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A portable, stable and precise laser differential refractometer

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In this work, we present a portable laser differential refractometer with real-time detection and high precision based on the Snell's law and a $2f$ - $2f$ optical design. The $2f$ - $2f$ configuration solves a traditional position drifting problem of the laser beam and enhances the signal stability, where a small pinhole is illuminated by the laser light and imaged to the detector by lens placed in the middle between the detector and the pinhole. However, it also leads to a larger dimension of the instrument, limiting its applications and its sensitivity that is proportional to the optical path. Therefore, for a portable device on the basis of the $2f$ - $2f$ design, a combination of a mirror and a lens was developed to minimize the optical path without affecting the $2f$ - $2f$ design. Our simple and compact design reaches a resolution of 10^{-6} refractive index units (RIU). Moreover, the dimension of such a modified differential refractometer is significantly reduced to be portable. Owing to its real-time detection speed and high precision, this newly developed refractometer is particularly attractive when it is used as an independent and ultra-sensitive detector in many research and industrial applications wherein there is a time-dependent concentration change, e.g., the concentration determination, quality control, and study of kinetic processes in solution, including adsorption, sedimentation, and dissolution, to name few but not limited. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4828350>]

I. INTRODUCTION

Differential refractometer has been often constructed as an accessory for modern laser light scattering spectrometers to measure the specific refractive index increment (dn/dc) of a polymer solution,¹ a value which plays a central role in determining the magnitude of the scattered intensity in light scattering techniques.² In a typical differential refractometer, the light beam is incident on a divided cell that contains solvent in one compartment and solution in the other (or solutions of two different concentrations). The beam is then refracted at the boundary and displaced, with a final deflection that depends on the refractive index difference (Δn) between the solvent and solution in the divided cell.³ For small Δn , the displacement of the refracted beam is proportional to Δn . As a result, by measuring the concentration (c) dependence of the refracted displacement, dn/dc can be obtained. In polymer science, the measurement of dn/dc is very important because the light scattering method of weight-average molecular weight (M_w) determination involves the measurement of dn/dc . Moreover, a small difference in refractive index (n) between the divided cells may be reflected to the difference in polymer concentrations or other physical properties. The differential refractometer, thereby, can also be considered as an independent, ultra-sensitive concentration detector which promises a great potential in many industrial processes, such as the *in situ* monitoring fermentation in wine industry and pollutants in waste water.⁴

During the past few years, we have successfully developed a differential refractometer (Jianke Instrument Ltd., China) based on the Snell's law of refraction and our novel

$2f$ - $2f$ optical design.⁵ In this differential refractometer, a pinhole ($200\mu\text{m}$) is illuminated by a laser beam and focused on the position sensitive detector by a lens located at an equal distance between the pinhole and the detector, while the sample cell is positioned just before the lens. Optically, it is equivalent to put the pinhole on the detector since the sample cell is unimportant due to its negligible size ($\sim\text{mm}$) compared with the focal length of the lens ($\sim\text{hundreds of mm}$). Therefore, this design overcomes the unavoidable drifting problem of the laser beam. Because the distance between the detector and the pinhole is four times the focal length of the lens, it is a so-called $2f$ - $2f$ design.⁵ The designed refractometer has been incorporated into commercial laser light scattering (LLS) to measure dn/dc in which the laser and computer are shared. Moreover, it has also been independently applied to precisely monitor the enzymatic degradation kinetics of some bio-nanoparticles by monitoring the change of the refractive index.⁶⁻⁹

However, the original $2f$ - $2f$ optical design requires a straightforward and long optical path, largely extending the size of the whole instrument as to preserve a moderate resolution. The enlarged geometry also induces difficulties to maintain the mechanical stability of the instrument and limits the related applications. Therefore, here we further improved the differential refractometer to a compact and portable one by generating a double refraction but kept the original $2f$ - $2f$ configuration with better performance. In this novel design, a combination of a convex lens and a laser mirror was placed just after the divided cells. Geometrical optics showed that by properly placing the laser source, sample cell, and the optical lens system, the beam signal passes twice through the cuvette producing a twice refraction through the sample cuvette and then reflected into a position sensitive detector which is still in a $2f$ - $2f$ manner. One key advantage of this is that the

