

PRELIMINARY ANALYSIS OF THE POSSIBILITY OF PHOTOACOUSTIC
SPECTROSCOPY IN PHOTOPHYSICS OF SOIL

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Abstract. In the present paper, an attempt was made to apply photoacoustic spectroscopy (PAS) i.e., the particular version of photothermal spectroscopy where a quantity of energy deactivated into heat is evaluated, to quantify photophysical processes in a soil sample. As light sources three diodes emitting at blue, green and red bands of visible light spectrum were used. The obtained dependences of photoacoustic signal amplitude versus light modulation frequency did not follow predictions of Rosenzweig-Gersho classic theory since an additional heat exchange mechanism characteristic of powdered solid samples was likely to occur. In visible light spectrum band, two independent transition processes, achievable to our apparatus, were distinguished. The principal parameters: the relative photoacoustic signal amplitude and characteristic times (1.28 and 0.64 ms) of each revealed process were obtained.

Key words: photoacoustic spectroscopy, photophysics, soil

INTRODUCTION

We know relatively little about the photophysical processes in soil (Orlov 2008). The electromagnetic waves in the form of solar radiation (direct or scattered) are a constant source of energy, especially great in equatorial zones. This energy is not only transformed into heat via thermal processes (including energy transfer and electron transfer pathways) but it also has direct photochemical effects. The effect of radiant energy on organic substances has been studied more thoroughly than on mineral substances. Under the effects of light, solutions of humic acids are more or less rapidly decomposed, being completely bleached by large doses of radiation (Brinkmann *et al.* 2003). The molecules of humic acids break down in the process into smaller units. On the other hand, other substances, for instance, some amino acids, are condensed under the effect of light to give rise

to dark products. Under natural conditions the photophysical and photochemical reactions involve only the uppermost soil layer, but due to the transfers of matter among various layers, the products penetrate into the subsoil.

In the present paper, we describe the application of photoacoustic spectroscopy (a version of photothermal spectroscopy where a quantity of energy deactivated into heat is evaluated) to quantify the photophysical processes in soil. The technique of photoacoustics has been successfully employed to study the thermal parameters of clays in Brazil (Alexandre *et al.* 1999, Manhaes *et al.* 2002), to estimate quantum yield of photophysical processes in various fulvic acids (Brucoleri 2000) and, in our group, soil surface evaporation (Żurawska *et al.* 2009) as well as photoacoustic spectra of different soil categories (Żurawska *et al.* 2010). At present, having recognised the limitations of photoacoustic signal generation attributed to both water evaporation and soil particle size distribution effects, an attempt was undertaken to detect photophysical processes in completely untreated samples (i.e., as collected). It seems that such an “in vivo” study ought to provide complementary data to traditional measurements performed on soil water solutions.

When a sample is exposed to modulated light, a part of the absorbed energy is emitted in the form of modulated heat resulting from the thermal deactivation of a sample. The part of the photoacoustic signal is reduced by a fraction equal to that part of the absorbed energy which can be used for photophysical and photochemical processes in the sample. By measuring heat emission in the presence or absence of a non-modulated saturating light background, the parameters (maximum of absorption, characteristic time, endothermic or exothermic character) of the processes can be evaluated. One of the advantages of the technique adopted is an opportunity to obtain a signal time-profile in the sample studied. By selecting different frequencies of the chopped light, one can obtain information about different time-resolved processes of various time constants.

MATERIALS AND METHOD

Soil samples used in this work originated from flower-pot plants growing in our laboratory. Only the upper 2 mm of soil was utilised for the measurements. Samples were air-dried. Chemical composition of samples was determined by the Regional Chemical-Agricultural Station in Gdansk (Tab. 1).

The photoacoustic signal measurement technique used is based on a diode (LED) as a light source which allows precise adjustment of the light modulation frequency with a very fine step. The measurements were done at three light bands (blue, green, red) (Fig. 1).

Pressure fluctuations in the closed-type photoacoustic cell (Fig. 2) were detected using a microphone (Type 4146, Brüel & Kjaer). The signal was selected and amplified with a lock-in amplifier (5105, EG&G). The output was connected to a PC-class computer for further data processing.

