NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (12), 3733—3734 (1979)

Cell Design for Simultaneous Measurement of Photoacoustic and Fluorescence Spectra

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(Received April 3, 1979)

Synopsis. A simple and convenient sample cell has been designed for the simultaneous detection of photoacoustic and fluorescent signals. Spectral measurement of natural zircon, using the designed cell, is presented.

There has been a growing interest in photoacoustic spectroscopy as a method for the characterization of solid materials, in addition to the conventional methods including fluorescence spectroscopy. Since photoacoustic spectroscopy depends on the radiationless process of de-excitation, it is complementary to fluorescence spectroscopy which deals with the radiative process of de-excitation. A combination of the two methods, and particularly the simultaneous measurement of photoacoustic and excitation spectra will be of great use in the study of the de-excitation process.

In this note, a cell design for the simultaneous detection of photoacoustic and fluorescent signals is presented together with a spectral measurement on natural zircon $ZrSiO_4$.

Cell Design

Figure 1 shows the sample cell which is designed for the simultaneous detection of photoacoustic and fluorescent signals of powdered specimens. The cell is composed of a cell body and a sample base. On the sample base, the powder specimen is spread with the aid of water, acetone, or alcohol. In the measurement, the cell body and the sample base are tightly coupled using a packing material such as PARAFILM (American Can Co., USA). The air space in the cell is approximately 0.4 cm^3 in the coupled state. The electlet-microphone attached onto the cell body is connected to the sample position *via* a channel (2 mm$\phi \times$40 mmL). The amount of sample necessary for the measurement is approximately 0.05 g.

Figure 2 shows the photoacoustic signal intensity of carbon black at the output terminal of the microphone with respect to the chopping frequency. The spectrometer was set at 500 nm as a filter with a slit width of 3.0 mm. The photoacoustic signal intensity is inversely proportional to the chopping frequency in the range 7 to 320 Hz.

The photoacoustic signal is considered to be generated in the boundary layer of gas (air) surrounding the sample. The thickness of the layer is given as

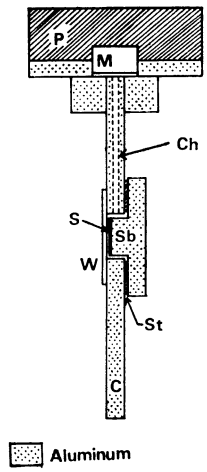

Fig. 1. Sample cell for simultaneous measurement of photoacoustic and fluorescent spectra. S: Sample, W: quartz window, St: sticky packing, Sb: sample base, Ch: channel, M: microphone, P: acoustic protector.

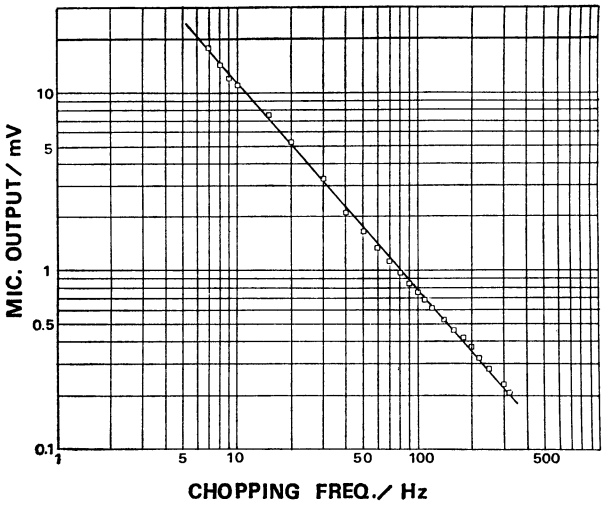

Fig. 2. Photoacoustic signal of carbon black at the output terminal of the microphone *vs.* chopping frequency.

$2\pi(2\alpha/\omega)^{1/2}$,[1] where ω is the chopping frequency and α, the thermal diffusivity of the gas. It is approximately 1 mm, at a chopping frequency of 100 Hz for example. This suggests that there is a limitation to the smallest air space in the coupled cell as well as to the lowest chopping frequency for effective detection of the photoacoustic signal. Beyond the limitation, losses

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occur in thermal generation, resulting in a reduction of the signal intensity.[2,3] The optimum chopping frequency was found to be approximately 100 Hz.

J. F. McClelland *et al.* have discussed the influence of scattered light in the photoacoustic cell.[4] They have suggested that the scattered light was absorbed by the microphone diaphragm and a resultant spurious signal was detected. In the sample cell designed here, the microphone is isolated from the sample, so that the obtained spectra are completely free from the scattered light, as seen in the Fig. 3.

Other properties of the designed cell are; i) the system of the cell body and the sample base are of a simple type, so that spare parts, especially of the sample base, can be readily provided, ii) the quartz sample base allows the observation of transmitted light, iii) since the sample base is inserted in the cell body, the air volume in the cell is very small contributing to the enhancement of signal intensity.

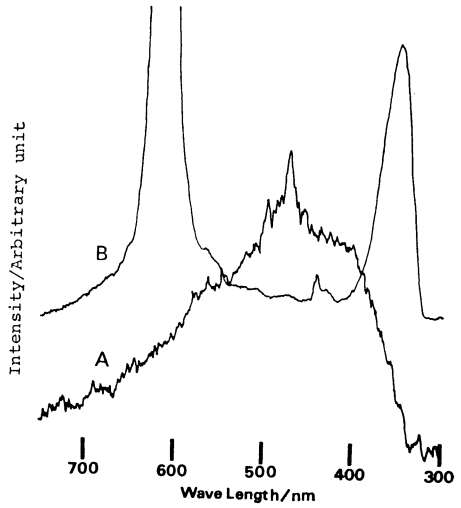

Fig. 3. Photoacoustic (A) and fluorescent excitation (B) spectra of natural zircon $ZrSiO_4$.

Simultaneous Measurement

Figure 3 shows the photoacoustic and excitation spectra simultaneously measured at room temperature for zircon $ZrSiO_4$ at a chopping frequency of 80 Hz. The scanning rate was 25 nm/min, and the slit of the spectrometer for incident light was 0.5 mm which corresponds to a resolution of 3 nm, and that for the emitted light was 1 mm. The time constant was 3 s for both of the lock-in amplifiers. Corrections for the light source intensity were not made, and the excitation spectra was monitored at 520 nm fluorescence output. The contrast between the photoacoustic and the excitation spectra is clearly seen and no additional signal due to the diaphragm was observed.

The authors wish to thank Prof. Kozo Nagashima of the University of Tsukuba, Institute of Chemistry, for his kind support during the course of this work.

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