Measurement of the refractive index of distilled water from the near-infrared region to the ultraviolet region

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By the minimum deviation method using a prism shaped cell, the absolute refractive indices of high-performance liquid chromatography distilled water were measured at the wavelengths from 1129 to 182 nm, at the temperature of 19 °C, 21.5 °C, and 24 °C, and then dn/dt at 21.5 °C was calculated. The coefficients of the four-term Sellmeier dispersion formula were determined by using the refractive indices at each temperature. As a result of the comparison of our refractive index data in the visible wavelength region with the formula by Tilton *et al.* at the National Bureau of Standards in 1938, both the refractive index data corresponded within 6×10^{-6}. In the UV region, the absolute refractive index at 193.39 nm calculated by the data measured nearby the wavelengths from 200 to 190 nm was 1.436517 (21.5 °C). The value was lower by 9×10^{-5} or 10×10^{-5} than the data measured by Burnett *et al.* at the National Institute of Standards and Technology. © 2007 Optical Society of America

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1. Introduction

Water is widely used as a standard material when the refractive index of liquid has to be measured accurately since it is easy to make water to high purity, and there are many measurements in the visible wavelength region of refractive index of water from previous research. Research for expressing refractive index by a formula as a function of wavelength, temperature, and density by integrating of these measurement results has also been performed [1–3]. In the visible region, the precise measurements of water were made by Tilton *et al.* [4] at the National Bureau of Standards [the NBS, which is the predecessor of the present National Institute of Standards and Technology (NIST)] in 1938, and these results have been adopted as the most reliable measurement values in the visible region in the formulas of Refs. 1 to 3. Recently, in the UV region, water is used as an immersion liquid for immersion photolithography by ArF laser, and the refractive index near 193 nm was measured by Burnett *et al.* [5] at the NIST. Because

measurement examples in the UV region are less than in the visible region, we tried to measure the refractive index with the shortest wavelength possible by the minimum deviation method using a prism shaped cell for liquid, which is described in Section 2, instead of a solid prism. In addition to these measurements, we measured the refractive index in the visible region and also part of the infrared region. We compared these with the measurement examples of the literatures.

2. Measurement Method

The refractive index n_{rel} of a specimen polished to a prism shape over surrounding environment is expressed by apex angle θ and minimum deviation angle δ as follows [6]:

$$n_{rel} = \frac{\sin[(\theta + \delta)/2]}{\sin(\theta/2)}. \qquad (1)$$

The refractive index of liquid can also be measured as a solid specimen by putting it into a prism shaped cell, which is made by plane-parallel plates of transparent and homogeneous material as indicated in
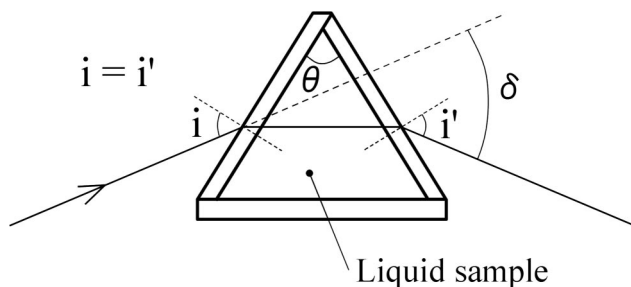
Fig. 1. Sketch of refractive index measurement of liquid by the minimum deviation method using a prism shaped cell.

Fig. 1. The prism shaped cell we used was what the plane-parallel plates of 6 mm thickness made of fused silica were assembled to by epoxy adhesive, and its apex angle was 60°, and the inner faces of the cell, which the light rays pass, was 20 mm in height and 30 mm in width. Although the parallelism of individual fused silica plates was controlled within 1 arc sec, the prism had been assembled so that the direction of the wedge of the plates was perpendicular to the direction of the deviation angle of the prism in order to minimize the error caused by the wedge angle. A stainless steel pipe 2 mm in diameter with a closed tip to insert a temperature sensor was placed in the glass lid. For sampling, we used distilled water used for high-performance liquid chromatography (HPLC) made by Wako Pure Chemical Industries, Ltd., Japan, and we put on a lid to the cell so that air was included in the inside upper space part of the cell.

Measurement was performed in a nitrogen gas environment by using the goniometer spectrometer model 1 UV-VIS-IR made by Moeller-Wedel-Optical, Germany, which was modified so that it could even measure in the vacuum UV region [7]. One set of the measurements of apex angle was the average of the eight measurements of apex angle by rotating the graduated circle of the spectrometer by 45° every time. To obtain the minimum deviation angle, the double deviation angle 2δ was measured by determining the positions of the left and right minimum deviations. The two ways to detect the position of the minimum deviation were first by observing the motion of the position of the slit image on the monitor and looking for its return point under the prism shaped cell turning in the wavelength range from 1129 to 289 nm, which can be measured by CCD camera, and, second, by using a reflection light from the incident surface of the prism [6] in the wavelength shorter than 289 nm with a photomultiplier tube.

For light sources of the wavelength from 1129 to 289 nm, we used six kinds of spectral lamps (H, He, Hg, Cd, Cs, and Rb), and from 283 to 182 nm we used a Pt-Ne hollow-cathode lamp [8,9]. We measured the refractive indices at 57 wavelengths in total. To compare our data with the measurement results of the NIST, in the region of wavelength 200 nm or less, more frequent intervals of the wavelengths were taken. To obtain the refractive index at 21.5 °C and

the temperature coefficient of the refractive index (dn/dt), the sample was measured at 19 °C, 21.5 °C, and 24 °C (within ±0.1 °C, respectively). The sample temperature and the atmospheric pressure of the environment were measured in every measurement at each wavelength. The atmospheric pressure during the whole period of the measurements was within the range from 989 to 1000 hPa. The light rays pass through the whole cell uniformly in the wavelength region with high transmittance over the sample, but the measurement error becomes large in the wavelength region with low transmittance over the sample because of the error effected by the flatness of the prism surfaces, since the light rays cannot pass through except for the neighborhood of the apex angle. To reduce the above effects in our measurements, under the conditions that only the width of 10 mm from the tip of the apex is left and the other part is masked, we measure the apex angles and the minimum deviation angles of the whole wavelengths.

