Several Factors Affecting the Detection Sensitivity of the Reaction Heat-Induced Optical Beam Deflection Method

Xing-Zheng Wu,*,# Hideki Kitatani, Katsumi Uchiyama, and Toshiyuki Hobo

Departmental of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03

(Received May 16, 1996)

In order to improve the detection sensitivity of the reaction heat-induced optical beam deflection method, the experimental factors that affect the detection sensitivity were investigated in detail. Firstly, different types of deflection detectors were compared. The experimental results showed that the bi-cell photodiode detector is most sensitive to the deflection signal. Secondly, the effect of the size of the reaction cell on the detection sensitivity was investigated. A small reaction cell gave a stable baseline and small noise in flow injection experiments, and thus gave a high detection sensitivity. Thirdly, the effects of the optical arrangements on the detection sensitivity were investigated. Focusing the probe beam close to the gold film/CCl_4 interface enhanced the detection sensitivity. Also, refocusing the deflected probe beam improved the sensitivity. Under the selected experimental conditions, the detection of the neutralization reaction between HCl and NaOH at sub-nanomol level became possible. Further improvements are also discussed.

The optical beam deflection (OBD) method[1,2] has been widely used for studying photothermal phenomena;[3,4] a mass diffusion process occurs in aqueous solution and the interfaces of an electrode/solution and polymer film/solution.[5—15] Recently, we investigated OBD induced by chemical reaction heat, and proposed a novel analytical method based on it.[16] In this method, a chemical reaction in aqueous solution occurs above the CCl_4 phase, and a probe beam is passed through the CCl_4 phase near to the water/CCl_4 interface. A part of the reaction heat of the chemical reaction is conducted to the CCl_4 phase, and thus, a temperature gradient is generated in the CCl_4 phase. This temperature gradient induces a refractive index gradient, which in turn induces a deflection of the probe beam. The amplitude of the deflection signal is applicable to a quantitative analysis of reactants or products in the reaction.[16—19] Also, the method can be applied for monitoring and analyzing a chemical reaction process.[20] Moreover, information concerning the one-dimensional distribution of a chemical reaction can also be obtained by the method.[18,23] This method is applicable to not only a batch experiment,[16,18] but also to a flow injection experiment.[17,19] It has been applied to neutralization reactions, redox reactions and enzyme reactions.

It is well known that the OBD method in photothermal spectroscopy (It is usually called photothermal beam deflection, (PBD))[1—4] is a highly sensitive method. In PBD, modulated excitation light is used to excite a sample, and a probe beam is applied to probe the temperature gradient, which is produced by a nonradiative relaxation process of the excited molecules of the sample. The PBD sensitivity depends on many factors, such as the power of the excitation light, the modulation frequency, the offset of the probe beam, and the focusing of both the excitation and probe beam. In general, a highly focused excitation beam with high power, an optimum offset between the probe beam and illuminated sample, and an optimum modulating frequency is selected so as to obtain the best ratio of the signal to noise (*S/N*). In spite of these factors influencing the detection sensitivity, a high sensitivity is usually easily achieved for PBD, since the signal is an alternating-current (a.c.) signal, which can be selectively detected by a lock-in amplifier. On the other hand, in reaction heat-induced OBD, since the deflection signal is not an a.c. signal, it contains many components with different frequency. Also, noise with different frequency are included in the signal. Therefore, the noise level is much higher than that in PBD, where only noise at the modulation frequency is picked up by the lock-in amplifier. The mixing and reaction processes also generate larger noise in the reaction heat-induced OBD. Another difference between the two methods is the size of the heat source. In PBD, the size of heat source is nearly equal to the illuminated area, usually from ca. 10 to ca. 100 μm. However, the size of heat source in the reaction heat-induced OBD is nearly equal to that of the reaction cell, usually about ~mm. Accordingly, the selections of the experimental conditions for the two methods are different.