Table 1. Physicochemical properties of investigated soil

Parameter	Value	Microelements (totally)	
pH	7.2 ± 0.3	Cu	$24.0 \pm 3.2 \text{ mg kg}^{-1}$
phosphorus P_2O_5	$> 125 (312.2) \text{ mg (100 g)}^{-1}$	Zn	$389.8 \pm 49.5 \text{ mg kg}^{-1}$
potassium K_2O	$> 200 (447) \text{ mg (100 g)}^{-1}$	Mn	$274.6 \pm 32.1 \text{ mg kg}^{-1}$
magnesium Mg	$> 200 (212.8) \text{ mg (100 g)}^{-1}$	Fe	$8.1 \pm 1.0 \text{ g kg}^{-1}$
nitrogen N	$1.72 \pm 0.26\%$		
organic matter	$56.0 \pm 6.4\%$	Microelements (assimilated)	
dry matter*	$89.5 \pm 1.8\%$		
Particle diameter		Cu	18.6 mg kg^{-1}
		Zn	279.5 mg kg^{-1}
2.00-0.05	95.26%	Mn	188.2 mg kg^{-1}
0.05-0.02	2.95%	Fe	3.7 g kg^{-1}
0.02-0.002	1.79%		
< 0.002	0.00%		

all concentration values (except *) refer to dry matter, the values outside the measuring range are given in brackets.

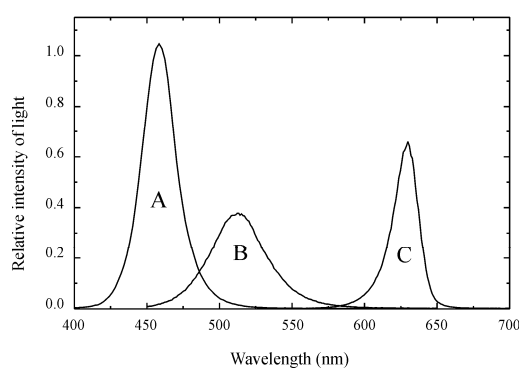


Fig. 1. Light emitting spectra of the LED used; A – blue, B – green, C – red

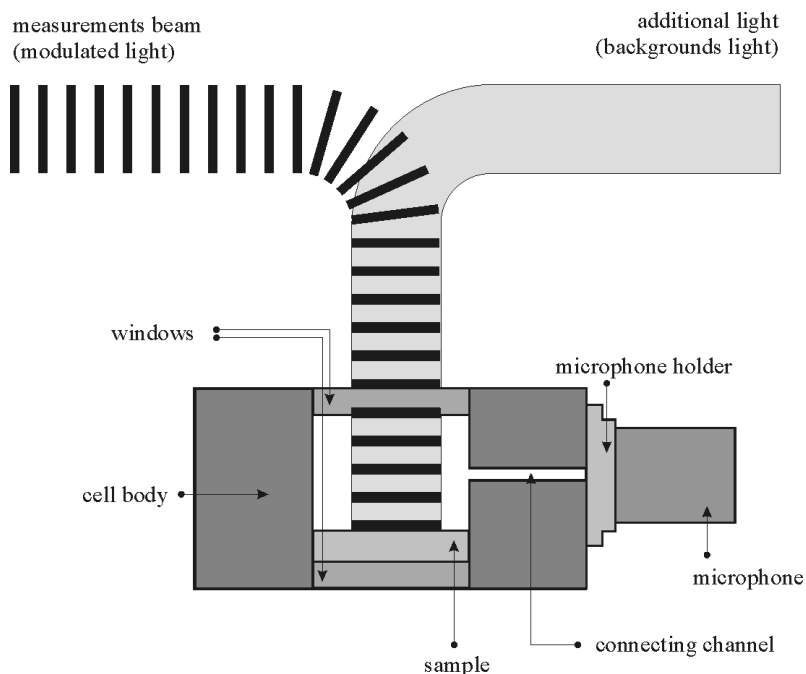


Fig. 2. Scheme of the closed-type photoacoustic cell

The application of a two-phase amplifier allowed the measurement of the characteristic time of the photoacoustic signal creation. It is widely used in fluorescence decay time studies (Lakowicz 1983). According to Lakowicz (1983), by using a fluorometer with a single modulation frequency (f), it is possible to determine the characteristic decay time (τ), assuming a one exponent decay from the equation:

$$\varphi = \text{arctg} (2\pi f\tau) \quad (1)$$

Although in our measurements the photothermal signal is studied instead of the fluorescence one, the same mathematical approach can be applied (Szurkowski *et al.* 2001).

