A Simple Transmitted Interference Method for Nanovolume Detection

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A transmitted interference method for nanovolume detection is developed for a square-capillary or microchannel. A He–Ne-laser beam passed along an interface of inner medium/capillary wall or microchannel. The inner medium- and capillary wall-passed parts of the laser beam interfered each other to form an interference fringe after exiting out of the capillary. Experimental results of intensity profiles of the interference fringe coincided well with theoretical ones. The method was demonstrated to be applicable as a new universal tool for nanovolume detection.

One trend of analytical science is down-sizing and miniaturization of analytical systems.[1,2] Capillary or chip-based analytical systems are the typical examples.[3] In the downsized or miniaturized systems, sample volume is usually on the order of nano- or subnanoliter. Thus, nanovolume detector is required. Detection methods based on the optical interference can be used for determination of any kind of chemical species since they detect the refractive index (RI) of analytes. Several interference detection methods for capillary or chip-based analytical systems have been reported. They are forward scattering,[4–10] backscattering,[11–15] Fabry–Perot,[16,17] retroreflected beam,[18] and waveguide-interference methods.[19] In these methods, a laser beam transmitted through the centre of a capillary or microchannel. A part of the laser beam was reflected, refracted, or scattered on the interface of capillary wall/air or inner medium. The transmitted, reflected, refracted, or scattered light interfered each other, yielding the forward scattering, backscattering, or other interference fringe patterns. These interference fringes have been used to determine RI of a saccharide mixture,[4] CE-separated metal ions,[5] carbohydrates,[10] and glycerol.[13,15] The forward scattering[4–10] is the simplest in optical configuration, where the interference fringe is detected at a forward scattering angle although a specially designed cell filled with refractive index matching fluids is used sometimes.[4,9] The other interference methods required more complex optical arrangements.

In this work, a simple transmitted interference detection method for nanovolume in a square-capillary or a microchip is proposed. The feature and difference of the configuration from other interference methods are that the laser beams do not pass through the center of the capillary or channel but along an interface of inner medium/capillary wall. This novel optical alignment makes half of the laser transmitting through the inner medium and the left half the capillary or microchip wall. The two transmitted rays overlap and form an interference fringe after existing the capillary or channel. Here, we call it as a transmitted interference method. The usefulness and simplicity of the method were demonstrated by flow injection analysis (FIA) of saccharose.

Figure 1A shows the schematic diagram of the interference detection system with a square capillary or microchannel. The 632.8-nm beam from a He–Ne-laser (1507P-0, Uniphase, USA) of 0.8 mW was used as a light source. A plano convex lens of 35-mm focal length was used to introduce the laser beam to a square capillary (o.d. 380 μm, i.d. 100 μm, length 35 cm, Polymicro, USA) mounted on a micrometer x–y–z stage. The diameter of the laser beam at focal point (sample point) was calculated to be about 60 μm. The capillary was vertical to the laser beam. Its upper and lower ends were immersed into two vials filled with water, respectively. The height difference between the two vials was about 22 cm. The outside-coated polymer in the capillary at the detection point was removed for letting the laser beam pass through. The capillary was adjusted to let the center of the laser beam passed along an inner medium/capillary wall interface as shown in Figure 1B. Either a CCD camera (C4742-95, Hamamatsu, Japan) or a photodiode with a pinhole of 1.0 mm was used to detect the interference fringe patterns, or intensity changes at center of the interference fringe. Sample injection was carried out by replacing the upper vial to a sample vial for 1 min.

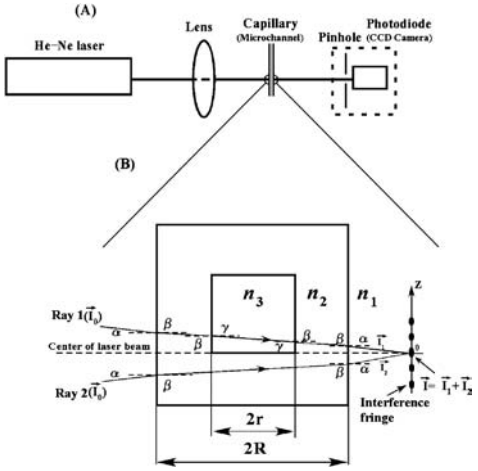

Figure 1. Schematic diagram of the interference detection system (A) and a cross section of the capillary with the ray paths of the laser beam (B).