In our early experiments concerning reaction heat-induced OBD, the water phase was placed directly on the CCl_4 phase.[16,17] It was found that the distance between the probe beam and the water/CCl_4 interface was an important factor for the detection sensitivity.[16] The closer the probe beam is to the interface, the greater is the deflection signal. A theoretical

Present address: Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, 3-9-1 Bunkyo, Fukui 910.

analysis of the reaction heat-induced OBD showed that the amplitude of the signal is proportional to the reciprocal of the distance between the probe beam and the interface.[22] Therefore, the probe beam should pass through the CCl_4 phase as close as possible to the interface. However, a disturbance of the interface caused by the addition of reactants generated a large noise near to the interface; thus, the probe beam could not be very close to the interface.[16] A further experiment showed that the disturbance could be greatly decreased by partitioning the reaction medium from the CCl_4 phase with a thin gold film.[18] When the reaction media is partitioned, the reaction heat is first transferred to the gold film, then to the CCl_4 phase. In this case, since the probe beam could be very close to the gold film, the detection sensitivity was improved.

In this work, we further investigated other factors that affect the detection sensitivity. The effects of detectors of different types, the size of the reaction cell, and the optical arrangements of the experimental system on the detection sensitivity were examined in detail, in both batch experiments and flow injection experiments.

Experimental

Experimental Setup: Figure 1 illustrates the experimental setup, which is similar to those reported before.[16—22] A He–Ne laser (wavelength: 632.8 nm, output power: 1 mW) provided the probe beam. The probe beam was focused on the reaction cell by lens 1. The deflection of the probe beam was detected by a deflection detector. A glass tube, with one end sealed by a thin gold film (thickness, 10 μm), was used as a reaction cell. The size of the reaction cell was changed by using glass tubes with different internal diameters. The reaction cell was immersed into another cell constructed from glass slide sheets. The cell was filled with CCl_4, above which water was added to prevent the evaporation of the CCl_4. The cell was placed on a X–Y–Z stage for adjusting the distance between the probe beam and the gold film/CCl_4 interface. The distance between the probe beam and the gold film was estimated to be less than 100 μm. After passing through the cell, the probe beam was focused onto the deflection detector by another lens 2.

Three kinds of deflection detectors were used in the experiments. They were a position sensor (C2399, Hamamatsu, Japan), a bi-cell photodiode (S2721-02, Hamamatsu, Japan), and the combination of a knife-edge and a photodiode (Fig. 2). The outputs of the detectors were monitored by a digital multichannel multimeter (SC7502, Iwatsu, Japan), and the data were recorded and treated using a personal computer.

A neutralization reaction between HCl and NaOH was used as a model reaction. In batch experiments, after a certain amount of HCl solution was first introduced into the reaction cell by a syringe, a certain amount of the NaOH solution was injected into the reaction cell by a microsyringe. If flow injection experiments, when the internal diameter of the reaction cell was larger than 2 mm, two Teflon® tubes (i.d.: 0.5 mm, o.d.: 1 mm) were immersed into the reaction cell, and were used as flow lines (Fig. 1B)). An aqueous solution of NaOH at a certain concentration was aspirated into the reaction cell by a pump. An aqueous solution of HCl at a certain concentration was injected into the flow line by an injector. When the internal diameter of the reaction cell was smaller than 2 mm, capillaries (o.d.: 150 μm, i.d.: 75 μm) were used as flow lines.

All of the reagents were used as received from Kantou Kagaku (Japan). The water used was deionizted water.

Results and Discussion

Comparison of Different Types of Deflection Detectors. Several kinds of deflection detectors have been reported. The most common ones are a position sensor,[24] a bi-cell photodiode,[5] and the combination of a photodiode and a knife-edge.[1,5,25] Although these detectors have been widely used in PBD, as far as we know no comparison has been reported. Here, we compare these detectors for the detection