For a thermally thick sample (our case), the time of signal creation results from two contributions (Lima *et al.* 1987). The first one corresponds to the non-radiative relaxation from excited states, whereas the second one is the contribution from the thermal diffusion in the optical-absorption depth. This latter time delay is a function of the optical-absorption coefficient and the sample thermal-

diffusion time. In the case of our samples, strongly absorbing, this component is relatively small. Additionally, we compare the changes in the photoacoustic signals with and without the non-modulated saturating light background and the time lag, if any, between the signals may be mainly attributed to the difference in the non-radiative relaxation times in soil samples.

RESULTS AND DISCUSSION

The amplitude of the photoacoustic signal versus modulation frequency ex-

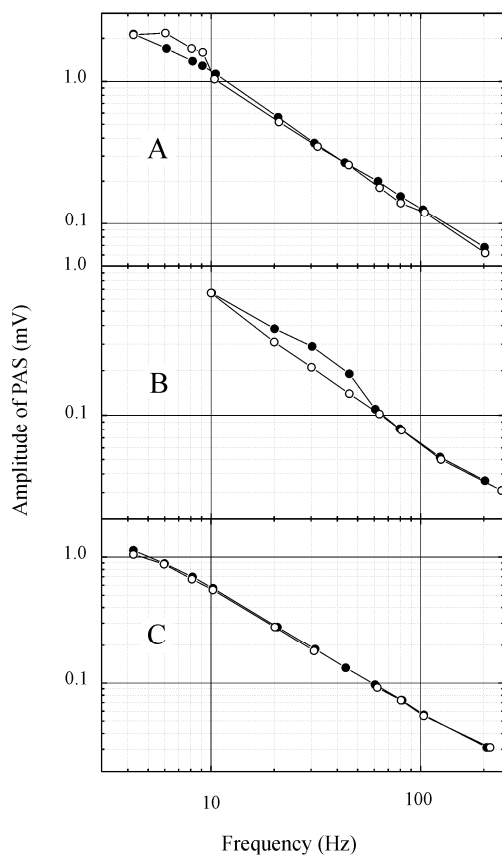


Fig. 3. Amplitude of the photoacoustic signal (PAS) versus modulation frequency for a soil sample. Measured signal data for LED excited modulated light alone (open circles) and with switched strong non-modulated white light (solid circles). Light band excitations; A – blue, B – green, C – red

cited by modulated LED diodes, at three light bands (blue, green, red) with and without additional non-modulated background light is shown in Figure 3. The signal plots did not exhibit strictly pure f^{-1} or $f^{-1.5}$ dependences as predicted by the model of Rosenzweig and Gersho (1976) for thermally thick, opaque or transparent samples. The obtained results suggest that an additional mechanism plays an important role in the generation of the photoacoustic signal. For powder samples (as is the case in the present work), non-radiative relaxation time is also affected by a contribution from heat exchange between the powder particles and the transducing gas in the PA cell. This heat exchange time depends not only on the shape of the particles but also on their size distribution. Additionally, non-modulated background light, unless directional influence on photoacoustic signal amplitude, changes the shape of the relation between amplitude and modulation frequency. The effect was exhibited in blue and green visible light excitation bands.

The situation, in our measurements is little similar to that found in well known differential thermal analysis (DTA) (Inczedy *et al.* 1998), a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to the same controlled programmed procedure. The record is the differential thermal or DTA curve; the temperature difference should be plotted on the ordinate with endothermic reactions downwards and temperature or time on the abscissa increasing from left to right. Multiple peak systems, showing shoulders or more than one maximum or minimum, can be considered to result from superposition of single peaks.

