2 Egypt. J. Phys. **Vol. 39**, No.1, pp.11 - 24 (2008)

Precise Determination of Refractive Index of Most Popular Environmental Pollutant Gases (1)

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IN PRESENT work a Mach- Zehnder Interferometer System (MZIS) was constructed by using a Multimode Argon Ion Laser (MAIL) with six different wavelengths. These wavelengths were selected by using a high-resolution monochromator. A gas flow system (GFS) was carefully designed and constructed which was linked to MZIS. This gas flow system was controlled by both pressure range from 60-90 cm Hg and temperature range between 308-358 K. The accuracy of pressure measurements was ± 0.5 mm Hg and for temperature was ± 1 °C. The MZIS and GFS were combined and used to determine the refractive index (RI) of two most popular pollutant gases, carbon dioxide (CO_2) and $freon_{12}$ (R_{12}), as a function of pressure, n_T (p), and temperature n_P (T). The thermo-optical coefficients, $(dn/dT)_P$, of the two investigated gases were determined. Also, the rate of change of refractive index with respect to gas pressure at constant temperature $(dn/dP)_T$ was also determined. In view of the presence of these gases within the atmosphere and its effect by the different wavelength, the dispersion behavior, the wavelength dependence of a refractive index $(dn/d\lambda)_T$, of that selected gases were studied. Also, the optical dispersion curves for both carbon dioxide and $freon_{12}$ gases were studied. Therefore the dispersion constants A and B of Cauchy's equation were determined.

In the attempt to study the behavior of some environmental pollutant gasses, one needs to provide an accurate experiment, which give us the behavior of these gases at different pressures and temperatures. Some of these experiments depend on the fact that the optical behavior of gases is related to gas density. Indeed the application of optical interferometer to gas dynamic began when Jamin[1] started to measure the refractive index of a gas. Also Hohm and Kerl[2] used a Michelson twin interferometer for precise measurement of the refractive index of gases between 100 K and 300 K.

Holmes and Cozens[3] made interferometric measurements of the gas density distribution in the dark space of an abnormal glow discharge in xenon .

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Also, Webb and Viskanta[4] used a Mach-Zehnder interferometer to determine the temperature field and fluorescence due to injection technique to illustrate the flow structure with water as working fluid. Betzler *et al.*[5] used a simple method for the measurement of the refractive indices of parallel plate sample to shift the interference pattern when rotating the sample in one arm of the Mach-Zehender interferometer.

The determination of refractive index[6,7], refractive index distribution[8], refractive index increment[9], nonlinear refractive index[10,11], group and phase refractive index[12], refractive index variation with temperature[13,14], pressure[15], and refractive index variation with both temperature and pressure[16] were determined.

Experimental Technique

The discussion of the experimental technique includes gas sample's cell, temperature control system, Pressure control system, evacuation system; and set-up and performance of MZI.

Gas sample's cell

For studying the change of the refractive index of a gas with temperature and pressure we used the cell shown in Fig. 1. The gas's sample cell was formed as two fixed coaxial cylindrical glass cell. The inner cylinder was filled with the gas under investigation. The length of this cell was 28 cm, its inner diameter was 1.6 cm, and the outside diameter was 2 cm. The cell has two open-longitudinal windows at the ends with a diameter of 1.6 cm. A fixed transparent parallel plate glass closes these windows. The cell has another two transverse-opposite and extended holes with about 1 cm in diameter far from the two opened-ends with 3.8 cm. These two holes were used for evacuation and filling the gas under study. The outer cylinder was used for heating the inner cylinder (gas's cell), the details of heating process will be considered in the next section.

The two transverse-opposite and extended holes (3,5) were used as follows: hole (3) was connected with the evacuation system to evacuate the gas's cell, hole (5) was connected with a ternary glass valve by which we could connect the gas container with the first path of the valve.

The second path of the ternary valve was connected with Hg- Manometer to measure the gas pressure inside the gas's cell. Through these two holes (3,5) there were two calibrated thermocouple fixed to measure the inner temperature of the gas's cell. The two open longitudinal windows were completely parallel and polished. Two windows of pure and good transparent glass were fixed to be parallel in such that the incident laser beam was perpendicular (incident angle was 0^o); Fig.1.