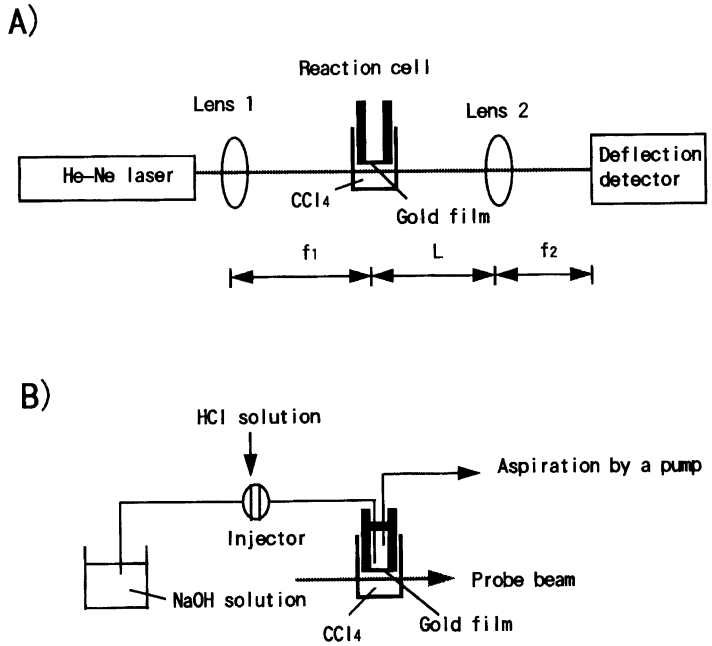

Fig. 1. Illustrations of the experimental setup (A) and flow injection system (B).

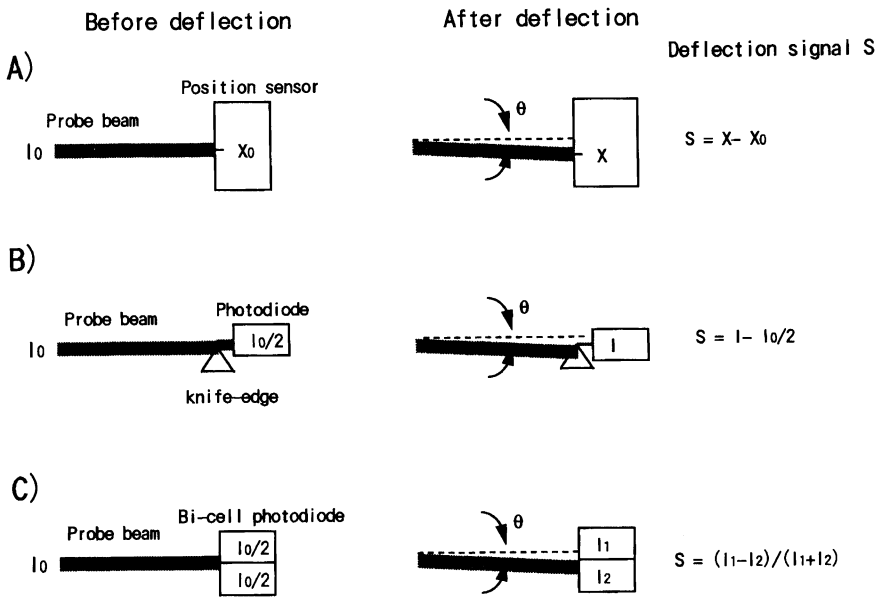

Fig. 2. Illustrations of the measurement principles for the deflection detectors of a position sensor (A), a combination of a photodiode and a knife-edge (B), and a bi-cell photodiode. I_0 is the intensity of the probe beam. In A), X_0, and X are positions of the light spot of the probe beam before and after deflection, respectively. In B), I is the intensity monitored by the photodiode after the deflection. In C), I_1 and I_2 are intensities monitored by the two photodiodes, respectively.

of reaction heat-induced OBD.

Figure 2 illustrates their measurement principles. The position sensor measures the position change of the light spot of the probe beam. For the case of the combination of a photodiode and a knife-edge, the knife-edge blocks one half of the probe beam; the other half is monitored by the photodiode. When the probe beam deflects, its intensity, monitored by the photodiode, is changed. The change in the monitored intensity is used as a deflection signal. For the case of a bi-cell photodiode, two photodiodes are placed close to one another. The probe beam is adjusted so as to ensure that the center of its intensity profile points to the area between the two photodiodes. When the probe beam deflects, the outputs of the two photodiodes are changed. The difference in the outputs between the two photodiodes has been used as a deflection signal.[5] In this work, the ratio of the difference to the sum of the outputs of the two photodiodes was used as the deflection signal (Fig. 2C). For the three kinds of detectors, accurate relationships between the measured signals and deflection angle θ are very complex. However, when θ is very small, the signals of the three detectors can be approximately proportional to θ.[5]