During preliminary measurements, we confirmed that the epoxy resin gluing the component parts of the cell was swelled by absorbing water. When we put water in the cell the apex angle of the cell changed during several days by 2 or 3 arc sec. To reduce this effect, we started the measurements after the change of the apex angle decreased by waiting 1 day after putting water in the cell. As the measurements of the minimum deviation angles took several days, the apex angle was measured at the beginning and the end of each measurement day. We used the average value of those apex angles measured before and after each measurement day as the apex angle used for determining the minimum deviation angles. The maximum value of the difference in apex angles measured in one day was 0.5 arc sec.

3. Measurement Results

The refractive indices calculated by substituting the measurement data of the apex angle and the minimum deviation angles for formula (1) were converted to the absolute refractive indices by multiplying the refractive indices of nitrogen gas. For calculating the refractive index of nitrogen gas, in a wavelength higher than 480 nm the formula of Peck and Khanna [10] was used, in a wavelength lower than 273 nm the formula of Griesmann and Burnett [11] was used, and in the middle of these wavelengths the formula of Koch [12] was used.

Since the change of refractive index in water attributable to temperature is not linear [4], the quadratic formula for the refractive index to the temperature was fixed from the three sets of the measurement data of the refractive indices and the temperatures. The correction of the temperature was done by substituting 19 °C, 21.5 °C, and 24 °C for this formula and calculating the absolute refractive index at each temperature. The refractive index at 20 °C was also interpolated by this formula. The temperature coefficient of the absolute refractive index at 21.5 °C was calculated by differentiating this formula with respect to temperature and substituting 21.5 °C for

Table 1. Absolute Refractive Indices and dn/dt of HPLC Water

| Vacuum Wavelength (nm)	Absolute Refractive Index				dn/dt abs. 21.5 °C ($\times 10^{-6}$/°C)
	19.0 °C	21.5 °C	24.0 °C	20.0 °C (interpolated)	
1128.95	1.323638	1.323435	1.323216	1.323559	−84.5
1083.33	1.324325	1.324125	1.323902	1.324248	−84.7
1014.26	1.325354	1.325147	1.324921	1.325273	−86.4
894.596	1.327152	1.326937	1.326702	1.327068	−89.9
852.344	1.327817	1.327601	1.327365	1.327733	−90.4
780.237	1.329041	1.328821	1.328583	1.328955	−91.6
706.714	1.330463	1.330240	1.329996	1.330376	−93.3
656.454	1.331597	1.331371	1.331126	1.331509	−94.1
644.025	1.331906	1.331679	1.331436	1.331817	−94.0
587.725	1.333489	1.333260	1.333012	1.333399	−95.3
546.227	1.334915	1.334684	1.334435	1.334825	−96.0
486.269	1.337575	1.337344	1.337091	1.337485	−96.9
480.126	1.337903	1.337669	1.337418	1.337811	−97.0
435.957	1.340669	1.340434	1.340179	1.340578	−98.0
404.770	1.343205	1.342968	1.342710	1.343113	−98.9
365.119	1.347494	1.347254	1.346994	1.347400	−100.1
334.244	1.352091	1.351848	1.351588	1.351996	−100.6
312.657	1.356306	1.356059	1.355795	1.356209	−102.1
296.814	1.360132	1.359885	1.359619	1.360036	−102.5
289.44400	1.362185	1.361938	1.361673	1.362089	−102.5
283.11246	1.364120	1.363872	1.363603	1.364023	−103.3
273.47659	1.367399	1.367152	1.366882	1.367303	−103.4
262.88107	1.371580	1.371332	1.371063	1.371483	−103.5
253.99695	1.375660	1.375410	1.375140	1.375563	−104.2
248.79191	1.378345	1.378094	1.377822	1.378247	−104.6
244.08006	1.380993	1.380742	1.380471	1.380895	−104.5
239.02641	1.384097	1.383847	1.383575	1.384000	−104.3
231.16733	1.389567	1.389317	1.389045	1.389469	−104.3
226.34187	1.393389	1.393138	1.392869	1.393291	−104.1
222.57015	1.396666	1.396417	1.396146	1.396569	−103.9
217.53669	1.401504	1.401257	1.400987	1.401408	−103.5
213.13806	1.406245	1.406001	1.405734	1.406151	−102.3
210.40121	1.409478	1.409236	1.408969	1.409385	−101.8
207.60622	1.413036	1.412797	1.412533	1.412944	−100.5
204.22306	1.417740	1.417506	1.417245	1.417649	−98.9
200.84066	1.422949	1.422718	1.422463	1.422859	−97.1
198.91056	1.426185	1.425958	1.425704	1.426097	−96.3
197.97647	1.427824	1.427601	1.427348	1.427738	−95.1
197.15374	1.429315	1.429093	1.428844	1.429229	−94.1
196.31429	1.430883	1.430662	1.430413	1.430798	−94.0
195.47439	1.432498	1.432280	1.432034	1.432415	−92.9
194.44617	1.434542	1.434328	1.434084	1.434460	−91.5
193.74245	1.435991	1.435775	1.435535	1.435907	−91.2
193.43690	1.436629	1.436417	1.436177	1.436547	−90.3
192.92449	1.437718	1.437512	1.437273	1.437640	−89.0
191.60818	1.440625	1.440420	1.440187	1.440546	−87.6
190.74940	1.442606	1.442404	1.442176	1.442529	−86.1
189.90445	1.444627	1.444427	1.444204	1.444550	−84.8
188.95226	1.446990	1.446797	1.446576	1.446916	−82.6
188.30587	1.448653	1.448465	1.448250	1.448581	−80.6
186.71302	1.452973	1.452796	1.452589	1.452905	−76.7
185.34523	1.456955	1.456787	1.456594	1.456891	−72.1
184.96831	1.458101	1.457938	1.457748	1.458039	−70.6
184.57517	1.459322	1.459163	1.458976	1.459262	−69.2
183.65075	1.462294	1.462140	1.461964	1.462235	−65.9
182.61377	1.465810	1.465671	1.465508	1.465757	−60.2
181.78736	1.468775	1.468645	1.468492	1.468725	−56.5
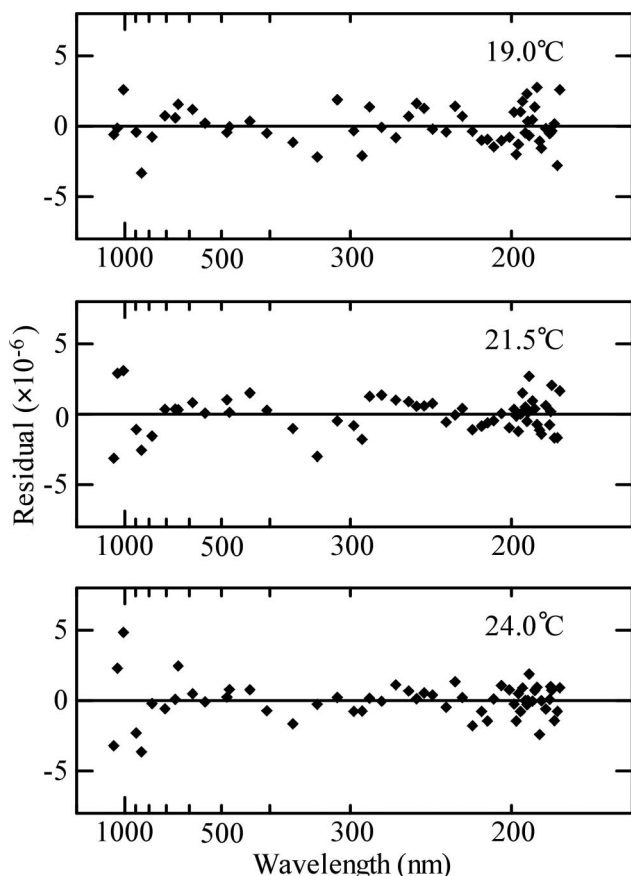
Fig. 2. Residuals in the approximation by Sellmeier dispersion formula for the refractive index measurements from 1129 to 182 nm.