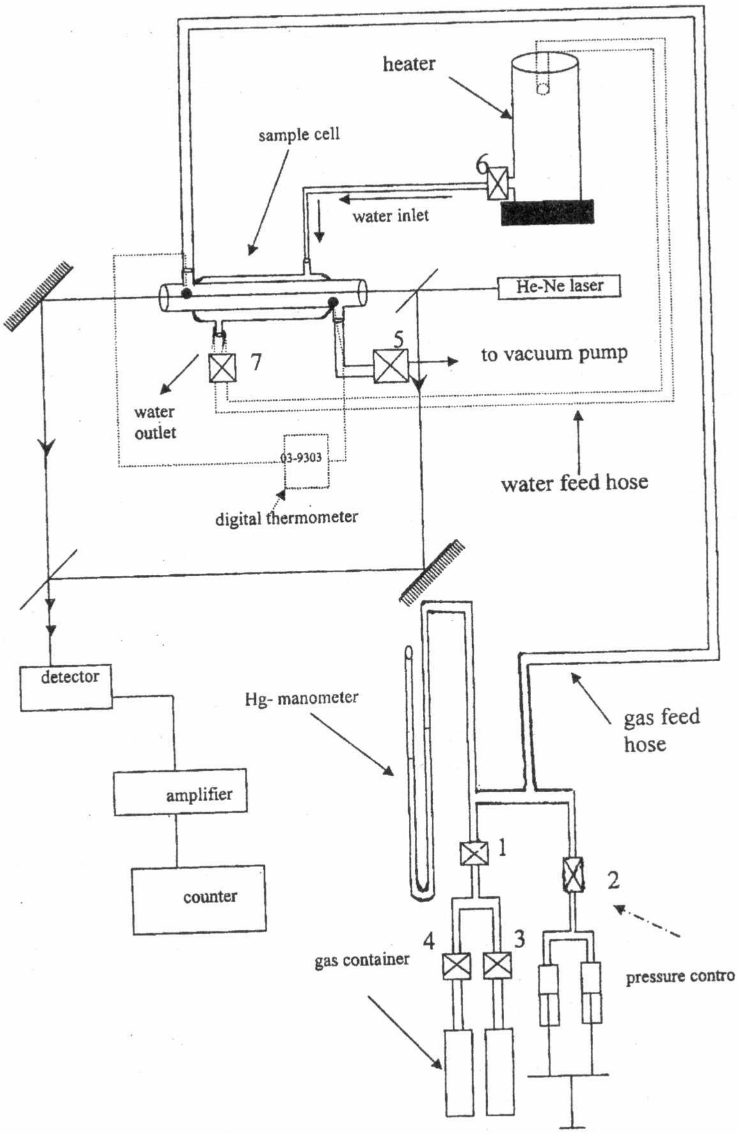

Fig. 1. The constructed set- up used for measuring the gas's refractive index.

Temperature control system

Figure 1 shows a schematic diagram of the temperature control system. To heat up the temperature of the gas under investigation we constructed the outer cylinder, which was used as a container of heating liquid water around the sample's cell. The outer cylinder (or heating cylinder) has another diameter 30 mm and length 186 mm welded at its ends together with the gas's cell. This cylindrical glass has two extended holes (4,5). One of them was used to get the hot water from an electric water heater and the other extended hole was used to outlet the water from the heating tube directing it back to the heater. The rate of water cycle was controlled by using two fixed valves on both inlet and outlet holes, which help to control the temperature of the gas under investigation. By using the two fixed thermocouples, (k-nickel chrome-nickel, which give one mV per 25^{o}) and a digital thermometer (Proskit, 03-9303) at the ends of the sample's cell, one could measure the temperature of the gas. The accuracy of temperature change was about $\pm$ 1°C. The range of temperature change was 308-358 K. The reading of both digital thermometers was the same which means that the temperature of the gas under investigation was homogenous.

Pressure control system

To study the effect of pressure on the gas under investigation we have to change the pressure of the gas inside the cell. This pressure should be under control. The change and control the gas pressure inside the cell was shown schematically in Fig. 1. At the end of the gas container, there was a valve, by which one could control the amount of the gas, which passes to the gas cell. There was a common tube with a diameter 2 cm, from which one path was opened to the Hg- Manometer and the other path is opened to the gas cell. To control the gas pressure inside the cell, two syringes, 100 ml, with a movable piston by two fine screws are used. The amount of the gas contained inside the gas's cell was controlled by using a Hg-manometer.