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optical path distance between the detector and pinhole is reduced from four times of the focal length of the lens to two times compared to the former design. Therefore, the dimensions of the instrument are significantly reduced to be compact and portable. In contrary, the precision of the measured Δn is improved close to $\sim 10^{-6}$ refractive index unit (RIU), which for example, corresponds to a common polymer concentration change as small as $\sim 10^{-5}$ g/mL assuming $dn/dc \sim 0.1$. By considering that more and more analysis in industry and also academic researches need dynamic and rapid measurements, such portable refractometer which incorporates precise temperature control is particularly attractive in quality control and dynamic monitoring of common processes in solution like adsorption, sedimentation, and solvation. To demonstrate this, we present a simple application in the determination of polymer adsorption before and after filtration which simulates a case in wastewater treatment.

II. INSTRUMENTATION

A. Optical design

Figure 1(a) shows a single-refraction light path of our former laser differential refractometer (Jianke Instrument Ltd., China) based on the Snell's law and $2f$ - $2f$ optical design.⁷ It showed that a homemade small pinhole with a diameter of 200 μm is illuminated with a laser light. The illuminated pinhole is imaged to a position sensitive detector (PSD, Hamamatsu Photonics, S3931) by a lens which is located at an equal distance between the pinhole and the detector. The distance between the detector and pinhole is two times the focal length ($f = 200$ mm) of the lens from the lens itself, i.e., we have used

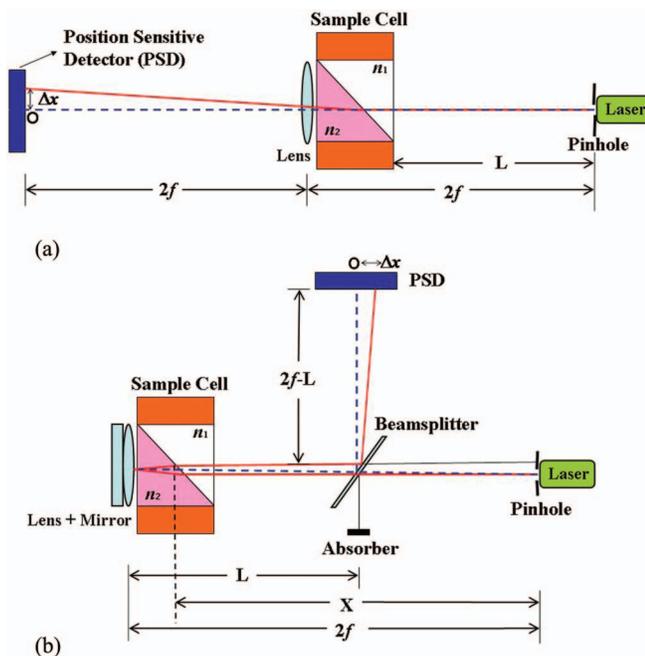


FIG. 1. (a) Schematic of former $2f$ - $2f$ design of the differential refractometer. (b) Optical design of the newly modified refractometer. L : distance between the beamsplitter and the reflection surface of the mirror ($L = 180 \pm 1$ mm); X : the distance between the pinhole and the center of the cuvette ($X = 300 \pm 1$ mm); the focal length of the lens, $f = 175$ mm.

a $2f$ - $2f$ design by placing the lens in the middle of the pinhole and the detector. The sample cuvette (Hellma, 590.049-QS), a flow cell with a volume of ~ 20 μL and divided by a glass plate at 45° into two chambers, is placed just in front of the lens. It has been shown that in comparison with the conventional ($1f$) design, where a parallel incident light beam is used and the distance between the detector and the lens is one time of the focal length, the developed refractometer decreases the root-mean-square (RMS) noise at least five times.⁵