it. About a group of absolute refractive indices (n) at each temperature, the eight constants in the following four-term Sellmeier dispersion formula were determined by the least-squares method, and the residuals between the values calculated by this dispersion formula and the measurement values were obtained:

$$n^2 - 1 = \sum_{i=1}^{4} \frac{A_i \lambda^2}{\lambda^2 - \lambda_i^2}, \qquad (2)$$

where λ is a vacuum wavelength in units of micrometers.

The absolute refractive indices at each temperature and the dn/dt at 21.5 °C are listed in Table 1, and the residuals are shown in Fig. 2. Table 2 shows the constants of the dispersion formula. The standard deviations of the residuals became 1.3×10^{-6} in all three temperatures, so the dispersion formula made it possible to approximate the measurement results to the sixth decimal place.

Table 3 shows the estimations of the major uncertainties in measurements. Although the effect of temperature to the uncertainty of the measurement results is different by dn/dt, by supposing $dn/dt = -105 \times 10^{-6}/°C$, the expanded uncertainty of the absolute refractive index becomes 8×10^{-6} and that of dn/dt becomes $2.2 \times 10^{-6}/°C$ as the results of estimating the expanded uncertainty based on the standard uncertainty with respect to each item. Here we adopted 2 to the coverage factor k. In the wavelength region lower than 185 nm, we expect that the uncertainty will increase somewhat because the transmittance of water declines rapidly [13–15], and the light rays pass through only part of the tip of the apex angle of the cell.

4. Comparison with the Results Measured by the Other Institutions

A. Comparison with the Measurement Results of the National Bureau of Standards (1938)

Within the measurement range (from 706 to 405 nm) of the NBS, Fig. 3(a) shows the results of comparison between our measurement values of refractive index and the values based on the dispersion formula of the NBS. Since the formula of the NBS [4] is the formula that shows the relative refractive index with respect to air, it was compared with the result converted to the absolute refractive index by multiplying it by the refractive index of air [16]. The maximum difference between our data and the formula of the NBS was 6×10^{-6}, and they corresponded within the range of both errors. Figure 3(b) shows the results of the comparison of dn/dt at 21.5 °C between the two. The maximum difference was $0.3 \times 10^{-6}/°C$, and they corresponded well within the range of both errors too.