Figure 3 shows the experimental results for the three detectors. The S/N of the position sensor is the worst. The maximum *S/N* is obtained by the bi-cell photodiode. As shown in Fig. 2C, since the ratio $[(I_1-I_2)/(I_1+I_2)]$ of the difference (I_1-I_2) to the sum (I_1+I_2) of the outputs of the two photodiodes was used as a signal in the bi-cell photodiode detector, the drift and fluctuation in the probe beam intensity was corrected. Therefore, it is better than a detector comprising a photodiode and a knife-edge. Especially, for a light source whose output drift and fluctuation are severe, the bi-cell photodiode detector would be superior. Therefore,

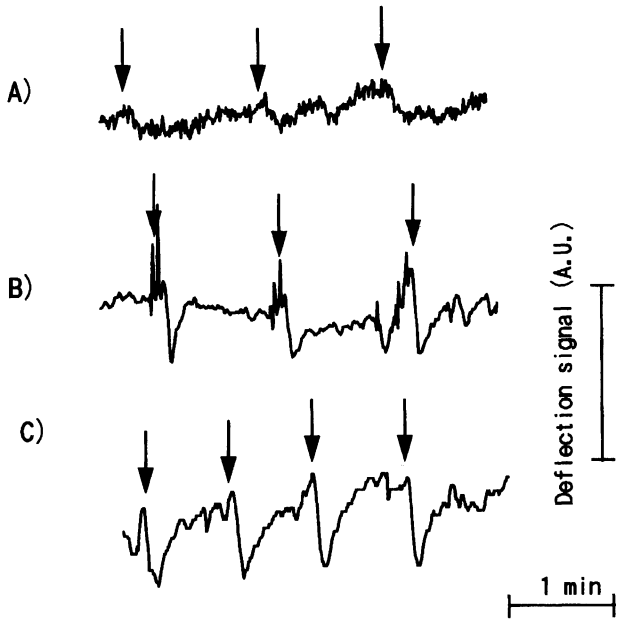

Fig. 3. Comparison of the deflection signals in a flow injection experiment for the detectors. A), B), and C) are results for the position sensor, combination of a photodiode and a knife-edge, and bi-cell photodiode, respectively. Arrows represent injections of 20 μl 0.01 M HCl solution into the flow line of 0.05 M NaOH solution.

in the following experiments the bi-cell photodiode detector was used.

Effects of the Size of the Reaction Cell on the Detection Sensitivity. In PBD, since the illuminated area of the sample in a cell due to focused excitation light is usually very small, the size of the cell has little influence on the

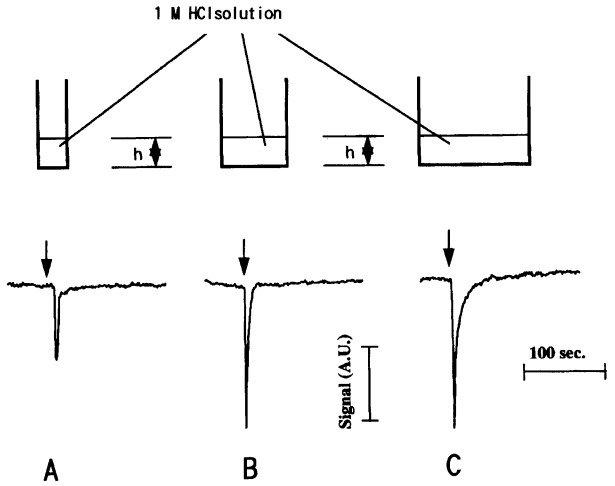

Fig. 4. Deflection signals for reaction cells with internal diameter of 1.2 mm (A), 2 mm (B), and 5 mm (C) obtained in batch experiments. Height h of 1 M HCl solution in the reaction cells was 2 mm. Arrows represent injections of 1 μl 0.05 M NaOH solution.

PBD sensitivity in most cases. However, in the reaction heat-induced OBD, the size of the reaction cell is related to the interaction pathlength between the probe beam and the reaction heat-induced temperature gradient (dT/dz). In the experiments, the internal diameter of the reaction cell can be considered as the pathlength. The relationship between the pathlength (l) and the deflection signal (S) is as follows:[1)]

$$S \propto l(dn/dT)(dT/dz), \tag{1}$$

where dn/dT is the temperature coefficient of the refractive index of CCl_4. The temperature gradient (dT/dz) is a function of the time and position (z), at which the probe beam passed through. For a fixed z, the maximum dT/dz is proportional to the temperature increase (ΔT) in the reaction media,[22)] which is induced by the reaction heat.