The initial design was encouraging; we then further modified the refractometer by introducing a double-refraction optical design in order to save the spaces inside the refractometer to achieve the compact and portable purpose. As shown in Figure 1(b), we replaced the lens just after the cuvette by a combination of a convex lens (CVI Melles Griot, LDX-25.0-362.7-C, $f = 350$ mm) and a laser mirror (Edmund Optics Inc., NT43-532, diameter = 25 mm). Note that the convex lens with such a smooth curvature is tightly clung to the reflection surface of the laser mirror by a homemade plastic holder producing little air gap existence between them. The combination of the lens and mirror therefore has the same functions as two equal lenses positioned along the optical axis. First, after passing through a 50/50 beamsplitter (Edmund Optics, BS Plate VIS 50R/50T, diameter = 25 mm), half of the initial laser beam (Edmund Optics, NT53-756, laser diode module 5 mW, 635 nm) is incident on the sample cuvette, passes through the lens, then reflected back by the mirror, and goes through the lens and the sample cuvette again. In this way, after passing through the beamsplitter again, the resultant signal has been refracted twice before they are reflected to the PSD. The optical path length between the detector and the pinhole is now only two times of the focal length of lens instead of four times as shown in Figure 1(a). Therefore, the dimension of the instrument can be significantly reduced.

On the other hand, according to geometrical optics, the combination of two same focal lengths of thin lenses without gap is equivalent to a single lens with a focal length half of the thin lens, i.e., $f/2$. Such an equivalent is illuminated in Figure 2. For two ideal thin lenses have the same focal length (f) and assume that there is no gap between them, the Gaussian equation in geometry optics is expressed as

$$\frac{1}{u_1} + \frac{1}{v_1} = \frac{1}{f} \quad (1)$$

$$\frac{1}{u_2} + \frac{1}{v_2} = \frac{1}{f}$$

where u and v are the objective and image distances of a lens, while the subscripts 1 and 2 represent lenses A and B, respectively. When two lenses are closely combined, $u_2 = -v_1$, Eq. (1) becomes

$$\frac{1}{u_1} + \frac{1}{v_2} = \frac{1}{\left(\frac{f}{2}\right)}. \quad (2)$$

Therefore, we conclude that placing closely the combination of a lens (focal length = 350 mm) and a mirror just after the cuvette is equivalent to one lens with $f = 175$ mm placing at the same position. On the other hand, the $2f$ - $2f$ design is maintained (now the term f in " $2f$ - $2f$ " is 175 mm) by placing both