The difference between PAS with and without additional non-modulated background light versus modulation frequency, for all the LEDs used, is shown in Figure 4. These are well known correlations of optical and thermal transitions (for example – Endicott and Uddin 2001). Opposite to DTA plots, PAS is dependent not only on the energy provided (in our case instead of temperature the energy borne by light of particular wavelength appears) but also on modulation frequency related to the characteristic time of the process involved. Analyses of such a relation lead to conclude that in the studied light band we are concerned with at least two phenomena characteristic for one exothermic and another endothermic reactions.

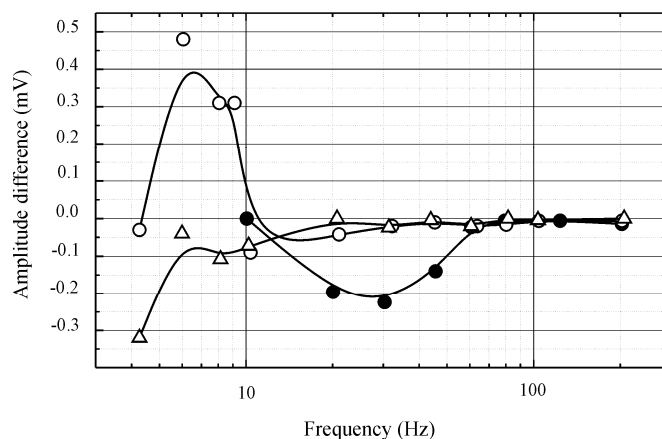


Fig. 4. Difference between photoacoustic signal amplitude with and without additional non-modulated background light versus modulation frequency. Light band excitations; ○ – blue, ● – green, △ – red

More information on characteristic times of the mentioned processes can be gained from Figure 5, where the signal phase differences are presented. Similarly to Figure 4, at least two individual processes can be distinguished, observed for

blue and green LED excitations. In opposite, for red LED data neither amplitude (Fig. 4) nor phase (Fig. 5) variations were observed.

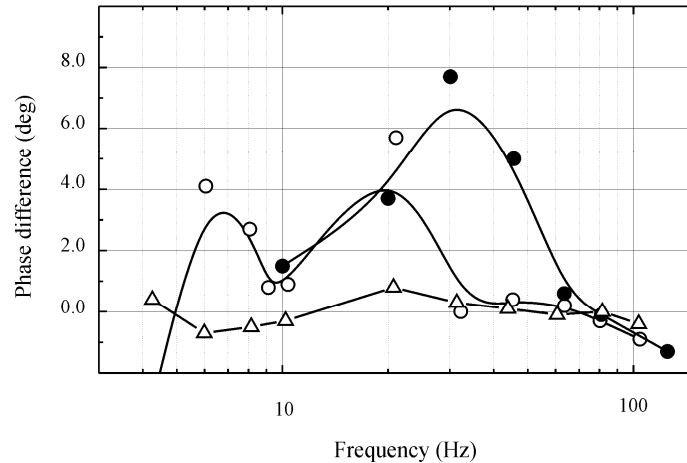


Fig. 5. Difference between photoacoustic signal phase with and without additional non-modulated background light versus modulation frequency. Light band excitations; \circ – blue, \bullet – green, Δ – red

Table 2. Parameters of the photo-processes measured by photoacoustic spectroscopy at a few light bands

LED	Amplitude difference			Phase difference			
	Frequency (Hz)	Amplitude (mV)	Time 1 (s)	Frequency (Hz)	Amplitude (deg)	Time 1 (s)	Time 2 (ms)
blue	6.5	0.4	0.15	6.5	3	0.15	1.28
				20	4	0.05	0.56
green	28	-0.21	0.04	30.2	7	0.034	0.64

Time 1 – time generation of PAS, Time 2 – influence of additional light to time generation of PAS.