Figure 1B shows the laser beam paths in the capillary. In the reported forward scattering method,[4,9] the interference fringe was calculated by overlapping of a total internal reflection ray at capillary/inner medium interface and a transmitted ray. Here, the interference fringe is calculated by considering overlap of the inner medium-transmitted Ray 1 and capillary wall-transmitted Ray 2. Their optical paths at incident angle α are as follows:

$$L_1 = 2 \cdot n_2 \cdot (R - r)/\cos\beta + 2 \cdot n_3 \cdot r/\cos\gamma, \quad (1)$$

$$L_2 = 2 \cdot n_2 \cdot R/\cos\beta, \quad (2)$$

where L_1, L_2, n_2, n_3, β, and γ, are optical paths of Ray 1 and

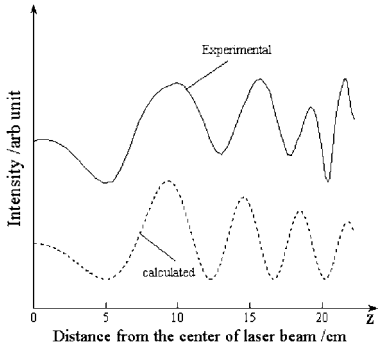

Figure 2. Experimental (solid curve) and calculated (dotted curve) interference fringe for a water-filled capillary.

Ray 2, RIs of capillary wall, inner medium, refractive angles in the capillary and inner medium; r and R are the inner and outer radii of the capillary, respectively. Their phase difference was

$$\delta = 2\pi \cdot (L_1 - L_2)/\lambda, \quad (3)$$

where λ is the wavelength of laser. The overlapped light intensity of Ray 1 and Ray 2 was

$$I = I_1 + I_2 + 2 \cdot \sqrt{I_1 \cdot I_2} \cdot \cos\delta, \quad (4)$$

where I, I_1, and I_2 are intensities of the overlapped ray, Ray 1, and Ray 2, respectively. For a given α, the overlapped intensity could be calculated from above equations by further considering Snell's law and Fresnel's equations.

Figure 2 shows one example of the calculated and measured interference fringes when the capillary was filled with water. The distance from the center of laser beam in horizontal axis corresponded to various α. Only half profile of the interference fringe was shown in Figure 2 because the left half was symmetric. The whole measured interference fringe coincided well with the calculated one, although there were small differences caused by experimental errors.

Next, the most sensitive detection position of the interference fringe was preliminarily investigated. Here, dI/dn (dn is the difference of RI between the sample and the inner medium, and dI is the corresponding intensity change caused by dn) is defined as sensitivity of the method. Theoretical results indicated that the maximum sensitivity was obtained at the center of the interference fringe. This was experimentally verified by filling the capillary with different ethanol and saccharose solutions. Therefore, the detector was placed at the center of the laser beam. This was different from the forward scattering methods where the detection position was away from the center of the laser beam. Position of the laser beam in the capillary was also studied, and the results showed that the center of the beam passing along the interface of the capillary wall/inner medium gave the highest sensitivity.

Furthermore, quantitativity of this method was investigated. Figure 3 shows the intensity changes at the center of the interference fringe for injections of different saccharose solutions into the water flow in the capillary. The intensity changes were nearly linear with the concentrations of saccharose solutions in range of 0.003%–0.3%. The detection limit was estimated to be about 0.0015% (S/N = 2), corresponding to a 2.1×10^{-6} RI unit change. Figure 3 also suggests that the method could be used as a new detector for FIA and square-capillary or chip-based

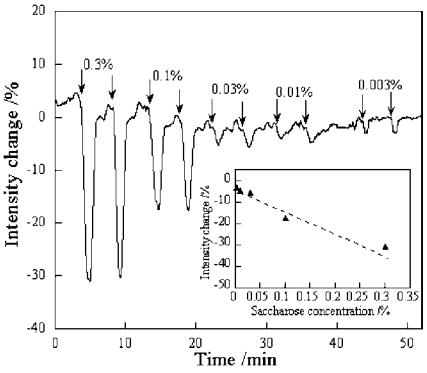

Figure 3. Intensity changes at the center of interference fringes corresponding to the injections of saccharose solutions with different concentrations. Arrows represent injections of saccharose solution.

electrophoresis. The detection limit could be further lowered by using a stabilized laser and controlling the temperature fluctuation around the capillary. The improvements, comparison with the forward scattering methods, and analytical applications will be reported in detail later.

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