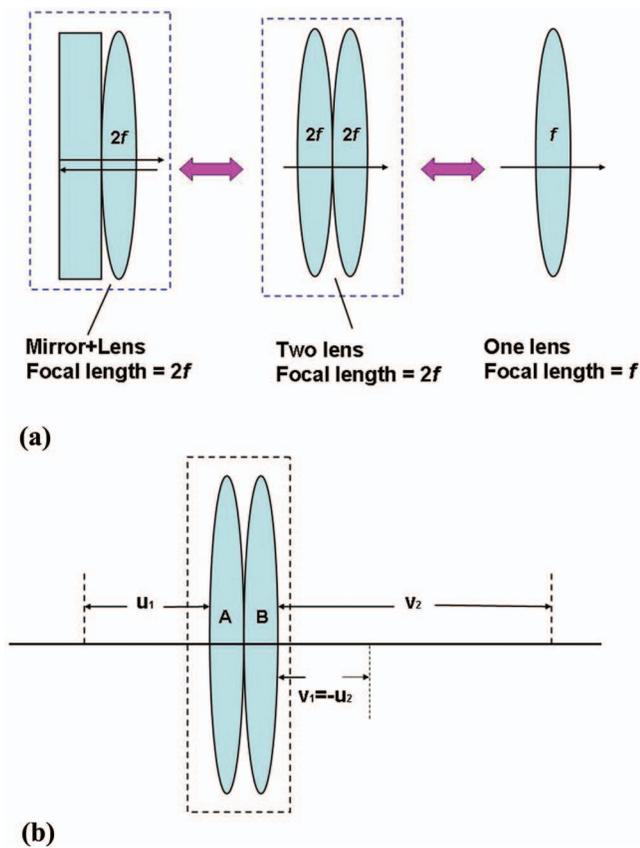


FIG. 2. Schematic shows that the combination of a lens and a laser mirror optically equals to a lens with focal length half of the combined lens, where u_1 and u_2 are the objective distances of lens A and B, respectively, and v_1 and v_2 are their corresponding image distances. Note that in this system, positive objective distance is defined on the left side of the lenses, while positive image distance is obtained on the right side.

the laser pinhole and the PSD at a distance of $2f = 350$ mm away from the combination of the lens and mirror.

B. Principle of refracted signal detection

Following the above optical design, if both the compartments of the sample cuvette are filled with the same solution (i.e., $n_1 = n_2$), the illuminated pinhole will be just imaged at the point O, as seen in Figure 1. However, if the solvent in one of the compartments is replaced by a dilute polymer solution with a slightly different refractive index (i.e., $n_2 = n_1 + \Delta n$), the image is shifted away from the point O at a distance of Δx which is proportional to Δn , which can be directly obtained from the measured voltage difference (ΔV) (-9.55 to $+9.55$ V) from the PSD signal processing circuit (Hamamatsu Photonics, C3683-01) and recorded with an analog-to-digital data acquisition system (Jianke Instrument Ltd., China) with a sampling rate up to 1 kHz.

As shown in Figure 3, the resultant position shift ΔX projected on the PSD equals

$$\Delta X = \tan(45^\circ - \theta_5)(2f - L + S) + S, \quad (3)$$

where now $2f = 350$ mm, L is the distance between the pinhole in front of the laser source to the beamsplitter, S is the distance between incident beam and refracted beam projected on the beamsplitter, and θ_5 is a specific angle shown in

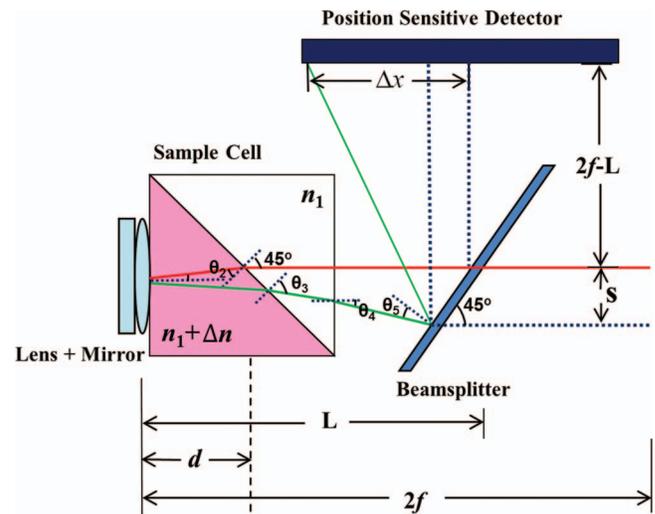


FIG. 3. Light path in the differential refractometer. One compartment of the sample cuvette is filled with solvent (n_1) and the other is filled with solution of slightly different refractive index ($n_1 + \Delta n$). The laser beam is incident into the cuvette at 45° , refracted, reflected, and refracted again at the cuvette interface, and refracted out from the cuvette, then the rest beam is projected into a position detector (PSD) reflected by a beamsplitter.

Figure 3. On the other hand,

$$S = (L - 2d) \tan \theta_4 + d \tan(\theta_3 - 45^\circ) + 2d \tan(45^\circ - \theta_2), \quad (4)$$

where d is the half optical path length (5.0 ± 0.1 mm) of the sample cuvette.

