Pergamon

Talanta, Vol. 41, No. 11, pp. 1861–1864, 1994

0039-9140/94 $7.00 + 0.00

PHOTOACOUSTIC SPECTROSCOPIC STUDIES ON THE SOLID PHASE CELL WITH A DIFFERENTIAL TYPE MICROPHONE USING A DIODE LASER AS RADIATION SOURCE

Junichi Shida[1], Hideaki Takahashi[1] and Kazuo Oikawa[2]
[1]Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Jonan-4, Yonezawa, 992, Japan
[2]Yamagata Research Institute of Technology, Numaki, Yamagata, 990, Japan

(*Received* 20 *January* 1994. *Revised* 25 *April* 1994. *Accepted* 27 *April* 1994)

Summary—The design and applications of the solid phase photoacoustic cell with a differential type microphone are described. This cell has higher sensitivity and reproducibility relative to a cell without a differential microphone. The method has been applied to the determination of phosphate ion in water samples. The detection limit for phosphate ion concentrated from 22.5 ml of sample solution on a membrane filter as molybdophosphate-*n*-dodecyltrimethylammonium bromide was 3.0 ng PO_4^{3-}/ml and the coefficient of variation for five measurements at 20 ng PO_4^{3-}/ml of phosphate ion was 3% using a diode laser (30 mW, 826 nm) as radiation source. The calibration graph for phosphate ion was linear over the range 5–50 ng PO_4^{3-}/ml.

Photoacoustic spectroscopy (PAS) has been used to study the optical and thermal properties of various opaque and transmitting condensed-phase samples.[1–3] The application of PAS has expanded in recent years as a result of the development of lasers with high monochromaticity and with high powers which significantly improves the detection sensitivity.[4–6] The authors applied PAS to the determination of phosphate as Molybdenum Blue species adsorbed on uniform anion-exchange beads.[7]

However, for the samples of low absorptivity, an accurate measurement of phase was difficult because of the acoustic background and the various structural factors of the photoacoustic cell and microphone.[8] Hence, we made an attempt at using a high sensitive differential type microphone for the photoacoustic cell in order to decrease the noise from various structural factors, and combined a diode laser head as radiation source in order to make a PAS apparatus compact for wide usage.

EXPERIMENTAL

Apparatus

The schematic block diagram of the photoacoustic spectrometer assembly is shown in Fig. 1. The light source was a 30-mW diode laser head (Melles Griot 06 DLL 507, wavelength 826 nm) controlled by diode laser drivers equipped with a thermoelectric cooler control (Melles Griot 06 DLD 003).

Measurement of the chopping frequency was accomplished with a function generator (Kenwood FG-273), and the photoacoustic signal was measured with an auto-phase lock-in amplifier (NF LI-574). Normalization of the photoacoustic signal to the lamp power was done with carbon black.

Photoacoustic cell

The photoacoustic cell, shown in Fig. 2, was machined from brass with a highly polished glass window. The differential type microphone (Knowles BW-1789, 8 × 5 × 2 mm) was located between the sample chamber and the reference chamber, sealed with a silicone rubber and electrically isolated from the brass cell. The photoacoustic signal was obtained by placing the molybdophosphate in the form of Molybdenum Blue precipitate on a membrane filter (Advantec Toyo, 13 mm in diameter, pore size 0.8 μm, filtration area 0.78 cm^2).

In the previous paper,[7] the photoacoustic cell was machined from brass with a single sample

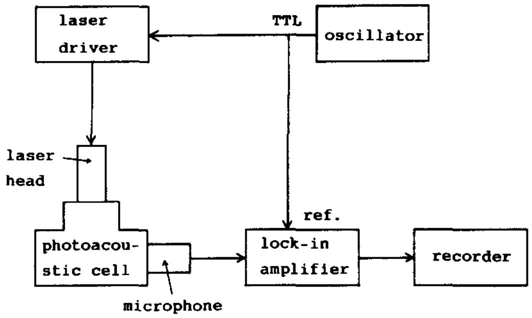

Fig. 1. The schematic block diagram of the photoacoustic spectrometer assembly.

chamber. The microphone (National WM-612, 0 8 mm) was sealed with an O-ring and electrically isolated from the brass cell. The cell used in this study had two chambers as described above. The former is termed cell A and the latter cell B. Cell B was used except when otherwise indicated.

Sample preparation

The samples as molybdophosphate–quaternary ammonium salt on a membrane filter were prepared following the previous paper.[9] Several reagents were added to a sample solution containing 0.1–1.0 μg of phosphate in a 25-ml polypropylene syringe. After the syringe was warmed to about 40°C, a filter holder with a membrane filter paper was attached to it, and the resulting precipitate was filtered off.

