CHEMISTRY LETTERS, pp. 783-786, 1980.

CORRELATION PHOTOACOUSTICS

Kenji KATO*, Shoichi ISHINO, and Yoshinori SUGITANI

Institute of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305

Cross correlation between the pseudo-random excitation signal and the resultant photoacoustic signal were recorded as a function of delay time τ. The correlation spectra showed peaks of transient phenomenon of heat generation for carbon black sample. This technique was found possible to observe the photoacoustic spectra at optionaly delayed time for spinach leaf sample.

Photoacoustic spectroscopy (PAS) enables to study the aspects of relaxation kinetic scheme in the mode of phase observation.[1] The kinetic aspects can be more definitely obtained by the introduction of the correlation method [2,3] into the photoacoustic measurement without comitting somewhat complicated analysis of phase information. The present study aims to realize the experimental combination of the correlation technique and the photoacoustic signal detection for measuring the thermal delay of the output signal of carbon black as well as observing the layer absorption of spinach leaf.

When a system is irradiated by a random excitation (white noise) F(t), the impulse response function (FID) of the system will be given as the cross correlation function $C(\tau)$ between the excitation input F(t) and the photoacoustic output G(t) as in the form of

$$C(\tau)=\frac{1}{2T}\int_{-T}^{T} F(t-\tau)G(t)\,dt,$$

where τ means the delay time in the reference signal with respect to the exciting input, T is a time span for the correlation integration. The correlation function will give a maximum at $\tau=\tau_0$ and after that will decrease monotonously since the degree of correlation will diminish with the increase of τ. Consequently the time τ_0 corresponding to the maximum $C(\tau)$ will reflect the time delay of the photoacoustic output signal with respect to the input excitation. This suggests that the measurement of τ_0 value would give an information concerning the thermal diffusivity in the sample studied.

Figure 1 shows the blockdiagram of the experimental setup for the present study. The exciting light from a 300W xenon lamp was modulated by a mechanical chopper so as to give an

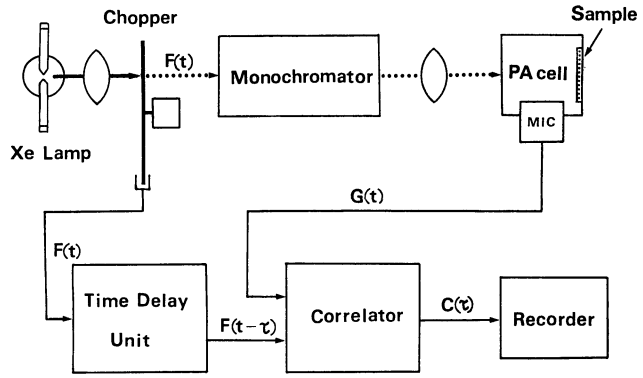

Fig. 1 Blockdiagram of correlation PAS system

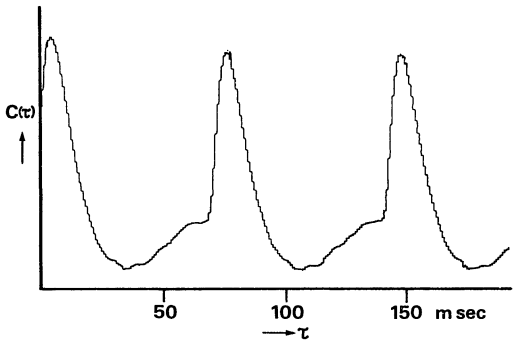

Fig. 2 Correlation PA spectra of carbon black powder as a function of τ at the irradiation of 475 nm

M-sequence pseudo-random excitation having 31 (2^5-1) on-off units in a period. The chopper used in this study has been made to contain two series of M-sequence for the experimental convenience. The output signal G(t) from the photoacoustic cell and the delayed reference signal F(t-τ) were introduced to the correlator, which gave the correlation function C(τ) in real time. The time delay unit was made by the use of a microcomputer (NEC, TK-80). The time resolution of the system is mainly limited as high as about 0.1 ms by the rotating speed of the mechanical chopper.

Figure 2 shows the correlation photoacoustic spectra of carbon black sample recorded as a function of the delay time τ. The spectra shows a maximum at $\tau=\tau_0$ and decays after that with the increase of delay time τ. The maximum time τ_0 corresponds to the time interval from a heat pulse generation at the surface layer of the sample to getting to a highest air pressure in the photoacoustic cell space. In the case of the carbon black sample the heat pulse generation is considered to occur at the uppermost surface layer, since the delay time τ_0 is almost constant of about 2 ms for each carbon black powder sample with different grain size.

The decay profile of C(τ) was approximately expressed as an exponential function $\exp[-(\tau-\tau_0) / \tau_R]$, with a fitting value of τ_R=6 ms. The τ_R value is considered to be dependent on the relaxation characteristics within the sample specimen and/or the properties of the inner-cell gas. Since the carbon black sample with different grain size gave the same τ_R value of about 6 ms, the origin of τ_R is probably attributed to the cooling characteristics of the inner-cell gas. The exact meaning of the parameters τ_0 and τ_R, especially the latter, is left for further study. The second and the third peaks in Fig. 2 are due to the correlations of the output signal with the respective second and third series of the random excitation. The peak to peak distance of 75 ms (Fig. 2) just coincides with the time interval between an M-sequence random exciation and the next

one, calculated from the rotating speed of the light chopper. The peak to peak distance proportionally changed with the time interval of the two M-sequence random excitations. Exactly the same decay profiles of the observed peaks are very much convincing the cause of the origin of them.