It is noted that Eq. (4) is an approximation assuming that the deflection of the beam inside the cuvette is comparably small since $d \ll L$, and the thickness of the beamsplitter d_b (3 mm) is small. The thickness of the beamsplitter does affect the value of S as the incident beam (red line in Figure 3) is actually shifted when passing through the beamsplitter. However, the effect is slight since this produces an additional shift $= d_b \sin(45^\circ - \sin^{-1}(\sin 45^\circ / 1.52)) \sim 0.297$ mm of the beam refracted at the reference/sample interface of the sample cell assuming the refractive index of the beamsplitter equals to 1.52 as glass. Compared with the half width of the cell $d = 5$ mm, this shifted variation is neglectable.

On the other hand, due to the Snell's law, if the initial incident angle of the beam (θ_1) into the cuvette is defined, the specific angles in Eq. (4) are all determined as

$$\begin{aligned} (n_1 + \Delta n) \sin \theta_2 &= n_1 \sin \theta_1 \\ n_1 \sin \theta_3 &= (n_1 + \Delta n) \sin(45^\circ - \theta_2) \\ \sin \theta_4 &= n_1 \sin(\theta_3 - 45^\circ) \\ \theta_5 &= 45^\circ - \theta_4 \end{aligned} \quad (5)$$

where n_1 is the refractive index of the reference solvent and ($n_1 + \Delta n$) is the refractive index of the solution on the other side. Usually, $\theta_1 \sim 45^\circ$ is adopted in our experiment by adjusting the incident angle of the laser beam into the sample cuvette. To achieve this, a pair of pinholes is used in the optical path before the beamsplitter which is fixed along calibration lines printed on the bottom metal plate. The initially drilled screw holes to fix the beamsplitter

holder on the bottom plate help to calibrate this angle as well. Therefore, $\Delta\theta = (45^\circ - \theta_2)$, $\Delta\theta' = (\theta_3 - 45^\circ)$, and $\theta_4 = (45^\circ - \theta_5)$ are all infinitesimals since $\Delta n/n_1 \ll 1$. As a result, based on Eqs. (3), (4), and (5), ΔX can be further approximated to be proportional to the refractive index change by⁷

$$\Delta X = [n_1(2f - 2d) + d]\Delta\theta' + 2d\Delta\theta, \quad (6)$$

where

$$\begin{aligned} \Delta\theta &= \frac{\Delta n}{n_1 + \Delta n} \\ \Delta\theta' &= 1 - \frac{n_1 + \Delta n}{n_1 \sin 45^\circ} \Delta\theta = 1 - \frac{\Delta n}{n_1 \sin 45^\circ}. \end{aligned} \quad (7)$$

Based on Eqs. (6) and (7), finally we can obtain

$$\begin{aligned} \Delta X &= k \cdot \Delta n + C \\ C &= n_1(2f - 2d) + d. \end{aligned} \quad (8)$$

In Eq. (8), C is a constant that depends on f , d , and n_1 . In our instrument, the PSD detector is placed on a two-axis translation stage with fixed distance to the beamsplitter, so C can be first eliminated by adjusting the PSD detector to be centered when the two sides of the sample cuvette are filled with the same reference solvent. On the other hand,

$$k = \frac{\Delta X}{\Delta n} = - \left(\frac{2f - 2d}{\sin 45^\circ} + \frac{d}{n_1 \sin 45^\circ} - \frac{2d}{n_1} \right). \quad (9)$$

From Eq. (9), k is a constant for a given optical setup and solvent. The value of it determines the sensitivity of the instrument, and the symbol “-” represents the projected direction on the one-dimension PSD. This constant $k = (2f - d/n_1)$ in an initial $2f$ - $2f$ design shown in Figure 1(a). From the above result, assuming with the same f , k of our refined instrument is estimated higher than the initial design for most commercial solvents, including water ($n_1 = 1.332$).

