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A New Development of Photoacoustic Detection for Microchip-CE Using a Simple Pick-up Device

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Abstract A new approach to laser-based non-fluorescence detection was developed for microchip-capillary electrophoresis (microchip-CE) utilizing an electrical pick-up device. An intensity-modulated laser beam was irradiated on the microchip, and an acoustic wave was then generated by the periodic thermal expansion. Detection of signals was performed by the measurement of the induced electromagnetic wave with the use of a pickup device. The signal magnitude showed a linear relationship with the laser power and applied voltage, while the acoustic signal displayed a linear dependence on the concentration of the sample over a wide range. The separation of dye mixtures is achieved by the use of this new detection method for microchip-CE.

Keywords Antenna · Electromagnetic wave detection · Microchip-CE · Photoacoustics

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1 Introduction

In recent years, a great attention has been paid to the chemical manipulation and separation in micro-analysis systems. The merits of the miniaturization are found in many aspects, such as smaller sample and reagent volumes, smaller space, large surface areas compared to capillaries, simple flow control using an electric field, fast analysis time, etc. Since the development of miniaturized chemical analysis systems utilizing electokinetic phenomena by Manz et al. [1] and Harrison et al. [2,3], the microchip-capillary electrophoresis (microchip-CE) has shown great promise in many chemical analysis systems, particularly in areas of biological analysis [4]. However, these nanoliter detection systems necessitate sophisticated detection technologies strongly demanding simple detection methods possessing high sensitivity. One of the most highly sensitive methods commonly used is a laser-induced fluorescence (LIF) [5–7]; however, its applicability is limited to fluorescent analytes. Other methods such as fully integrated electrochemical (EC) detection [8], normal Raman spectroscopic detection [9], and on-line chemiluminescence detection [10] have been reported for microchip-CE systems. Recently, a method based on the thermal lens effect, considered a non-fluorescent-based method, has also been developed to obtain much higher sensitivity than previous techniques applicable to microchip-CE [11,12].

The electromagnetic (EM) induction by ion movements has been studied since the 1960 s [13–15], and fluctuating magnetic fields around the human torso produced by ion currents from the heart have been detected by Cohen [14]. When an electrically active tissue produces a bioelectric field, a biomagnetic field is simultaneously produced, so that the detection of the electromagnetic field using a coil from a fine current source in a bioelectric field can be achieved to monitor brain waves [16]. Recently, by analogy of the electromagnetic induction from ion movements as described above, we have discovered the signal of an induced electromagnetic wave generated by the photoacoustic effect in a capillary tube, where the sample is irradiated by an intensity-modulated laser and detected with a simple antenna [unpublished results]. In this aricle, we report the detection scheme for microchip-CE with the use of a metal pick-up plate based on the mechanism of an electromagnetic induction process followed by the generation of the photoacoustic signal.

2 Measurements

A block diagram of the experimental arrangement used in this study is shown in Fig.1. The microchip is a 2 mm thick piece of quartz (Digital Bio Technology, Korea) and contains two intersecting channels, where both the ends of each channel have accompanying reservoirs. A cover plate with holes drilled for reservoirs is joined to the top of the channel plate using a direct bonding technique. Four pipet tips are epoxied to the cover plate to make reservoir volumes. The four channels extending from the injection cross have lengths of 6 mm, 5 mm, 5 mm, and 58 mm for the buffer, sample, sample waste, and analysis channels, respectively. Each channel is 100 μm width and 20 μm depth. A 30 kV high-voltage power supply (Model SL30P150, Spellman) is employed as a potential source for the separation. The high voltage from the power supply is

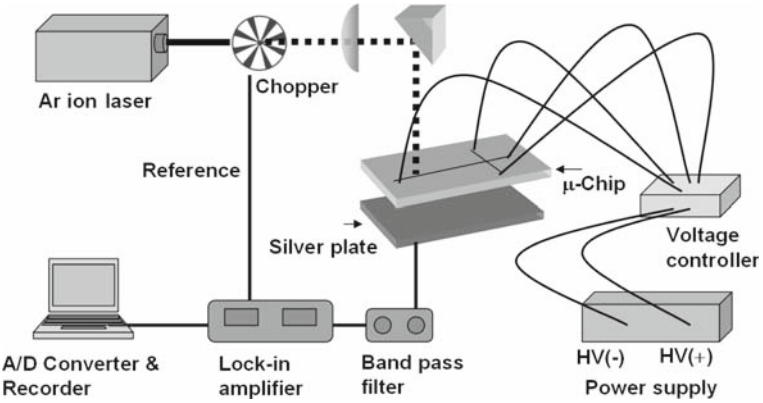

Fig. 1 Schematic diagram of experimental setup

divided and loaded into the microchip by the use of a simple circuit divider to provide proper voltages for the sample loading and dispensing steps [17]. In most cases, the induced potential of approximately $150\,\mathrm{V}\cdot\mathrm{cm}^{-1}$ is applied in the channel for the sample separation. The output beam of a cw Ar ion laser (Innova 300, Coherent) operating in the multiline mode (457.9 nm to 514.5 nm) at 300 mW is intensity-modulated at 40 Hz by the use of a chopper. The laser beam is then focused onto the detecting point located 50 mm downstream from the center of the injection cross by a convex lens with a focal length of 25 cm.