The precipitate as molybdophosphate-*n*-dodecyltrimethylammonium bromide and a membrane filter were dried under silica gel in a desiccator.

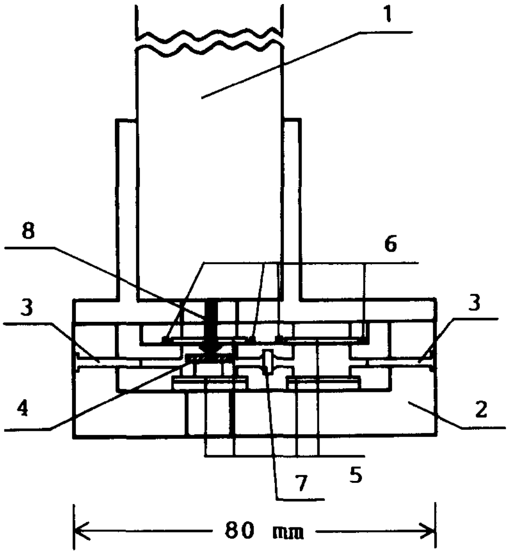

Fig. 2. Cross-sectional view of the differential type solid phase photoacoustic cell: (1) diode laser head, (2) cell body, (3) leak valve, (4) sample, (5) glass window, (6) O-ring, (7) differential type microphone, (8) incident light.

RESULTS AND DISCUSSION

Effect of source power and modulation frequency

The predicted proportionality between the amplitude of the photoacoustic signal and the source power was readily confirmed using both a carbon black and phosphate sample by varying the operating power (0.1–50 mW) of the diode laser head. Results were obtained utilizing a source power of 30 mW owing to consideration of the lifetime of the source.

For the modulation frequency, the signal magnitude decreases monotonically upon increasing the chopping frequency from 10 to 1000 Hz, and show a f^{-1} dependence, where f is the chopping frequency. This means that there is no effect from the system frequency characteristics within this frequency range. The chopping frequency was fixed at 39 Hz in further work so as to obtain the highest S/N ratio.

Effect of the distance between the sample surface and the window

In PAS of solid phases, the sample to be studied is placed inside a closed cell containing a gas, such as air, and a sensitive microphone. As the photoacoustic signal is ultimately governed by the magnitude of the thermal diffusion length of the solid phase,[10,11] the dependence of photoacoustic spectrometer sensitivity on the physical dimensions of sample cell was investigated for sizes larger than the gas thermal diffusion length. The relationship between the photoacoustic signal and the head space (l_g) is shown in Fig. 3. The sensitivity was the most

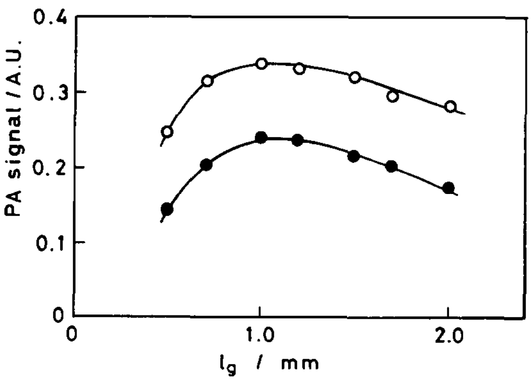

Fig. 3. Dependence of the distance between the sample surface and the window: PO_4^{3-}; —○— 200 ng/ml, —●— 20 ng/ml.

suitable when l_g was 1 mm. Therefore, the sample was set at the place where the length between the sample surface and the window was 1 mm.

Merit of differential type microphone

The differential type microphone (cell B) can be expected to decrease the noise of photoacoustic signal. To find the differential effect, the S/N ratio was investigated using a membrane filter. The patterns of photoacoustic signal are shown in Fig. 4. The values for cell A and cell B were 0.19 and 0.25, respectively. It was recognized that the S/N ratio of cell B increased about 13 times compared to that of cell A.

Reproducibility of the photoacoustic signal for the cells

Table 1 shows the results of reproducibility on the photoacoustic signal obtained from Phosphomolybdenum Blue species in cells A and B. As is obvious from Table 1, it becomes clear that cell B, with the differential type microphone, had a higher sensitivity and reproducibility than cell A.

Effect of moisture on the surface of sample

The dependence of the photoacoustic signal on the amount of water in the surface region of sample was measured. The surface of a filter paper (Toyo 5C, Ø 13 mm) was wetted with water by a capillary tube, and the filter paper was set quickly in the cell. After 5 min, the photoacoustic signal magnitude was measured. The results are plotted in Fig. 5. The photoacoustic signal magnitude increased in proportion to the amount of water until about 8 mg, and was constant over 8 mg of water. Although the magnitude of increase was the order of 1% compared to that of the phosphate sample at 0.5 μg, the surface of the sample was kept dry.