The effect of size of the reaction cell on the detection sensitivity was first investigated in batch experiments. Since the detection sensitivity is determined by S/N, the effects of the size on both the signal and noise were examined. The experimental results showed that the noise level was nearly the same for reaction cells of different size. In order to investigate the effect of the size on the signal, two kinds of experiments were carried out. The first involved different amounts of reactant (NaOH and HCl) solutions being added into reaction cells of different size, so that the same ΔT occurred in the reaction media. In this case, the signal was proportional to the internal diameter of the cell. This is also expected based on Eq. 1, which states that the signal is proportional to the pathlength of the same ΔT. The second experiment involved the same volume of 0.5 M NaOH solution (1 μl, 1 M=1 mol dm^{-3}) being added into the reaction cells, where the height of the HCl solution was the same for the different cells, as illustrated in Fig. 4. In this case, ΔT was calculated using,

$$\Delta T = (\Delta H \cdot M)/(C \cdot V \cdot \rho), \tag{2}$$

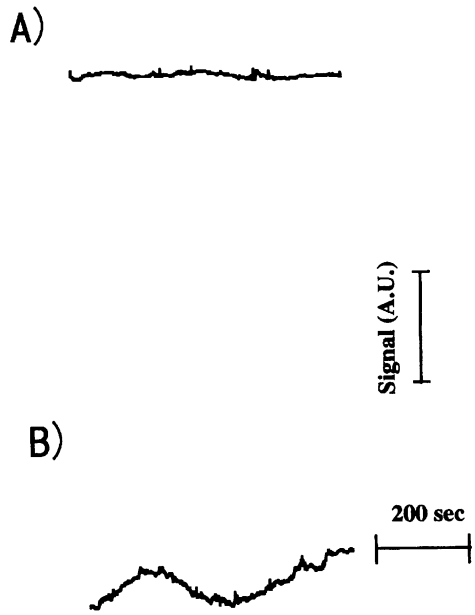

Fig. 5. Comparison of baselines of the deflection signal before (A) and after (B) start of flow. Flow rate was 0.94 ml min^{-1}. Internal diameter of the reaction cell was 5 mm.

where ΔH and M are the molar reaction heat (J mol^{-1}) of the reaction and the amount of the reactant (mol); C, V, and ρ are the specific-heat capacity (J $g^{-1}°C^{-1}$), volume (ml), and the density (g ml^{-1}) of the water phase, respectively. The volume (V) was calculated from the internal diameter (d) of the cell and height (h) of the water phase (Fig. 4), i.e.,

$$V = (\pi d^2 h)/4. \tag{3}$$

From Eqs. 2 and 3, it is clear that ΔT is proportional to $1/d^2$, since M is the same for the different cells. Therefore, the deflection signal should be proportional to $1/d$ according to Eq. 1. However, the experimental results are beyond the above predictions. Figure 4 shows that the magnitudes of the deflection signals are nearly the same for cells with internal diameters of 2 and 5 mm. This might be because the added 1 μl NaOH solution reacted locally in the cell, since the reaction rate of the neutralization reaction was very fast and no stirring occurred in the cell. At the local position where the reaction occurred, ΔT was nearly the same, regardless of the size of the reaction cell. Regarding the smallest cell with an internal diameter of 1.2 mm, because of a difficulty to introduce of a reactant solution, some of the reactant solution might have adhered on the wall of the glass tube. Therefore, the actual reactant solution might have been smaller than the others. On the other hand, the decay of the deflection signal depended on the internal diameter of the cell. The larger was the cell, the slower was the decay. The decay of the deflection signal reflects the cooling process of the hot reaction medium heated by the reaction heat.[22)] Since the heat dissipation from the wall of the cell was fastest for the smallest cell, the cooling process of the hot reaction medium was also the fastest.