The induced electromagnetic signal is detected by using a simple metal pick-up device. The pick-up device, made of silver plate (20 mm × 60 mm × 2 mm, 92.5 %), is supported rigidly with a holder beneath the microchip. The silver plate is connected to the input of a lock-in amplifier (SR 850, Stanford Research System) with the aid of a bare cable, similar to an open circuit of an antenna. The induced current from the silver plate is amplified and detected by the lock-in amplifier tuned to the chopper modulation frequency. Electropherograms are collected through an A/D converter (PCL-711B, Advantech) and a personal computer.

All chemicals are used without further purification. Three samples of sunset yellow (TCI, purity is not known), amaranth (Aldrich, 80 %), and erythrosine B (Aldrich, 91 %) are used as standard analytes, which have absorption peaks in the range of 480 nm to 530 nm for an Ar ion laser. A 10-mM sodium borate solution ($Na_2B_4O_7/H_3BO_3$) at pH 8.74 is prepared as a buffer for all experiments. Freshly deionized and distilled water is used to make all solutions.

3 Results

The signal of the electromagnetic wave is detected with respect to the chopping frequency for sunset yellow dye. The magnitude of the signal exhibits a dependence on the reciprocal of the chopping frequency. This result confirms that electromagnetic signals produced by the periodic optical heating are inversely proportional to the chopping frequency, giving rise to the same dependence easily seen in photoacoustic

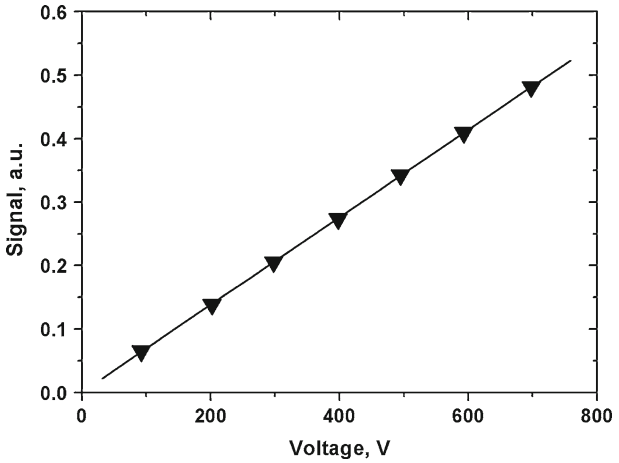

Fig. 2 Plot of electromagnetic induction signal versus applied voltage in the channel for sunset yellow with concentration of 1×10^{-3} M and 300 mW laser power at modulation frequency of 40 Hz

experiments. Note that the magnitude of the signal at very low frequencies below the chopping frequency of 40 Hz drops substantially. It is believed that the decrease of the signal at low frequencies in this experiment is due to the damping of the electromagnetic signal transmitted to somewhat wide areas in the silver plate at these low frequencies. In separate experiments [unpublished results] with metal wires, however, the signal is clearly observed to possess a $1/f$ dependence down to 10 Hz.

A study was carried out to characterize the dependence of the electromagnetic signal for sunset yellow on the voltage applied to the microchip for separation. As shown in Fig. 2, the electromagnetic signal is directly proportional to the separation voltage applied in the channel. Note that no signal is detected unless an electric field is applied, implying that the acoustic signal produced in the channel cannot generate the electromagnetic wave without an electrical potential. The result shown in Fig. 2 indicates that a high electrical field is needed to produce high electromagnetic induction as is found in the case of conventional radio wave transmission.

Within the narrow channel, the periodic heat generation due to the radiation absorption results in ion acceleration and deceleration in each direction with respect to the point of absorption of the laser beam, inducing a potential increase and drop with respect to the point of absorption. In this experiment, the periodic heat production in the channel of the microchip by the intensity modulated laser beam causes the generation of symmetric pressure waves inside the channel at the center of the focal point of the laser beam. Since a high voltage is applied into the narrow channel, the ion movement in one side by the electroosmotic flow (EOF) brings about an induction of the current in the channel. The periodic potential changes, caused by the ion movement due to the photoacoustic wave in the narrow channel of the microchip, emits electromagnetic waves of two inverse phases in both directions from the focus of the laser beam at the chopping frequency of the laser. The induced currents generated by the resonance between the electromagnetic wave and the antenna in one direction of the