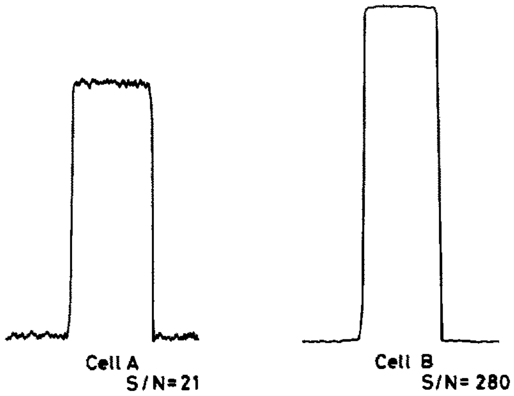

Fig. 4. Responses of Phosphomolybdenum Blue species in the photoacoustic signal.

Determination of phosphate ion in water samples

When 22.5 ml of a sample solution was used, the calibration graph obtained was linear over the range 5–50 ng PO_4^{3-}/ml. The detection limits of phosphate ion were 3.0 ng PO_4^{3-}/ml and the value was one-half compared with the detection limit (6.0 ng PO_4^{3-}/ml) of the method[7] based on

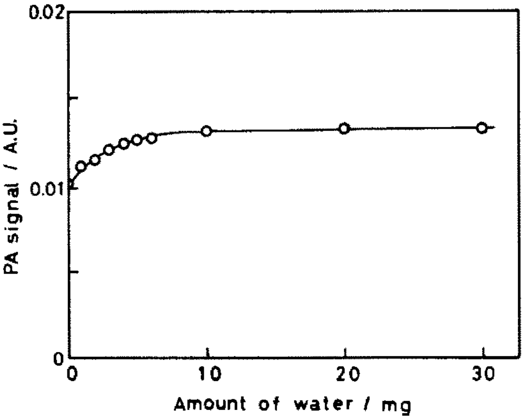

Fig. 5. Dependence of the amount of water on a filter paper.

Table 1. Reproducibility on the photoacoustic (PA) signal obtained from Phosphomolybdenum Blue species in the cells

Cell A		Cell B	
Average of PA signal *(A.U.)*	Relative standard deviation *(%)*	Average of PA signal *(A.U.)*	Relative standard deviation *(%)*
*0.190 ($n = 5$)	5.0	0.253 ($n = 5$)	3.0
†0.185 ($n = 3$)	6.3	0.248 ($n = 3$)	5.5

*The membrane filter was fixed in the cells.

†The membrane filter was turned for 45° on the same plane each time the PA signal was measured.

PO_4^{3-}: 20 ng/ml, n: number of measurements.

Table 2. Determination of phosphate ion in water samples

Water sample	PO_4^{3-} added	PO_4^{3-} found*	Recovery of added PO_4^{3-}	
	(μg)	*(μg)*	*(μg)*	*(%)*
Tap	None	0.46 (2.8)	—	—
	0.15	0.61 (2.5)	0.15	100
	0.30	0.77 (3.0)	0.31	103
	0.45	0.90 (3.2)	0.44	98
Rain	None	0.52 (2.6)	—	—
	0.15	0.68 (2.3)	0.16	107
	0.30	0.81 (3.2)	0.29	97
	0.45	0.97 (3.4)	0.45	100
Snow	None	0.38 (3.0)	—	—
	0.20	0.58 (2.5)	0.20	100
	0.40	0.76 (2.6)	0.38	95
	0.60	0.96 (2.8)	0.58	97
River	None	0.25 (3.8)	—	—
	0.20	0.44 (3.6)	0.19	95
	0.40	0.62 (3.7)	0.37	93
	0.60	0.82 (4.0)	0.57	95

Sample volume: 10.0 ml.

*Mean of five determinations; values in parentheses are coefficient of variation (%).

measuring the photoacoustic intensity of phosphate as Molybdenum Blue species adsorbed on anion-exchange beads using apparatus equipped with a xenon lamp (500-W) and cell A. The coefficient of variation for five measurements at 20 ng PO_4^{3-}/ml of phosphate ion was 3%. The proposed method was applied to the analysis of water samples and the results are shown in Table 2.

CONCLUSIONS

This work demonstrated that PAS with a diode laser as a radiation source can be successfully applied to the determination of ng/ml levels of phosphate ion in water samples, and that the space for assembly of apparatus was reduced to one-tenth in comparison with the apparatus[7] equipped with a xenon lamp. Further experiments are in progress in order to improve the apparatus, and should lead to a compact PAS apparatus for wide usage.

Acknowledgement—This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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