The effect of the size of the reaction cell on the detection

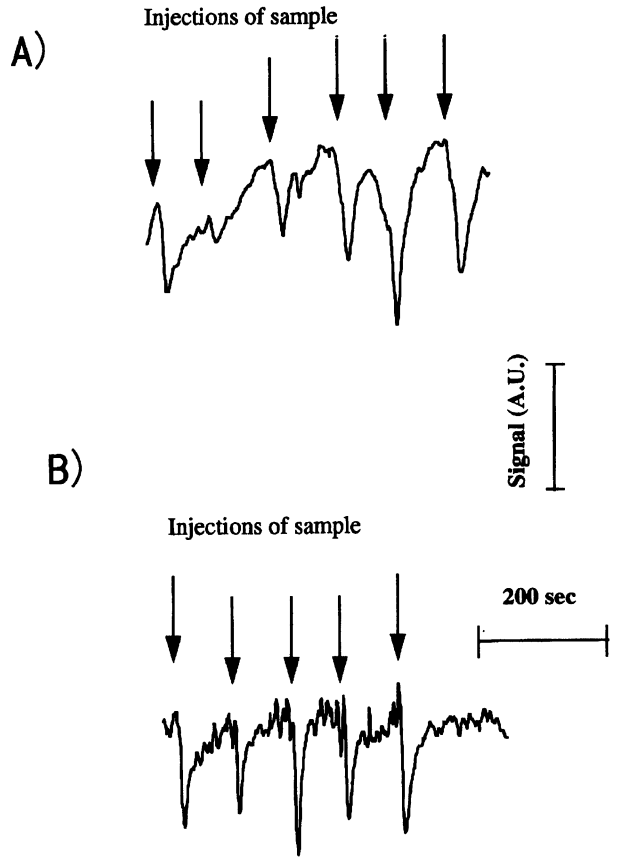

Fig. 6. Comparison of the deflection signals for flow reaction cells with internal diameter of 5 mm (A) and 2 mm (B). Aqueous solution of 0.5 M NaOH was flowed at a flow rate of 0.94 ml min^{-1}. Arrows represent injections of 20 μl 0.01 M HCl solution.

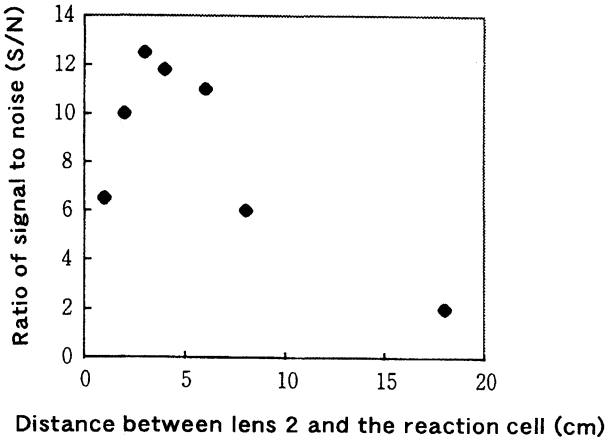

Fig. 7. Relationship between *S/N* and *L* for the lens 2 with f_2 of 3 cm.

sensitivity was further investigated in flow injection experiments. In flow experiments, the baseline was not stable, and the noise level was higher than that in the batch experiments. Figure 5 shows the baselines and noise levels before and after the start of flow. The flow of an aqueous solution in the reaction cell generated a fluctuation of the gold film. This fluctuation was the main noise source in the flow ex-