B. Comparison with the Dispersion Formula Presented by Harvey et al.

Figure 4 shows the result of comparison at 21.5 °C between our measurement values of refractive index

Table 2.   Sellmeier Dispersion Constants for Absolute Refractive Index of HPLC Water

	19.0 °C	21.5 °C	24.0 °C	20.0 °C
A_1	$5.672526103 \times 10^{-1}$	$5.689093832 \times 10^{-1}$	$5.666959820 \times 10^{-1}$	$5.684027565 \times 10^{-1}$
A_2	$1.736581125 \times 10^{-1}$	$1.719708856 \times 10^{-1}$	$1.731900098 \times 10^{-1}$	$1.726177391 \times 10^{-1}$
A_3	$2.121531502 \times 10^{-2}$	$2.062501582 \times 10^{-2}$	$2.095951857 \times 10^{-2}$	$2.086189578 \times 10^{-2}$
A_4	$1.138493213 \times 10^{-1}$	$1.123965424 \times 10^{-1}$	$1.125228406 \times 10^{-1}$	$1.130748688 \times 10^{-1}$
λ_1^2	$5.085550461 \times 10^{-3}$	$5.110301794 \times 10^{-3}$	$5.084151894 \times 10^{-3}$	$5.101829712 \times 10^{-3}$
λ_2^2	$1.814938654 \times 10^{-2}$	$1.825180155 \times 10^{-2}$	$1.818488474 \times 10^{-2}$	$1.821153936 \times 10^{-2}$
λ_3^2	$2.617260739 \times 10^{-2}$	$2.624158904 \times 10^{-2}$	$2.625439472 \times 10^{-2}$	$2.620722293 \times 10^{-2}$
λ_4^2	$1.073888649 \times 10^{1}$	$1.067505178 \times 10^{1}$	$1.073842352 \times 10^{1}$	$1.069792721 \times 10^{1}$

Table 3. Estimation of Uncertainty

Cause	Standard Uncertainty
Apex angle	0.1″
Change of apex angle by swelling of epoxy resin	0.15″
Double minimum deviation angle (2δ)	0.5″
Temperature	0.03 °C
Distribution of temperature	0.02 °C
Nitrogen pressure	0.1 hPa
Refractive index of nitrogen gas	2×10^{-7}

Object	Expanded Uncertainty (k = 2)
Refractive index	8×10^{-6}
dn/dt	$2.2 \times 10^{-6}/°C$

Fig. 4. Comparison between refractive index measurements of HPLC water at 21.5 °C and the formula of Harvey.

and the dispersion formula of Harvey *et al.* [3], and Fig. 5 shows the difference of our measurements from the dispersion formula of Harvey *et al.* [3] at three temperatures. In the visible region having adopted the measurement results of the NBS to the determination of this formula, both data correspond to each other. However, in the infrared region and the UV region, the differences between the two become large. However, since under the room temperature and the atmospheric pr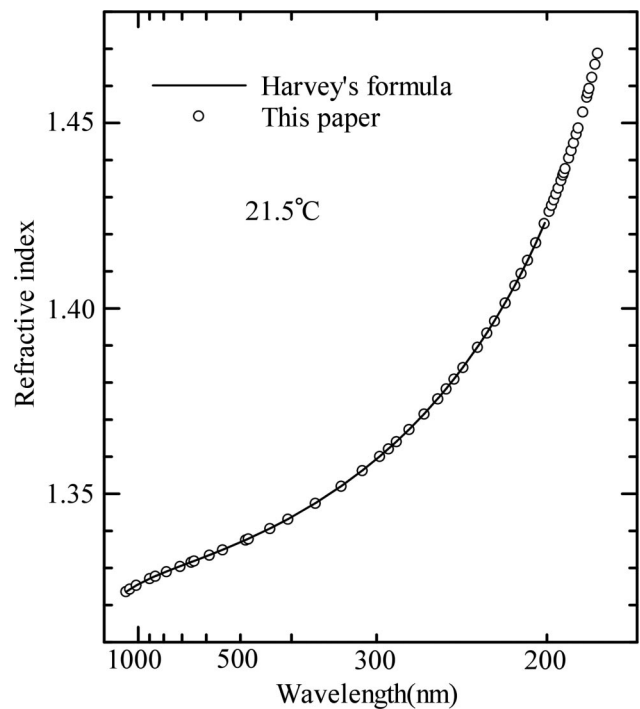essure, the uncertainty of the formula of Harvey *et al.* [3] is 1×10^{-3} in the infrared region and 5×10^{-4} in the UV region, both correspond as for these uncertainty ranges.
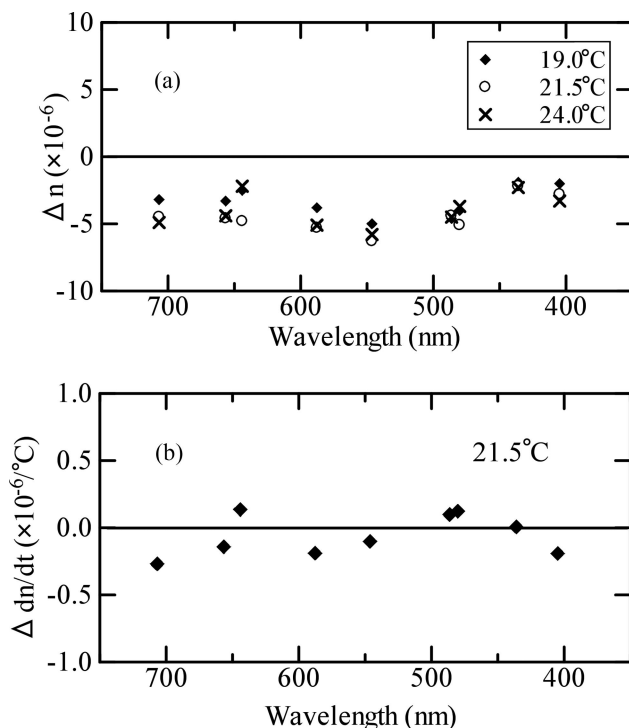