Evacuation system

For evacuation the system and charging it with the gases under investigation we used the vacuum gauge (cod 07-d361-48-000) which was made by Edwards's industry for high vacuum. The system was divided to two sections (the rotary and the diffusion). The rotary has three ranges for pressure range the first from 1 to 10^{-1} mbar, the second from 10^{-1} to 10^{-2} mbar, and the third from 10^{-2} to 10^{-3} mbar. After the rotary arrived to the range of 10^{-3} mbar we could use the diffusion. The diffusion has three ranges for pressure, range one from 10^{-2} to 10^{-5} mbar, the second ranges from 2×10^{-5} to 10^{-6} and the third from 2×10^{-6} to 10^{-7}. The ionization voltage for the pump supply for penning gauge head 2.3 kv source impedance 3MΩ approx. and the power supply 100-125/200-250 v s.ph 50/60 Hz. And their dimensions 133 high × 110 wide × 194 (mm) depp. And 2.25 kg weight.

Set-up of MZI

The set-up of used version of MZIS was explained in details by Ghazy[17]. Without the gas's sample cell the total path difference is therefore zero and it is:

$$\Delta s = (n-1)t \qquad (1)$$

With the sample having the refractive index (n) in one arm for every substance. The sample was fixed in one arm of MZI. By changing the pressure of the gas in the sample, the number of fringes in the field of view will change. By counting the number of shifted fringes ΔN passing the field of view by changing the pressure p in the cell, one can obtain the index of refraction at any arbitrary pressure by using the equation[18];

$$n(p_s)=(\lambda/t)(\Delta N/\Delta p)p_s+1 \tag{2}$$

where

$n(p_s)$: the refractive index at pressure P_s;
λ : is the wavelength of the laser light;
t : is the length of the cell;
ΔN : is the change in the number of fringes count and
Δp : is the change in the pressure.

Measurements

To measure the refractive index (n) of the gas under investigation the experiment is arranged as shown in Fig. 1. The gas's cell was evacuated by using the vacuum system to the pressure 2×10^{-5} mbar where the gas's valve was closed then the gas's valve was opened to transport the gas to the gas cell. There are two cases of study, one is the studying of the change of refractive index (n) with the temperature (T) at constant pressure, $n_p(T)$. Second is the studying of the refractive index (n) as a function of the pressure (p) at constant temperature $n_T(p)$.

The temperature of the gas under investigation was changed by passing the heated water, by opening the left valve (4), around the gas's cell through the outer cylinder. The temperature was controlled at definite temperature (T_1) by controlling the rate of heated water flow by using the outlet valve (5). Here the temperature becomes constant at T_1 we started to change the gas's pressure by using the micrometer screw and recording the pressure by using the Hg-manometer to be p_1. Then the change in the number of interfering fringes ΔN is counted by eye. The pressure of the gas is increased to become p_2 at the same temperature T_1 and recording the change in the fringes number. And so on at different gas pressures p_3, p_4 ..., therefore, now we have a relation between ΔN and Δp at constant temperature, and by using the following relation[19] the value of $n_T(p)$ was calculated.

$$(\Delta N/\Delta p)=[n_T(p)-1]/p(t/\lambda) \tag{3}$$

The temperature of the gas is increased to a higher value T_2 and the change of N as a function of p is plotted at the value of T_2. This step was repeated at different temperature T_3, T_4... .

The relationships between the refractive index (n) and the pressure (p) at constant temperature T, which denoted as $n_T(p)$, were plotted on the same graph. From which the values of $(dn/dp)_T$ were estimated at different values of temperature to be $(dn/dp)_{T1}$, $(dn/dp)_{T2}$,… .

In correspondence, to study $(dn/dT)_p$, the pressure is controlled to be constant at value p. Then the temperature T was changed and the number of the interfering fringes would change by N. The refractive index of the gas (n) is calculated.

The relationship between (n) and T at a constant value of pressure p_1 is plotted. Then we repeated last step for another values of gas pressure p_2, p_3, … by plotting the relation between n, T on the same graph. The temperature T of the gas was changed in the range from (308 to 358 K) and the pressure p of the gas was changed in the range from (60 to 90 cm Hg).

