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Improvement of Magneto-Optical Rotation Detector for High Performance Liquid Chromatography

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Performance of a magneto-optical rotation detector has been improved. Light intensity is stabilized using a semiconductor laser. A large and high frequency modulation of polarization plane is provided with the use of an external modulator. Detectability is in the μg range and linearity of an analytical curve is more than two orders of magnitude.

1. Introduction

Magneto-optical rotation (MOR), the so-called Faraday effect, is the phenomenon that the polarization plane of linearly polarized light rotates on propagating through substances in a magnetic field parallel to the direction of the light beam. MOR is a general physical property for all substances and can be utilized for a universal detector in high performance liquid chromatography (HPLC).[1-3] A change in composition of a solution modifies its rotatory power. A small rotation of the polarization plane can be measured using a technique similar to laser-based polarimetry.[4]

In our first paper,[1] the first application of the MOR-based flow detector was demonstrated and a simple additivity in MOR was confirmed for the quantitative analysis. In the second paper,[2] a semiconductor laser was used as a light source because its light intensity is more stable than that of a gas laser.[5] Recently, Xi and Yeung also developed a MOR detector using a He-Cd laser (442 nm), an external polarization modulator and a strong static magnetic field (ca. 6000 G).[3]

In this paper we will show an improved detection limit of the MOR detector using a semiconductor laser and an external modulator.

2. Experimental

The experimental apparatus is basically similar to that previously reported.[2] It consisted of a semiconductor laser (Sharp LT023MC, 3 mW at 784 nm) light source, a pair of Glan-Thompson prisms, an external polarization modulator, a flow cell and a photo-detection system with a lock-in amplifier, as shown in **Fig. 1**. The improvement in the present paper is the use of an SF10 flint glass rod (length: 20 mm) as an external modulator. A magnetic coil wound around it and it rotated the polarization plane of linearly polarized light at an angle of ± 0.4 degree and a frequency of 100 Hz through its Faraday effect.

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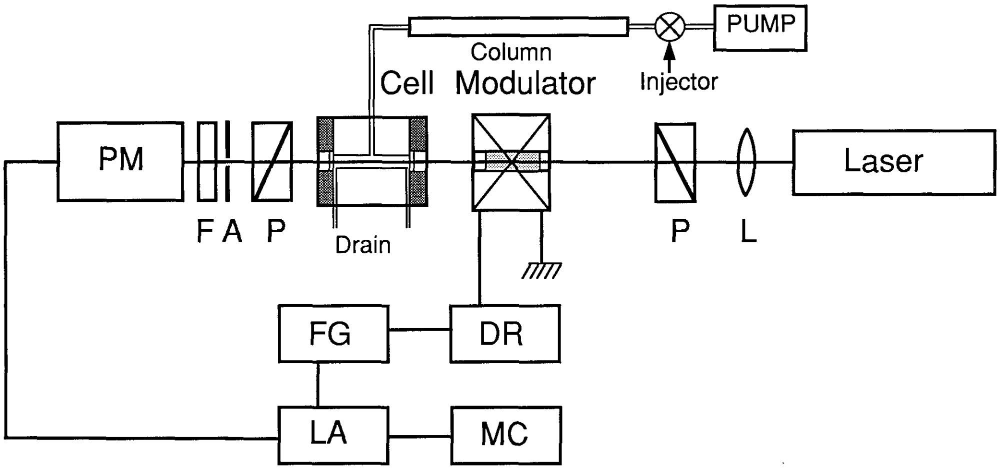

Fig. 1 Experimental setup for the MOR detector.
A, aperture; DR, current amplifier; F, optical filter; FG, function generator; L, lens; LA, lock-in amplifier; MC, microcomputer; P, Glan-Thompson prisms; PM, photomultiplier.

To obtain the large modulation angle, the flint glass is useful because it has a larger Faraday effect (Verdet constant: 6.4 x 10^{-4} degree cm^{-1} G^{-1}) than water has (2.1 x 10^{-4} degree cm^{-1} G^{-1}).

The flow cell was made of aluminum with 8-μl volume bores (10-mm long and 1-mm in diameter) and had a central inlet and two side outlets. Such a design can reduce the laser beam deflection due to the concentration gradient in the flow. A solenoid and a pair of permanent magnets were set around the cell to vary the strength of the magnetic field (0—670 G). The permanent magnets were ring-shape rare earth cobalt magnets (Edmund, 5800 Oe), and placed at both sides of the cell. The static magnetic field on the cell was calibrated with the static MOR measurement of water.

The chromatography system consisted of a pump (JASCO 880-PU), an injector (Rheodyne 7413) and a gel chromatography column (Asahipak GS-310M). The eluent was distilled water.

3. Results and Discussion

The chromatography for optically transparent samples is an appropriate demonstration of the universality of the MOR flow detector. A gel chromatogram of polyethylene glycol (PEG) 6000 and 2000 (average molecular weight: 7400—9000 and 1800—2200, respectively) was measured by using the semiconductor laser and the external polarization modulator, as shown in **Fig. 2**. The injection amount is 25 μg each and the concentration is 0.25% (w/w). The modulation frequency, strength of the static magnetic field and time constant of the lock-in amplifier is 200 Hz, 670 G and 10 s, respectively. The noise mainly depends on stabilities of the light intensity and the pressure of the chromatography system. A temperature change resulting from the heat of the coil produces slow increase in the chromatographic baseline.