Fig. 3. Comparisons of (a) our refractive index measurements, and (b) our dn/dt measurements with the formulas of NBS. Δn and $\Delta dn/dt$, which are vertical axes, show the differences (our measurements-formula of NBS).
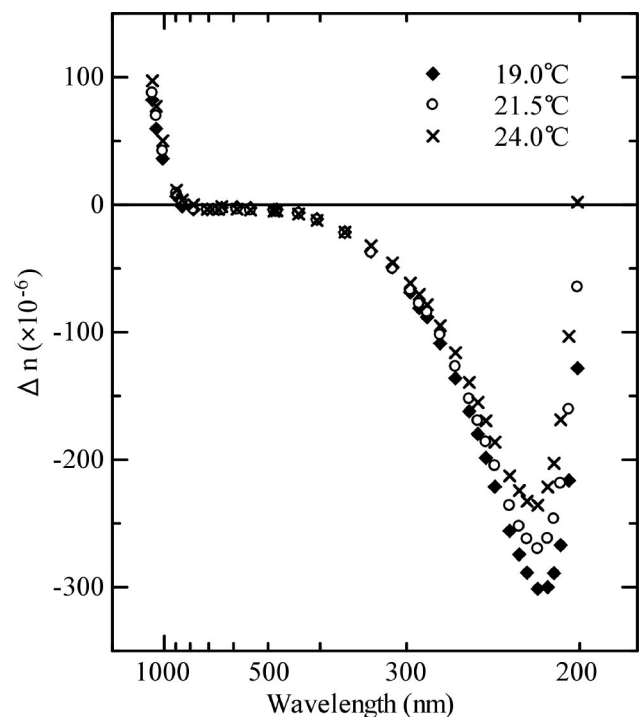

Fig. 5. Comparison of our refractive index measurements with the dispersion formula of Harvey. Δn shows the difference (our measurements-dispersion formula of Harvey).

## C. Comparison with the Measurement Results of the NIST

The NIST [5] has measured the refractive index of HPLC water by the two kinds of methods. The first method is the minimum deviation method using the prism shaped cell. The second method is the interferometric method. In this method, an etalon cell filled with water is illuminated with white light, and the peak wavelength of the light passed through the etalon cell is measured by the spectrometer [17]. The dispersion formula was determined by using the refractive indices at five wavelengths between 191.608 and 198.986 nm, which were measured at 21.5 °C by the method of the minimum deviation angle, and the refractive index at 193.39 nm (the wavelength of the ArF laser) was calculated. Regarding the wavelength of 194.5 nm, the value of dn/dt at 21.5 °C was obtained by the index measurements at various temperatures between 20 °C and 23 °C. The values of dn/dt in the other wavelengths including the visible region have also been shown in the graph. Regarding the measurements by interferometric method, as well as the method of the minimum deviation angle, the refractive indices at five wavelengths and at 193.39 nm were shown, and the dn/dt at 194.5 nm was indicated. In addition, the refractive indices and the dn/dt, at the other wavelengths were given in the graphs. It was stated that the uncertainties of the refractive index measurements were 2×10^{-5} in both methods, and the uncertainties of the dn/dt measurements were $4 \times 10^{-6}/°C$ in the method of the minimum deviation angle and $7 \times 10^{-6}/°C$ in the interferometric method.

The NIST is using a high electric current Cu-Ne hollow cathode lamp as a light source for the minimum deviation method. Therefore a common measurement wavelength between this NIST lamp and our Pt hollow cathode lamp is only 191.608 nm in the spectral lines of Ne. To compare our results with the NIST results, the coefficients of the same type of dispersion formula as that of the NIST (Table 4) were calculated by using the refractive indices of ten wavelengths selected among the wavelengths from 191.60818 to 198.91056 nm, which we measured this time. Figure 6 shows the residuals between the measurement values and the values calculated by using this dispersion formula [substituting 2 for m of Eq. (3)]:

$$n = \sum_{i=0}^{m} a_i(\lambda - 193.39)^i. \qquad (3)$$

Table 4. Dispersion Constants of Absolute Refractive Index of Distilled Water Between 198.9 nm and 191.6 nm at 21.5 °C

i	a^i	
	Quadratic Equation	Third-order Equation
0	1.4365243	1.4365170
1	-2.11491×10^{-3}	-2.11540×10^{-3}
2	3.6729×10^{-5}	4.0848×10^{-5}
3	—	-7.520×10^{-7}
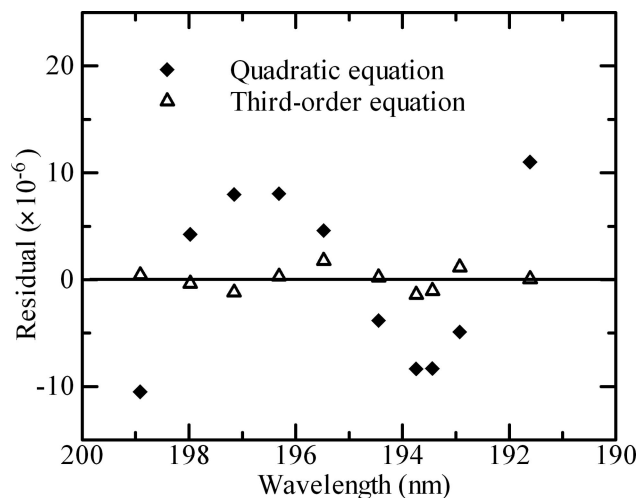
Fig. 6. Residuals between the measurement values arid the quadratic and the third-order dispersion formula determined by using the refractive index measurements from 198.9 to 191.6 nm (21.5 °C).

