability of the PA method, additional experiments using soils originating from more than one region are needed to investigate the effect of variations in chemical composition and content, specific heat capacity, distribution of particles, etc. Although the spectral feature at 1801 cm^{-1} proved to be quantitative for our test samples, a wide range of other soils containing various types of carbonate (ranging, for example, from amorphous to flocked to crystalline; the effect of spiking and synthetic dilutions must be considered too) should also be studied to establish whether the intensity of the 1801 cm^{-1} spectral feature is morphology sensitive. The effect of charcoal or the coal dust present in soils from burned-over areas (either natural or intentional) on the PA signal is another important issue worth further investigation. Because the PA method uses a microphone as a wavelength-independent detector, this technique might prove useful for quantitative determination of other constituents present in the soil as well.

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