From the above analysis, in principle, in order to enhance the sensitivity of the instrument, $2f$ should be set as long as possible but in this way it unavoidably increases the dimension of the refractometer. To compromise that, we set $2f$ closely to 350 mm, which equals to the focal length of the lens to obtain an excellent sensitivity. However, in real experiment, the PSD converts the position shift ΔX into voltage ΔV in a proportional way. Therefore, we define a new instrument constant K where $\Delta n = K\Delta V$ in the later experiment section. A smaller K corresponds to a higher sensitivity of the instrument.

C. Industrial design

Figure 4 shows the front view of our finished product. The outer dimension is 485 mm (length) \times 325 mm (width) \times 170 mm (height) so that it is compact and portable. All the components are built inside the box with the exception of two units: the sample inlet/outlet and a homemade mechanical unit for the planimetric adjustment of the PSD mentioned in Sec. II B. The mechanical unit possesses refined movement control in X-Y plane achieved by the internal two-axis translation stage with a maximum displacement of 20 mm at each



FIG. 4. Front view of portable refractometer with a dimension of $485 \times 325 \times 170$ mm³.

direction. This unit is specially prepared for position calibration in portable applications. Through it, the operator can easily calibrate and reset the position of the PSD if necessary.

To induce temperature variation, an internal thermoelectric module is used as a built-in thermostat to control the temperature so that no external heating bath is required. A pair of thermoelectric modules based on the Peltier effect (Guang-Tong Yuan Industry, TEC1-12703T125) together with cooling fan is employed to regulate and stabilize the temperature of the sample cell, ranging from 15 to 50 °C with an accuracy of 0.1 °C. A temperature sensor (Analog Devices Inc., two-terminal IC temperature transducer, AD590LF) is fixed onto the sample cell holder to monitor the temperature variation. Temperature feedback control unit is integrated on the same analog-to-digital data acquisition card used. The temperature is controlled by proportional-integral-derivative (PID) algorithm which is designed in a way that least mechanical fluctuation is induced by the fan.

In order to minimize the solvent evaporation during the long-time measurement, premium lockable stopcocks for sample input (Sigma-Aldrich, Perfektum one-way spring-clip stopcock) and output (Germany, Bfohlender, HPLC-Distributors 4-sockets W/Stopcocks) are used to form a close circle during the measurements so that the baseline drifting can be reduced. Furthermore, homemade program is developed that incorporates signal intensity and position monitoring, PID temperature control, instrument calibration and dn/dc measurements. The program is capable for long-term and real-time measurements and the data can be recorded and saved as individual txt files after each measurement with variation sampling rate according to the operator's requirements.

III. RESULTS

A. Instrument calibration

Before each experiment, the intensity and the position of the incident laser beam shed on the PSD is adjusted to the middle of the PSD sensor with two sides in the same solution.

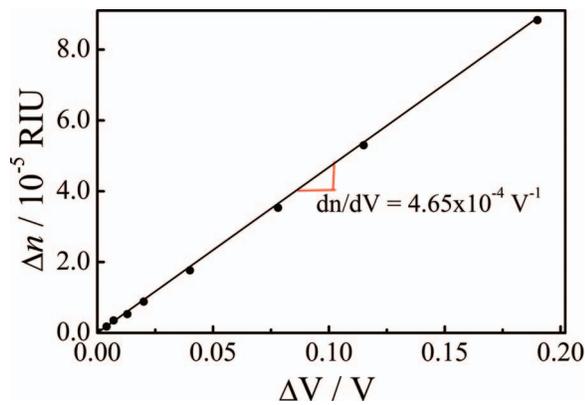


FIG. 5. Calibration curve of differential refractometer obtained by using a set of aqueous sodium chloride (NaCl) solutions ranging from 0.001 to 0.05 g/mL, corresponding to a Δn range of $\sim 1.76 \times 10^{-6}$ to $\sim 8.80 \times 10^{-5}$ RIU. The least-squares fit shows $dn/dV = 4.65 \times 10^{-4} \text{ V}^{-1}$.