Cauchy's dispersion equation

The first successful attempt to represent the curve of normal dispersion by an equation was made by Cauchy in 1836. This equation may be written as[19]

$$n= A+B/\lambda^2 + C/ \lambda^4 \quad (4)$$

where A, B, and C are constants which are characteristic of any substance. This equation represents a curvature behavior of refractive index,n, in the visible region. To find the values of the three constants, it is necessary to know values of n for three different wavelengths. Then, three equations may be set up which when solved as simultaneous equations, give A, B, and C. For some purposes it is sufficiently accurate to include only the first two terms and the two constants can be found from values of n at only two wavelengths. The Cauchy's equation is then[20];

$$n =A+B/\lambda^2 \quad (5)$$

From which the dispersion becomes, by differentiation;

$$dn/d\lambda=-2B/ \lambda^3 \quad (6)$$

This shows that the dispersion varies approximately as the inverse cube of the wavelength. At 4000 A° it will be about 8 times as large as at 8000 A°. The minus sign corresponds to the usual negative slope of the dispersion curve.

The theoretical reasoning on which Cauchy based his equation was later shown to be false, so that it is to be considered essentially as an empirical equation. Nevertheless it holds very satisfactorily for cases of normal dispersion along a limited spectral bandwidth and is a useful equation from a practical standpoint.

Results and Discussion

Refractive index measurements

We devoted to the experimental measurements of the refractive index and it's variation with pressure and temperature for carbon dioxide (CO_2) and $freon_{12}$ (R_{12}) gases.

From our measurements we can illustrate the dispersion curves for the two gases. Also the measured data for carbon dioxide gas is used to determine some physical constants, which are related to the refractive index.

We have used our experimental technique to determine the refractive index of the investigated gases. At constant temperature, any change of the pressure of the gas in the gas cell leads to a path difference between the two interfering beams of Mach-Zehnder interferometer, and a number of circular fringes start to cross the field of view. By counting this number which depends on the pressure, one can get the relation between them.

Figure 2 shows the dependence of the number of fringes ΔN on the pressure Δp at constant temperature and at 488 nm wavelength for carbon dioxide gas. This process was repeated over a range of temperatures from 308 up to 358 K and curves like that of Fig. 3 were obtained. From this figure we calculated $(\Delta N/\Delta p)$ at constant temperatures. The values of the refractive index could be calculated with the aid of Eqn. 3.

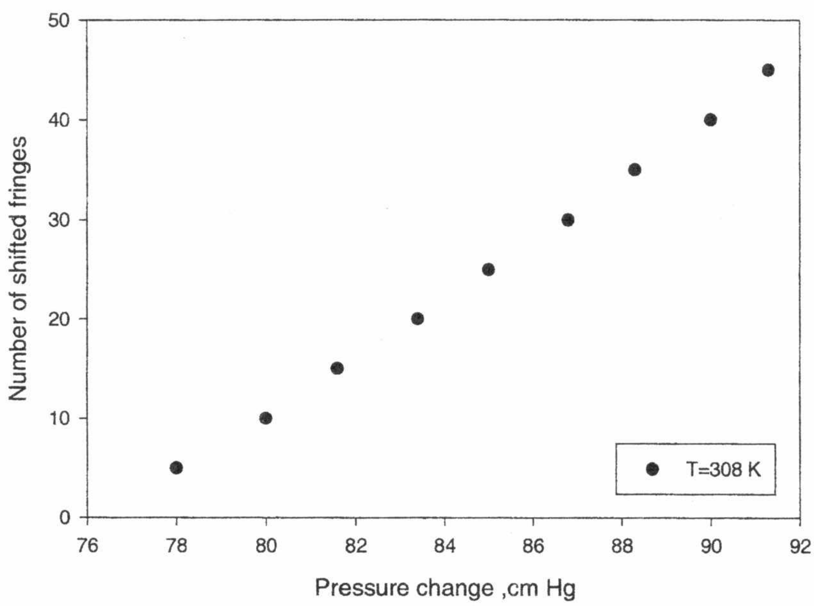

Fig. 2. An example of determination of gas's refractive index as a function of gas's pressure at constant temperature by using the constructed MZIS of Carbon dioxide gas.