The τ_0 data similarly obtained for spinach leaves at four different irradiation wavelengths are shown in Table 1. The τ_0 values for the whole leaf are always larger than those of the leaf without cuticle and the cuticle itself. This is reasonably understood that the heat signal generated within the leaf takes more time to come out through the whole leaf than in the cases of the leaf without cuticle or the cuticle itself. The apparent peak widths observed for the whole leaf were fairly larger than for the components, as in the case of the delay time data.

Figure 3 shows the correlation spectra of a natural spinach leaf recorded as a function of the wavelength of the exciting light at a fixed delay time τ_D. The spectra thus obtained are considered as reflecting the photoacoustic signal from the thin layer at a certain depth of the spinach leaf corresponding to the given τ_D value. The spectra at smaller τ_D value will correspond to the layer

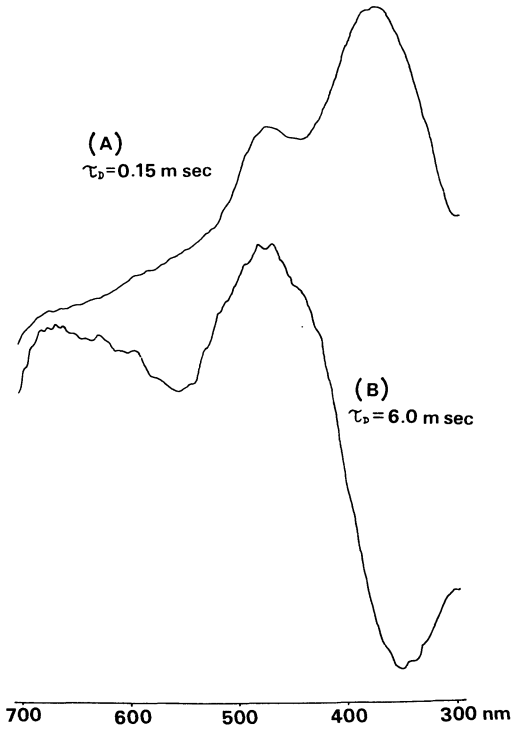

Fig. 3 Correlation PA spectra of the whole leaf of spinach as a function of wavelength at the fixed delay time: τ_D=0.15 ms (A) and 6.0 ms (B)

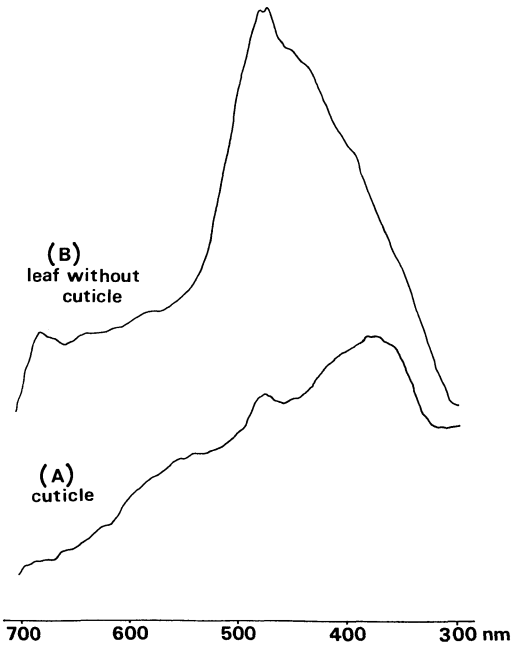

Fig. 4 Ordinary PA spectra of spinach leaf for the cuticle (A) and the leaf without cuticle (B)

Table 1. Delay time τ_0 of spinach leaves

Sample	Wavelength/nm			
	380	475	550	675
Whole leaf	1.4 (ms)	1.6 (ms)	1.4 (ms)	2.0 (ms)
Leaf without cuticle	1.2	1.1	1.1	1.1
Cuticle	1.1	0.8	0.9	0.9

near the surface, while those at larger τ_D value will correspond to the deeper layer of the spinach leaf. The spectra at τ_D=0.15 ms (Fig. 3) show a close resemblance to the ordinary photoacoustic spectra of the cuticle (Fig. 4A), while those at τ_D=6.0 ms (Fig. 3B) are very similar to Fig. 4B in peak positions. The large absorption at around 350 nm (Fig. 3A) contributes to protecting of the leaf body from UV light, while the large absorptions at around 470 nm and 670 nm are indicative of the active use of the solar energy for the photosynthesis.

*Present address: *National Chemical Laboratory for Industry, 1-1 Yatabe-cho Higashi, Ibaraki 305.*

References

1) M. B. Robin, "Optoacoustic Spectroscopy and Detection", ed. by Yoh-Han Pao, Academic, New York (1977), Chap. 7.

2) "Correlation function and Spectra (in Japanese)", ed. by T. Isobe, Tokyo Univ. Press, (1967).

3) M. H. Butterfield, G. F. Bryant and J. Dowsing, *Trans. Soc. Instr. Tech.* 13, 111(1967).

(Received April 11, 1980)