In this manner, maximum deflection of the beam can be detected. After that, calibration can be performed using a series of sample solutions with known concentrations and refractive indices. Figure 5 shows the calibration results by a set of aqueous NaCl solutions at concentrations from 2×10^{-5} to 10^{-3} g/mL with known Δn at 25°C ¹⁰. The calibration result shows that the output voltage ΔV is proportional to Δn at diluted condition, i.e.,

$$\Delta n = K \Delta V = 4.65 \times 10^{-4} \Delta V, \quad (10)$$

where Δn and ΔV are in the units of RIU and volts, respectively. In our former differential refractometer design with $2f = 200$ mm, the instrumental constant $K = \Delta n/\Delta V = 3.92 \times 10^{-3} \text{ V}^{-1}$ was achieved.⁵ The much smaller value of K indicates that the sensitivity of the newly developed refractometer is increased by ten-fold. This remarkable improvement is contributed to the introducing of the double-deflection design, the modification of the focal length, and also the components refinement. With calibrated K , the deviation $\Delta n = K\Delta V$. Thus, with known concentrations (c) of a series of solution, dn/dc can be obtained. Otherwise, with known dn/dc , the concentration can be determined.

B. Signal stability

We further test the long-time signal stability of this instrument. Once the sample is filled in the cuvette by syringe, the stopcocks are locked and the measurement is then recorded. Figure 6 shows that the fluctuation of the output voltage signal (ΔV) as a function of time (t) at 25°C is less than 5×10^{-3} V with temperature control turning on. Based on Eq. (10), it corresponds to Δn uncertainty $\sim 2.33 \times 10^{-6}$ RIU, which is sufficient for determining any small difference in chemical concentrations or compositions or any other properties related to refractive index. For example, the measured Δn close to $\sim 10^{-6}$ RIU corresponds to a polymer concentration change as small as $\sim 10^{-5}$ g/mL. Such low RMS noise also indicates that the introduction of double reflection does not change the original $2f$ - $2f$ configuration which minimizes the optical shifting. On the other hand, in terms of the good

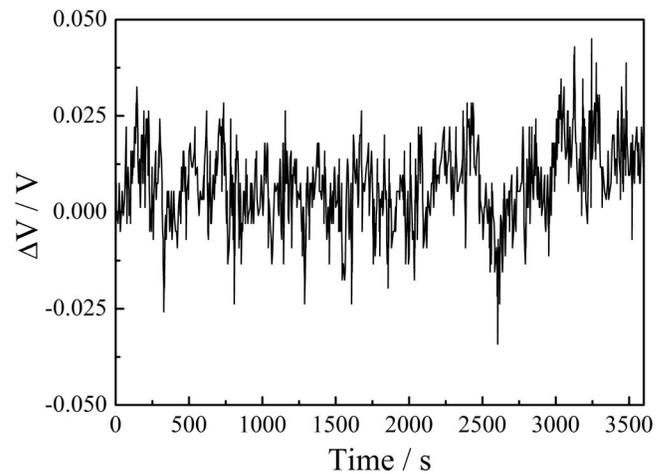


FIG. 6. Fluctuation of output voltage signal (ΔV) with pure water as a sample at 25°C , where peak-to-peak noise is less than 5×10^{-3} V, which corresponds to $\Delta n \sim 2.33 \times 10^{-6}$ RIU.

linear range (± 9.5 V) of the position sensitive detector, the maximum measurable range of the modified refractometer will be at least 0.0084 RIU, corresponding to a detectable concentration difference between the sample and reference NaCl solution as high as 4.76×10^{-2} g/mL.

On the other hand, Figure 7 shows the temperature fluctuation of this differential refractometer at 25.0°C for 1 h. It can be seen that even using the thermoelectric module and feedback control algorithm, the long-term stability of $\pm 0.2^\circ\text{C}$ can be achieved in the temperature range from 15 to 50°C .