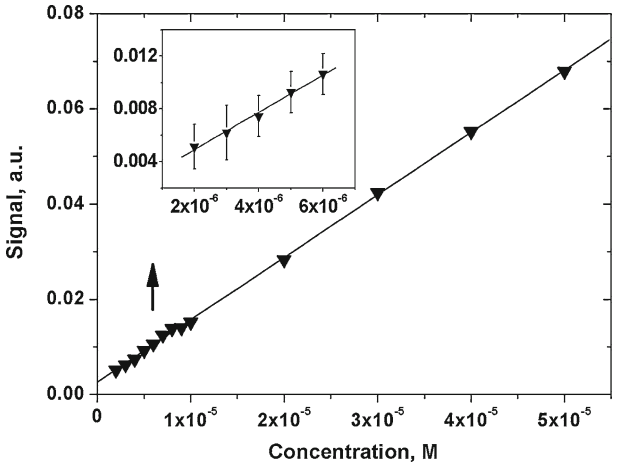

Fig. 3 Concentration dependence of the signal magnitude for sunset yellow with an induced potential of 1 kV and 300 mW laser power at a modulation frequency of 40 Hz. Inset: expanded low concentration region (2×10^{-6} M to 6×10^{-6} M)

electromagnetic waves can be amplified and detected as the signal. Thus, the emission magnitude of an electromagnetic wave caused by the generation of an acoustic wave in the narrow channel is directly related to the magnitude of the generated photoacoustic signal.

In light of the properties mentioned above, the signal dependence on the optical energy and the concentration of the sample is interesting. The electromagnetic signals observed in the experiments are found to be linearly-dependent on the laser input power; likewise, in Fig. 3, the observed dependence of the electromagnetic signal on the concentration of sunset yellow in the range of 1×10^{-6} M to 5×10^{-5} M is also linear. The linear relationship of the signal with concentration also extends into higher concentration regions. The results demonstrate that the electromagnetic signal is directly proportional to the concentration of the sample over a fairly wide concentration range. This linear dependence of the signal on the concentration of samples demonstrates the general applicability of this new methodology for quantitative analyses. From Fig. 3, the detection limit is obtained to be 3×10^{-6} M at a signal-to-noise ratio of two for sunset yellow dye. Considering the optical detection volume estimated to be 1×10^{-10} L, the absolute detection limit in terms of number of moles is calculated to be 3×10^{-16} mol. The results illustrate that the new electromagnetic wave detection for microchip-CE is more sensitive than a conventional spectrophotometric detector. It is still possible to increase the sensitivity by further optimization of the experimental conditions such as improved design of the microchip, separation media, buffer composition, etc.

To evaluate the separation capability of this detection method for mixed species of different chemical origins, experiments are carried out with a mixture of different samples. In this study Fig. 4 illustrates the separation of the mixture of three dye solutions. The electropherogram is obtained with a potential of 1 kV and a laser power of 300 W at a modulation frequency of 40 Hz, with each dye concentration at 5×10^{-4} M.

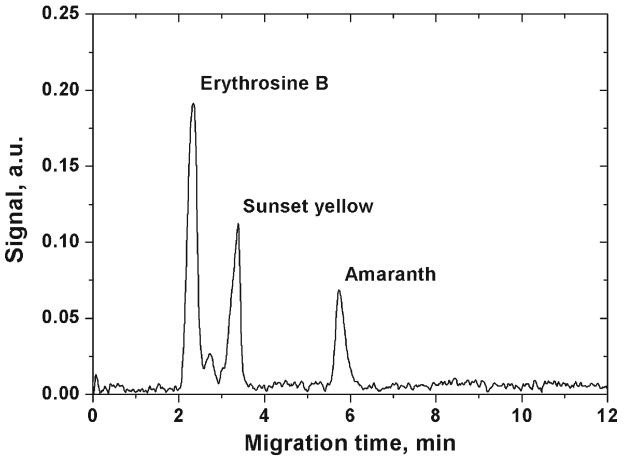

Fig. 4 Electropherogram of a three dye mixture with the electromagnetic detector obtained with a separation potential of 1 kV and 300 mW laser power at a modulation frequency of 40 Hz. All sample concentrations are 5×10^{-4} M before mixing

Figure 4 clearly shows a well-resolved separation of the three different components and a high signal-to-noise ratio for the detection of each species.

In conclusion, this paper demonstrates a very simple and new detection method for microchip-CE based on what might be called a "photoacoustic antenna." The advantages of the electromagnetic wave detection include wide applicability for the quantitative analysis, high sensitivity, and elimination of the signal induction and transmission between the capillary electrophoresis medium and the detector. Moreover, the method has the potential of being used for micro-sample separation and detection without the requirement of sophisticated optical or electrical devices used in highly sensitive detection methods.

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