Data obtained in these differential measurements are collected in Table 2. Modulation frequencies from the first columns correspond to resonance frequencies of the observed processes, for which maximal variations of both amplitude and phases of PAS signal were found. In addition, data placed in the third columns, giving the time required to signal generation, demonstrate a good agreement despite the kind of the measured parameter (amplitude or phase). The phase measurement performed for blue LED suggests the occurrence of two independent

photophysical processes in the spectra range of its emission. However, comparisons of the parameters characteristic of the second process with the parameters of the process taking place under green light LED illumination leads to the conclusion that rather the same process is observed for blue and green case light exposures. The most interesting data appears to be in the column where variations of the generation time are given under the radiation supplemented with non-modulated background white light. The observed changes within the range of 0.56-1.28 ms are attributed to an additional time required for the particular process being realised.

So far, we are not capable of pointing to the particular mechanisms responsible for the observed PAS signal variability in the studied soil samples. There are known several photophysical reactions taking place in the light energy region from 25000 cm^{-1} (400 nm) to 17000 cm^{-1} (600 nm). The visible region has been widely used for the identification of Fe oxides and hydroxides in soil (Manhaes *et al.* 2002). The Fe(II), taking part in Fenton reaction, is produced from photo-reduction of Fe(III) (436 nm) (Zepp 1992).

The studied soil sample is of a very particular structure and composition, soil humus accounting for as much as 56% of the sample dry mass (Tab. 1). As known, humus sorptive capacity is 15-36 times higher than that of the mineral part of soil. That leads to the formation of differentiated complexes within a soil structure. One of them are the metal-soil organic matter complexes (Protti *et al.* 2008). Spectrum bands where the additional background light effect on PAS is evidenced ought to be related to a metal-to-ligand charge-transfer (MLTC) mechanism, and resemble the spectra of analogous one-electron-ligand-reduction products. Chemical compounds contained in fertilisers absorb in the visible light band. The collected soil sample was high on manure and contained $1.72\pm 0.26\%$ of assimilable nitrogen. Moreover, visible light possesses enough strong radiative energy to induce photochemical reactions in compounds of NO_x type (Johnston and Graham 1974). As a result, a contribution of such photochemical reactions during light-soil interactions can not be excluded. leading to the observed PAS variability to a certain extent.

CONCLUSIONS

1. The obtained relations of PAS amplitude versus light modulation frequency did not follow the classic dependences of Rosencweig-Gersho theory since an additional heat exchange mechanism, characteristic of solid samples in a powdered form, is active.

2. Photoacoustic spectroscopy allowed one to reveal two photophysical processes characteristic of one exothermic and second endothermic reactions taking place in the studied soil samples. PAS technique provided the principal pa-

rameters characterising light-soil interaction phenomenon such as: the process threshold light energy, its relative intensity, and main characteristic processes time scales. Since PAS methodology is not an effective tool for dynamics studies of very fast and slow processes, other transition photochemical processes could likely escape detection. At the current stage of soil PAS studies, it is not possible to unequivocally link the discovered photochemical processes with the responsible source mechanism.

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WSTĘPNA ANALIZA MOŻLIWOŚCI ZASTOSOWANIA SPEKTROSKOPII FOTOKUSTYCZNEJ W FOTOFIZYCE GLEBY

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Streszczenie. W niniejszej pracy podjęto próbę zastosowania spektroskopii fotoakustycznej (PAS), t.j. szczególnej wersji spektroskopii fototermałnej, w której ocenia się ilość energii dezaktywowanej do postaci ciepła, dla ilościowej oceny procesów fotofizycznych zachodzących w próbce glebowej. Jako źródło światła zastosowano trzy diody emitujące w pasmach niebieskim, zielonym i czerwonym widma światła widzialnego. Uzyskane zależności amplitudy sygnału fotoakustycznego od częstotliwości modulacji światła nie były zgodne z przewidywaniami klasycznej teorii Rosencwaiga-Gersho, co mogło być spowodowane wystąpieniem dodatkowego mechanizmu wymiany ciepła, charakterystycznego dla sproszkowanych próbek glebowych. W paśmie widma światła widzialnego wyróżniono dwa niezależne procesy przejściowe, wykrywalne dla naszej aparatury. Otrzymano podstawowe parametry: względną amplitudę sygnału fotoakustycznego oraz czasy charakterystyczne (1,28 oraz 0,64 ms) dla każdego z tych wykrytych procesów.

Słowa kluczowe: spektroskopia fotoakustyczna, fotofizyka, gleba