C. Application in detecting polymer adsorption

In this demonstration, we simulate a case in water purification to test the filtration ability of a membrane filter (Millipore, Nylon hydrophilic, pore size: 200 nm) on a common polymer: poly(acrylic acid) (PAA) chains in water (hydrodynamic diameter of ~ 20 nm, determined by laser light scattering). PAA aqueous solutions at concentrations at 10^{-4} , 2×10^{-4} , and 3×10^{-4} g/mL are prepared and pumped in the sample cuvette before and after the filtration, respectively, while one compartment of the cuvette is always filled with

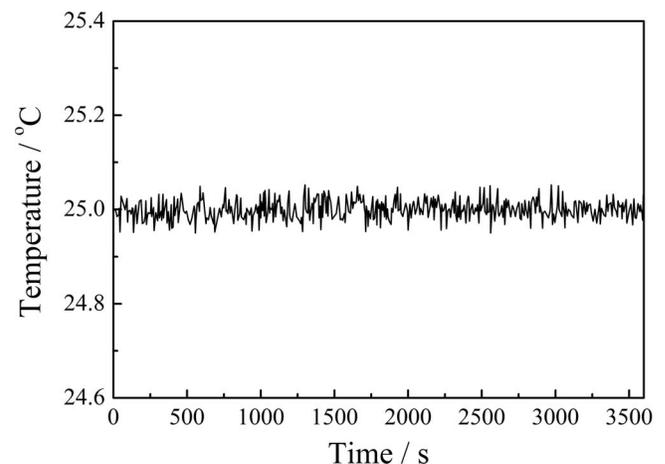


FIG. 7. Fluctuation of temperature inside measured solutions.

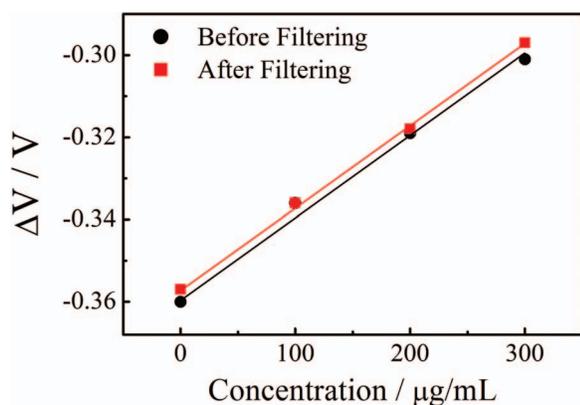


FIG. 8. Position voltage variation in dependence of concentration of PAA aqueous solution before (black circle) and after (red square) passing through a nylon hydrophilic filter with pore diameter = 200 nm, assuming the concentration is not changed. The fitting results of the slopes of the two curves give $dn/dc = 0.177$ and 0.180 , meaning that the concentration remains unchanged and filter shows little adsorption on PAA chains.

water. As shown in Figure 8, ΔV shows slight change at all the specific PAA concentrations as long as they are passing before and after the filter at such diluted concentrations. In addition, dn/dc of the resultant solution is compared with the solution before filtering to check whether the filter wall adsorbs these polymer chains or not. Fitting the linear lines in Figure 8 yields $dn/dc = 0.177$ and 0.180 before and after passing the filter, respectively, by assuming that the concentration is not changed. It indicates that the filter shows little adsorption with the polymer chains, mainly due to the large size differences between the polymer and the filter.

IV. CONCLUSION

Using a combination of $2f$ - $2f$ and a double-refraction optical design, we have developed a small and portable

refractometer with a long-term instrument drifting less than 2.33×10^{-6} RIU and a remarkable improved resolution. Such an instrument is proved to be suitable for use as a stand-alone static device to measure differential refractive index increment (dn/dc) determination or as a detector to monitor any kinetics processes that involve a time-dependent concentration change. We have clearly demonstrated in the current report that this novel portable differential refractometer developed is stable and sensitive to detect a very small concentration variation in real-time (a concentration change of 1 mg/mL with $\pm 1\%$ precision); namely, its precision is $1 \mu\text{g/mL}$. It can be used to monitor the adsorption and desorption from a substrate and detect the controllable release of active chemicals from a matrix under external stimulus like temperature and pH, to name but few.

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