The unit of λ in this formula is the nanometer. This dispersion formula does not sufficiently approximate the measurement results since the third-order components are remaining as seen obviously in Fig. 6. To improve the approximation, the increased degree of Eq. (3) to the third order was used by putting $m = 3$ in Eq. (3), and the results were shown in Table 4 and Fig. 6 as well. The dispersion formula was approximated to the level of the maximum residuals 2×10^{-6}. On the basis of this dispersion formula, Fig. 7 shows the plotting result of the values of the NIST, and Table 5 shows the result of the comparison of the
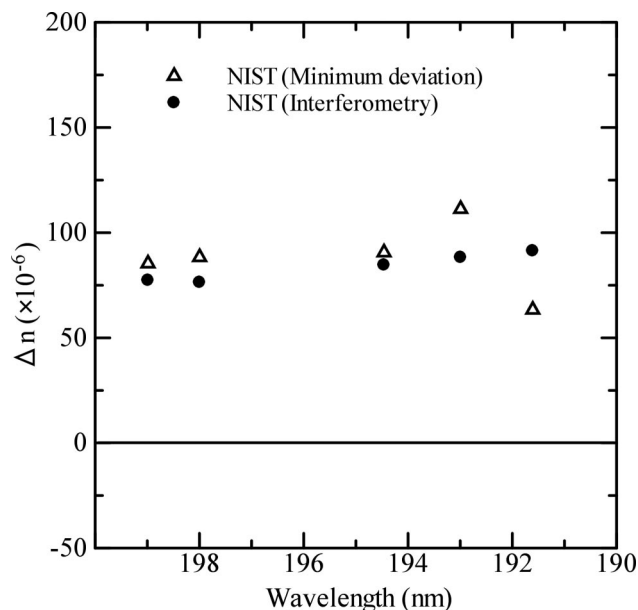
Fig. 7. Comparison of the measurements of NIST with the dispersion formula determined by using our refractive index measurements. Δn shows the difference (NIST measurements–our third-order dispersion formula).

Table 5. Comparison of Absolute Refractive Index Measurements at 193.39 nm and 21.5 °C
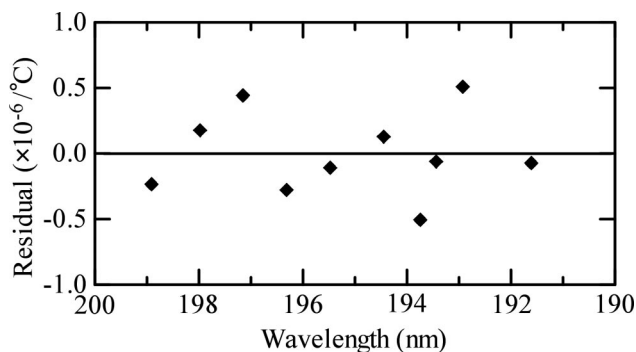
	Refractive Index	Difference From Our Measurements ($\times 10^{-5}$)
Our measurements	1.436517	—
NIST (Minimum deviation method)	1.43662	+10
NIST (Interferometric method)	1.43661	+9

Table 6. Comparison of dn/dt_{abs} Near 193 nm at 21.5 °C

Vacuum Wavelength (nm)	194.5	193.39
Our measurements	-91.7×10^{-6}/°C	-90.2×10^{-6}/°C
NIST (Minimum deviation method)	-100×10^{-6}/°C	—
NIST (Interferometric method)	-90×10^{-6}/°C	—

refractive indices at 193.39 nm. The refractive index at 193.39 nm measured by the NIST has the difference of $+10 \times 10^{-5}$ in the minimum deviation method, and $+9 \times 10^{-5}$ in the interferometric method compared with our value. The differences widely exceeded the range of the uncertainty by both the NIST's and ours.

To compare the measurement values of dn/dt the following dispersion formula (4) of dn/dt was evaluated from the measurement values of dn/dt at the same ten wavelengths as the refractive index measurement, and the residuals of its dispersion formula were within 0.5×10^{-6}/°C so as to be shown in Fig. 8:

$$\frac{dn_{abs}}{dt} = -9.020 \times 10^{-5} - 1.39 \times 10^{-6} \times (\lambda - 193.39)$$
$$+ 6.1 \times 10^{-8} \times (\lambda - 193.39)^2. \qquad (4)$$

The unit of λ in this formula is the nanometer. Table 6 shows the results of the comparison between the dn/dt at 194.5 nm calculated from formula (4) and the dn/dt values of the NIST. The dn/dt at 193.39 nm calculated in the same manner was also described. The value of dn/dt at 194.5 nm measured by the NIST has the difference of -8×10^{-6}/°C in the minimum deviation method, and $+2 \times 10^{-6}$/°C in the interferometric method compared with our value. The difference in the interferometric method was within the ranges of the uncertainties of both of the NIST's and ours. On the other hand, in the minimum

deviation method the difference exceeded the ranges for the uncertainties of both values. The values of dn/dt at other wavelength regions were read off the graph on the paper of the NIST, and they were plotted once again to the graph together with our measurement values and the values that were calculated from the formula of the NBS to compare with one another (Fig. 9). The values of the NIST by the minimum deviation method have the difference in degree of a maximum of -10×10^{-6}/°C compared with our data, but the data by the interferometric method correspond to our data within the difference in degree of $\pm 2 \times 10^{-6}$ all over the wavelength region.

5. Consideration About Cause of the Difference and Additional Experiments

To investigate the cause of differences between the NIST's results and ours, the considerations and the additional experiments were done about the following items.

Fig. 8. Residuals between the measurement values of dn/dt and the quadratic dispersion formula determined by using the dn/dt measurements from 198.9 to 191.6 nm (21.5 °C).
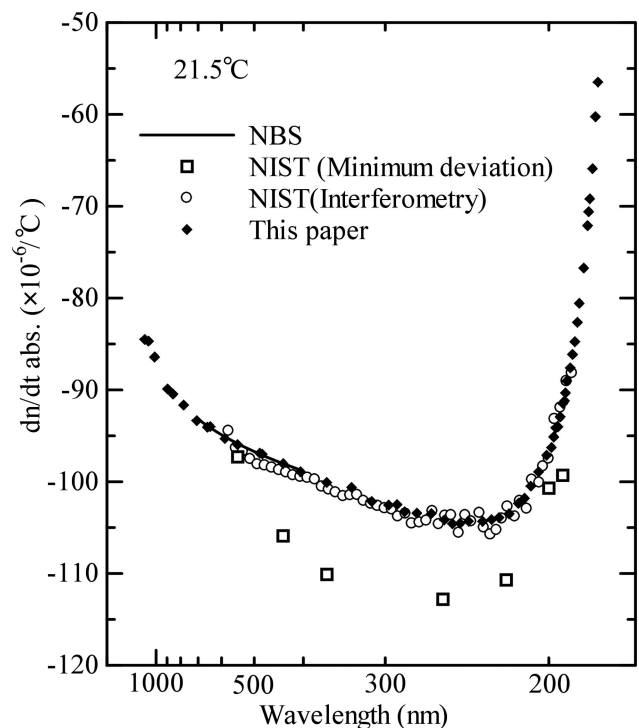