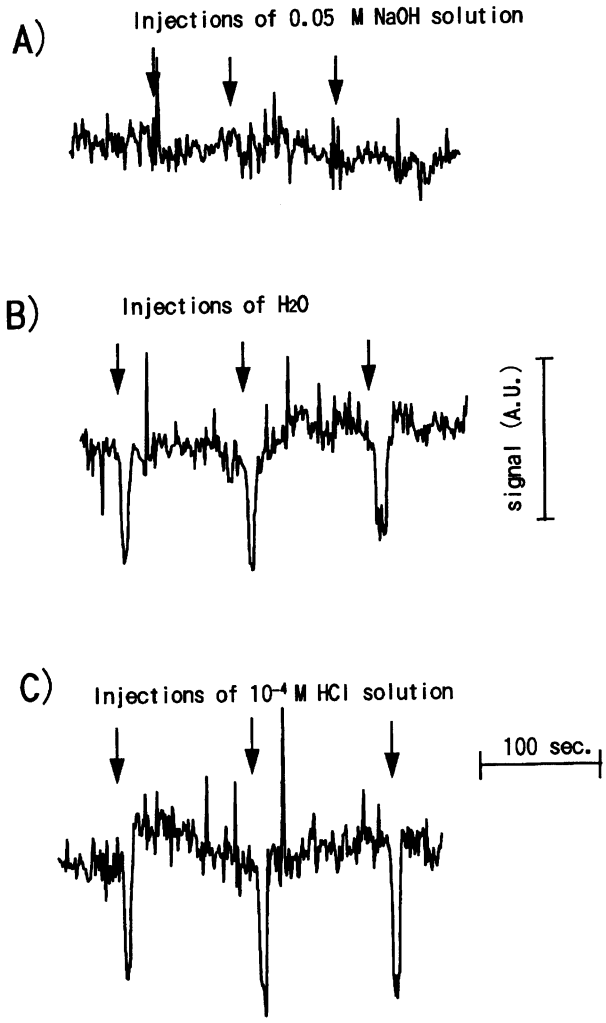

Fig. 8. Deflection signals obtained when 0.5 M NaOH solution (A), H_2O (B), 10^{-4} M HCl (C) were injected into the flow line of 0.5 M NaOH solution. Injected volume was 1.2 μl. Internal diameter of the reaction cell was 0.6 mm.

periments. The bigger was the cell, the higher was the noise level. On the other hand, the deflection signal for a single injection was nearly the same (Fig. 6) for both cells with different sizes. However, the stable baseline and small noise in the small cell gave a better *S/N*, thus resulting in a better detection sensitivity. Also, the reproducibility for multiple injections was improved.

Optical Arrangements of the System. Focusing of the probe beam to the gold film/CCl_4 interface was found to improve the detection sensitivity. This might have been due to the fact that the focused probe beam was closer to the gold film/CCl_4 interface than in the unfocused case. In PBD, the probe beam is also usually focused to the maximum temperature gradient. Since the size of the heat source in this experiment was much larger than that in PBD, a focal lens with long focal length was desirable for focusing the probe beam. In the following experiments, a lens with a focal length of 20 cm (lens 1 in Fig. 1) was used.

The use of lens 2 between the reaction cell and the detector (Fig. 1A) was also found to improve the detection sensitivity.

Moreover, the detection sensitivity depended on the distance (L) between lens 2 and the reaction cell. Figure 7 shows the relationship between S/N and L when the local length (f_2) of lens 2 and 3 cm. The maximum S/N was obtained when L was about 3 cm. On the other hand, the optimum L was about 10 cm for lens 2 with an f_2 of 10 cm. These results suggest that the optimum L is equal to f_2, i.e., refocusing of the deflected probe beam is desirable.

Detection Limit of the Method. Based on the above results, the following experimental conditions were selected for investigating the detection limit of the method: the detector was a bi-cell photodiode, the probe beam was focused on the gold film/CCl_4 interface as close as possible, the flow cell was as small as possible, and the distance between lens 2 and the reaction cell was equal to f_2. Here, a capillary (i.d., 0.6 mm, o.d., 0.7 mm) was used as the flow cell; the results are shown in Fig. 8. When 1.2 μl of a 0.5 M NaOH solution was injected into the flow line of 0.5 M NaOH, no detectable signal was observed (Fig. 8A). However, injections of water and 10^{-4} M HCl gave deflection signals (Figs. 8B and 8C). Because of the dissolution of CO_2 in water, the pH of the water was about 5.2. Therefore, the water was a weak acid, and a neutralization reaction also occurred when it was injected into the flow line of a NaOH solution. The dilution heat of the NaOH solution generated by the injection of water might also have contributed to the deflection signal. Although the exact amounts of the dilution heat are unknown, Fig. 8 shows that the detection limit for the neutralization reaction was below 10^{-4} mol dm^{-3} (the absolute detection limit is calculated to be below 0.12 nmol). In our previous work,[16,17] the concentration detection limit for the neutralization reaction was about 5×10^{-2} mol dm^{-3} (the absolute detection limit was about 5 μmol). Therefore, the detection sensitivity was improved by about 3 orders in the work. The reasons for the improvements are summarized as follows: a remarkable decrease in the noise by partitioning the reaction medium from the CCl_4 phase with thin gold film, and using a small capillary cell; an increase in the signal by focusing the probe beam close to the gold film/CCl_4 interface, the use of a bi-cell photodiode as the detector, and optimization of the optical arrangements.