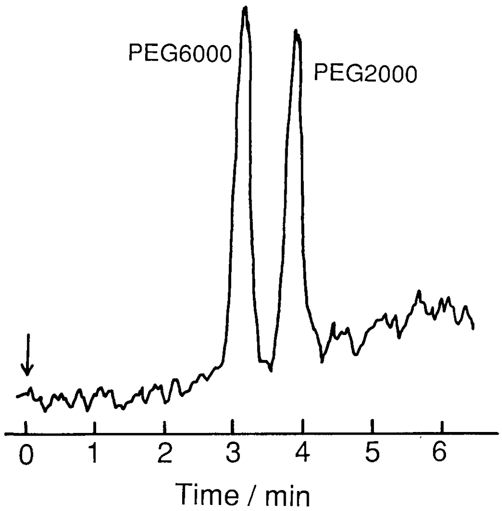

Fig. 2 Gel chromatogram of polyethylene glycol (PEG) 6000 and 2000. Mobile phase, water; flow rate, 0.5 ml/min; sample, 0.25% (w/w) each (10-μl injection); magnetic field, 670 G (sample) and 450 G (flint glass).

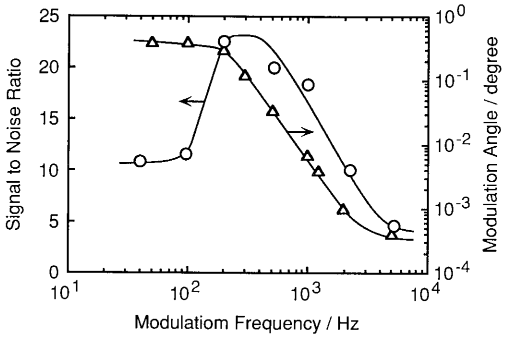

Fig. 3 Dependence of modulation frequency on signal to noise ratio and modulation angle. The signal to noise ratio was determined with the chromatogram of 0.25% (w/w) PEG 6000. Time constant of lock-in amplifier, 3 s.

The signal to noise ratio (S/N) in chromatograms depends on the modulation frequency as shown in **Fig. 3**. An optimum operation frequency is around 200 − 1000 Hz. The flicker and drift noise of the semiconductor laser light can be as low as 0.001% at more than tens Hz by using a light intensity feedback circuit.[2] The mechanical system stability such as an external vibration and a pressure fluctuation is better at the higher frequency.[6] On the other hand, the modulation angle decrease rapidly at the higher frequency, because the magnetic field on the modulator decreases owing to an induction effect of the coil. As the MOR signal intensity is proportinal to the modulation angle, the induction effect compensates the improvement of S/N at the high frequency modulation.

A dependence of the MOR signal intensity on the static magnetic field is shown in **Fig. 4** to confirm the proportionality to the magnetic field strength applied on the sample in the principle of the Faraday

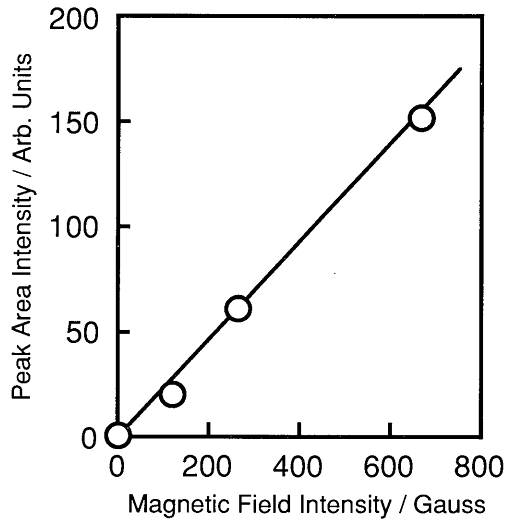

Fig. 4 Dependence of MOR signal intensity on static magnetic field applied the flow cell. The static magnetic field was calibrated with the static MOR measurement of water.

effect. As the static magnetic field can be esasily increased using Nd-Fe-B permanent magnets,[3,8] the detectability can be improved straightforwardly and no temperature effect appears.

An analytical curve of PEG 6000 was measured with the peak area intensity in the chromatogram. A linear relationship can be obtained up to 1.5% (w/w). A detection limit at $S/N=3$ is 1.3 μg (0.013% (w/w)). The singal increases monotonically to 3% (w/w) with a preceding negative peak which is resulting from an effect of a large refractive index change at the high concentration. The detection limit is 6 times as low as the previous one[2] and comparable to one reported by Xi and Yeung[3] when the static magnetic field is accounted for. An ordinary Z-type cell design provided a dynamic range of about one order.[3] Our cell design can prevent the distortion of the MOR signal due to the refractive index change and increase the linearity of the analytical curve up to more than two orders of magnitude.

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