Fig. 9. Comparison of dn/dt among our measurements, the NIST measurements and the NBS formula. The values of NIST were read off the graph in its paper.
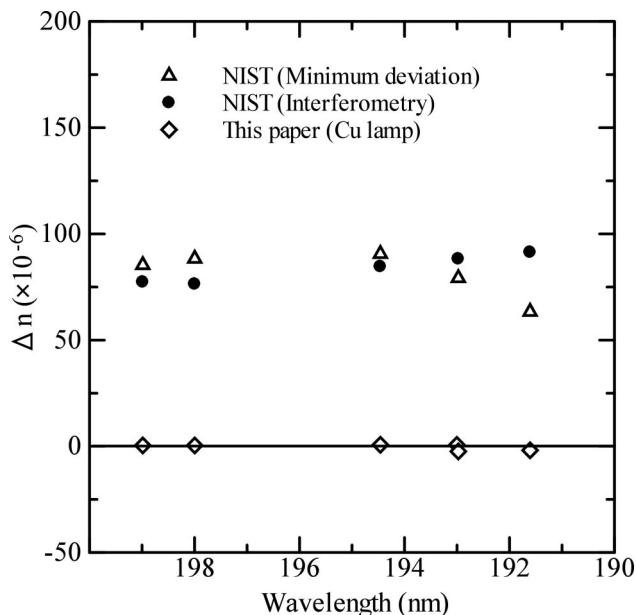
Fig. 10. Comparison between each measurement value of NIST and our measurement values with Cu lamp after revising its wavelength. Δn shows the difference (each measurement value minus our third-order dispersion formula).

A. Measurement by Using Cu Lamp

We tried to measure by using a Cu hollow-cathode lamp (which is not the high-current type) to measure at the same wavelengths as the NIST. Since the line near 192.990 nm separated into two lines, we measured the refractive index at both lines. According to the literature (Ref. [18]) these lines are considered 193.00345 nm of Ne and 192.97510 nm of Cu. Figure 10 shows the results that the measurements by using the Cu lamp were compared on the basis of the third-order dispersion formula (Table 4), which was determined in advance by the measurement by using a Pt hollow-cathode lamp. The difference between the measurement data by Cu lamp and the data derived from the dispersion formula determined by Pt lamp became 2×10^{-6} in maximum and we were not able to recognize the difference between the light sources of the Pt lamp and the Cu lamp. As it is supposed that these 193.00345 and 192.97510 nm lines may not be observed separately depending on the slit width, there is the possibility that the NIST showed 192.990 nm as the average of these two lines. Actually the ratio of the intensities of the two lines changes by the conditions of emission of light, so in the case the line does not separate, the practical wavelength of the measurement is not clear. By assuming that the NIST measured the refractive indices at 192.97510 nm, the result that we took the difference between the NIST data and our data evaluated from the coefficients of the third-order dispersion formula in Table 4 is shown in Fig. 10. When we compare Fig. 10 with Fig. 7, we see that the difference of the measurements near 193 nm by the minimum deviation method between our data and the NIST data decreased from 11×10^{-5} to 8×10^{-5}.

B. Effect by Dissolution of Components of Resin to Water

The prism shaped cell that the NIST used was assembled by the way of optically contacting the parts made of fused silica, and it has been considered so that the water of the sample contacts with only fused silica. The prism shaped cell that we used this time was assembled by using epoxy adhesive. For this reason, during the measurement, there may be the possibility of the dissolution of some components of resin to the distilled water of the sample and the possibility of the effect to the refractive index. To confirm the existence of this effect, we abandoned the distilled water which was in the prism shaped cell for 4 days when the refractive index measurements from 200 to 182 nm were finished and immediately put the distilled water in the glass bottle into the prism shaped cell and then we again measured the refractive index at 193.43690 nm within 30 min. Nevertheless the difference of the refractive indices before and after the exchange of the sample was within 2×10^{-6}. With this result, even if there may be the effect of dissolution of the adhesive, it is considered that the uncertainty of this factor is less than the uncertainty of other factors in this measurement.

C. Effect About Dissolution of Air to Water

The NIST used air-saturated HPLC water as the measurement sample. We also used the distilled water of HPLC grade, but we have not confirmed the degree of its saturation. However, it is considered that the measurement was done with water nearly saturated with air, because when we received the HPLC water packed in a glass bottle of the reagent maker, air was in the upper part of the bottle, and, further, after putting water into the prism shaped cell it was exposed to air for approximately one day until we started the measurement. According to Harvey *et al.* [19], the change of refractive index in the case that air dissolves to water until the saturated state is approximately -7×10^{-6} at 193 nm. Therefore even if the degree of air saturation in our sample was not sufficient, the difference from the NIST cannot be explained.