Further Improvements of the Method. Recently, it has been reported that PBD is more sensitive for a small single microparticle sample, because of an enhancement of the temperature gradient due to the microparticle curvature.[26] This enhancement is expected to also be useful for this method. Therefore, the design of a smaller reaction cell with a curvature is expected to enhance the sensitivity. Also, a more stable probe beam source having small deflection noise is desirable. Another important factor is to control the temperature change of the surroundings around the reaction cell. These studies are now being conducted.

The present work was partially supported by a Grant-in Aid for Scientific Research No. 06650936 from the Ministry of Education, Science and Culture, and a fund for Scientific Research No. 116 from the Academic Promotion Committee of Japan.

References

1) A. C. Boccara, D. Fournier, and J. Badoz, *Appl. Phys. Lett.*, **36**, 130 (1980).
2) J. C. Murphy and L. C. Amaodt, *J. Appl. Phys.*, **51**, 4580 (1980).
3) N. J. Dovichi, *CRC Crit, Rev. Anal. Chem.*, **17**, 357 (1987).
4) T. Kitamori and T. Sawada, *Spectrochimi. Acta Rev.*, **14**, 275 (1991).
5) J. Pawliszyn, *Spectrochim. Acta Rev.*, **13**, 311 (1990).
6) J. Pawliszyn, Michael F. Weber, M. J. Dignam, R. D. Venter, and Su-Moon Park, *Anal. Chem.*, **58**, 236 (1986).
7) J. Pawliszyn, Michael F. Weber, M. J. Dignam, R. D. Venter, and Su-Moon Park, *Anal. Chem.*, **58**, 239 (1986).
8) J. Pawliszyn, *Anal. Chem.*, **64**, 1552 (1992).
9) L. R. Lima and R. E. Synovec, *Anal. Chem.*, **65**, 128 (1993).
10) C. N. Renn and R. E. Synovec, *Anal. Chem.*, **62**, 558 (1990).
11) C. N. Renn and R. E. Synovec, *Anal. Chem.*, **60**, 558 (1988).
12) V. Murugaiah and R. E. Synovec, *Anal. Chim. Acta*, **246**, 241 (1991).
13) G. Chen and E. S. Yeung, *Anal. Chem.*, **60**, 864 (1988).
14) A. Mandelis, R. Takaue, Z. Zhen, J. Szurmak, and W. D. Baines, *Anal. Sci.*, **8**, 131 (1992).
15) J. D. Rudnicki, G. M. Brisard, H. A. Gasteiger, R. E. Russo, F. R. Mclarnon, and E. J. Cairns, *J. Electroanal. Chem.*, **362**, 55 (1993).
16) X-Z. Wu, H. Shindoh, M. Yamada, and T. Hobo, *Anal. Chem.*, **65**, 834 (1993).
17) X-Z. Wu, H. Shindoh, M. Yamada, E. Kobayashi, and T. Hobo, *Anal. Sci.*, **10**, 203 (1994).
18) X-Z. Wu, H. Shindoh, and T. Hobo, *Microchem. J.*, **49**, 213 (1994).
19) X-Z. Wu, H. Shindoh, and T. Hobo, *Anal. Chim. Acta.*, **299**, 333 (1995).
20) X-Z. Wu and T. Hobo, *Anal. Chim. Acta*, **316**, 111 (1995).
21) X-Z. Wu, T. Hobo, T. Kitamori, and T. Sawada, *Netsu Sokutei*, **22**, 143 (1995).
22) X-Z. Wu, *Bunseki Kagaku*, **45**, 55 (1996).
23) X-Z. Wu, K. Uchiyama, and T. Hobo, *Anal. Lett.*, **29**, 1993 (1996).
24) C. Barbero, M. C. Miras, R. Kotz, and O. Haas, *Solid State Ionics*, **60**, 167 (1993).
25) J. Wu, T. Kitamori, and T. Sawada, *Appl. Phys. Lett.*, **57**, 22 (1991).
26) J. Wu, T. Kitamori and T. Sawada, *J. Appl. Phys.*, **69**, 7015 (1991).