D. Effect About Purity of Sample

To confirm the influence by the purity of the sample, we measured several kinds of water at 21.5 °C and compared them with HPLC water. The samples we used were the deionized water prepared in our laboratory, the distilled water distilled from this deionized water, and the water before refinement (tap water). Figure 11 shows the refractive index result between each sample compared with HPLC water. The differences of the refractive index for both the deionized water and the distilled water from HPLC water were less than 5×10^{-6} in maximum, and each value corresponded well within the range of uncertainties. The difference of the refractive index for the water before refinement (tap water) from that of HPLC water was $+32 \times 10^{-6}$ in maximum. With
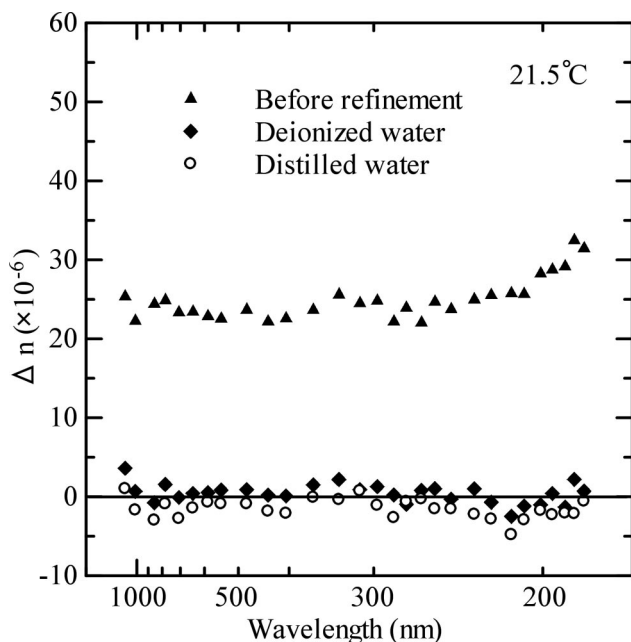
Fig. 11. Differences of refractive indices between three kinds of water and HPLC water. Δn shows the difference (refractive index of each kind of water-refractive index of HPLC water).

these results, once the water is refined, it is considered that the difference of 10^{-5} order does not happen.

E. Effect About Atmospheric Pressure to Water

Although the absolute refractive index of water rises according to the rising of pressure, the pressure coefficient of the refractive index (dn/dp) is very small, and it is approximately 1.5×10^{-8}/hPa in the visible region [3]. Therefore the difference of refractive index of only approximately 4×10^{-7} is caused by the difference of 24 hPa between the standard atmospheric pressure 1013.25 hPa and 989 hPa, which was the lowest one from the standard atmospheric pressure in this measurement. This amount is negligible in this measurement.

The above consideration and the additional measurements from Subsections 5.A–5.E were done regarding the items that were not included in the estimates of uncertainties, but none of them were able to reduce the difference of nearly 1×10^{-4}. Our measurement data correspond well with the data of the NBS whose accuracy has been announced as 1×10^{-6} in the visible region. Since the residuals from the dispersion formula are within $\pm 3 \times 10^{-6}$ even in the UV region, where the intensity of light or the detector are different from the visible region, and the factors of uncertainty about the measurements of angle and temperature are common to the visible region, we think that the measurement results in the UV region are also sufficiently trustworthy. Although it has been pointed out recently [19] that estimating the change of the refractive index due to the solution of air is not sufficient regarding the data of the NBS,

nevertheless it is considered that the error might not reach 1×10^{-5}.

The NIST measured by the minimum deviation method and by the interferometric method, and it showed that each result corresponded within each uncertainty (2×10^{-5}). Since the Gaertner goniometric spectrometer used by the NIST cannot directly measure the minimum deviation angle owing to its mechanics, it is necessary that the minimum deviation angles in the visible region be measured by another spectrometer in advance [20]. The NIST admits that its results in the visible region are approximately 4×10^{-5} higher than the NBS data, and it announced that it was investigating the causes. The interferometric method also cannot measure refractive index alone. To fix the order of the interferogram, it is necessary that the refractive indices of some wavelengths be known already. We do not consider that the results by the two kinds of perfectly independent measurement methods corresponded to each other because it is supposed that NIST used the refractive indices in the visible region that were measured by a spectrometer, although they were the refractive indices that were used as the basic values of interferometric method.

The interferometric method that the NIST performed has the possibility of improvement in accuracy of measurement by thickening the sample in the region of high transmission. We look forward to the completion of its investigation as we see some advantages of its method. For example the interval of the measuring wavelength can be set regularly and frequently.

6. Conclusion

By the minimum deviation method using a prism shaped cell, the absolute refractive indices of HPLC distilled water were measured at the wavelengths from 1129 to 182 nm, and at the temperature of 19 °C, 21.5 °C, and 24 °C, and then dn/dt at 21.5 °C was calculated. As a result the coefficients of the four-term Sellmeier dispersion formula were determined by using the refractive indices at each temperature, and the standard deviation of the residual was 1.3×10^{-6}. The absolute refractive index at 193.39 nm and 21.5 °C that was evaluated from these measurements was 1.436517, and then dn/dt at the same wavelength and at the same temperature was -90.2×10^{-6}/°C. The expanded uncertainties ($k = 2$) of the above refractive index measurement and the dn/dt measurement are estimated to be 8×10^{-6} and 2.2×10^{-6}/°C, respectively. A comparison of our refractive index and dn/dt data in the visible wavelength region to the formulas of the NBS shows that both refractive index data corresponded within 6×10^{-6}, and the both dn/dt data corresponded within 0.3×10^{-6}/°C, respectively. As a result of the comparison of our refractive index at 193.39 nm with the data that were measured by the two kinds of methods of the NIST, there were differences of $+10 \times 10^{-5}$ in the minimum deviation method and

$+9 \times 10^{-5}$ in the interferometric method from our measurements. Either method did not correspond within the range of the uncertainty to our data. The value of dn/dt at 194.5 nm measured by the NIST had the difference of $-8 \times 10^{-6}/°C$ in the minimum deviation method compared with our value, and we were not able to find the correspondence with both results. However, in the interferometric method its difference became $+2 \times 10^{-6}/°C$, and both results corresponded within the range of the uncertainty.

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