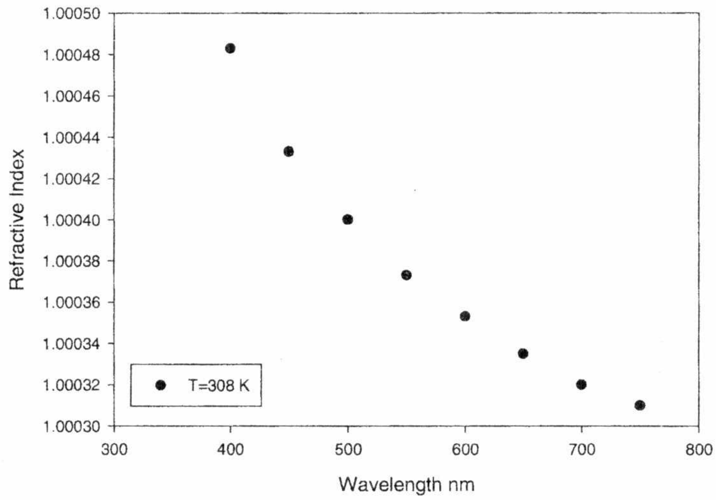

Fig. 3a. Wavelength dependence of refractive index for Carbon dioxide at constant temperature and pressure, $(dn/d\lambda)_{p,T}$.

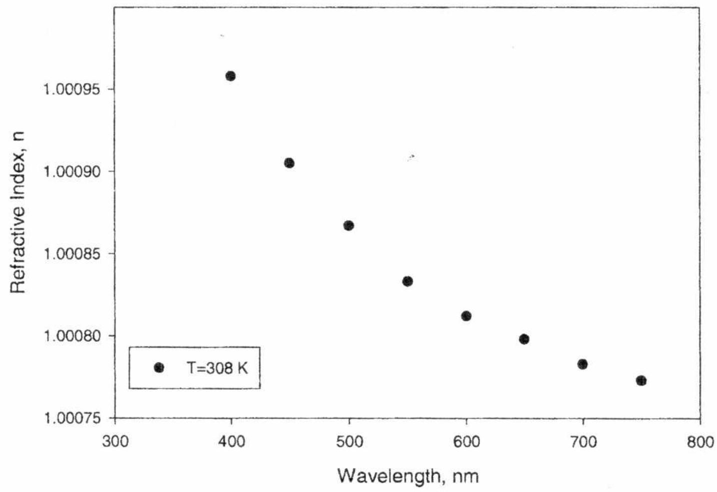

Fig. 3b. Wavelength dependence of refractive index for $Freon_{12}$ at constant temperature and pressure, $(dn/d\lambda)_{p,T}$.

Pressure dependence of refractive index $n_T(P)$

Figure (4 a,b) shows an example of refractive index, n, variation of Carbon dioxide (CO_2) and $freon_{12}$ (R_{12}) gases with the pressure p at constant temperature and selected wavelength, 488 nm. The pressure values were in the range from 60 up to 90 cm Hg, and the temperature was fixed at different values within the range from 308 up to 358 K. From that figure it was noted that the refractive index increases by increasing the pressure at constant temperature. This leads the increasing of gas's pressure, the density of the gas increases, this leads the refractive index to increase.

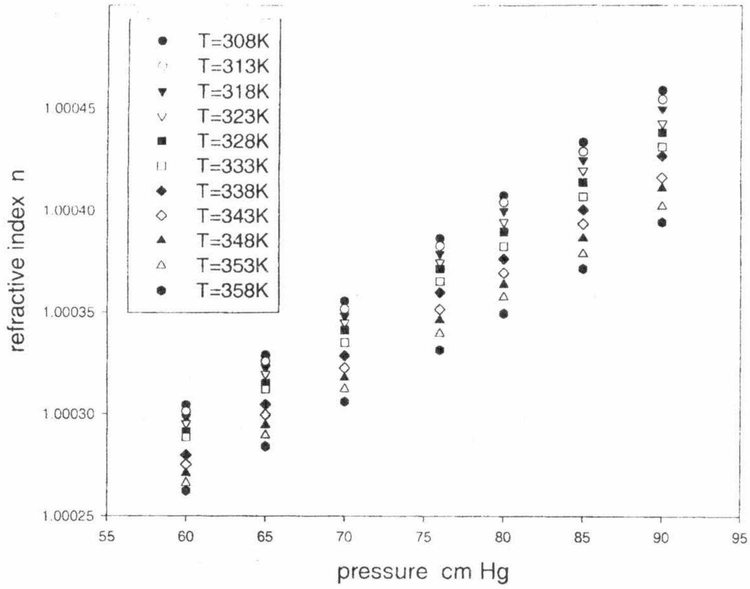

Fig. 4a. An example of pressure dependence of refractive index at constant temperature and laser wavelength, for Carbon dioxide, $(dn/dp)_{T,\lambda}$.

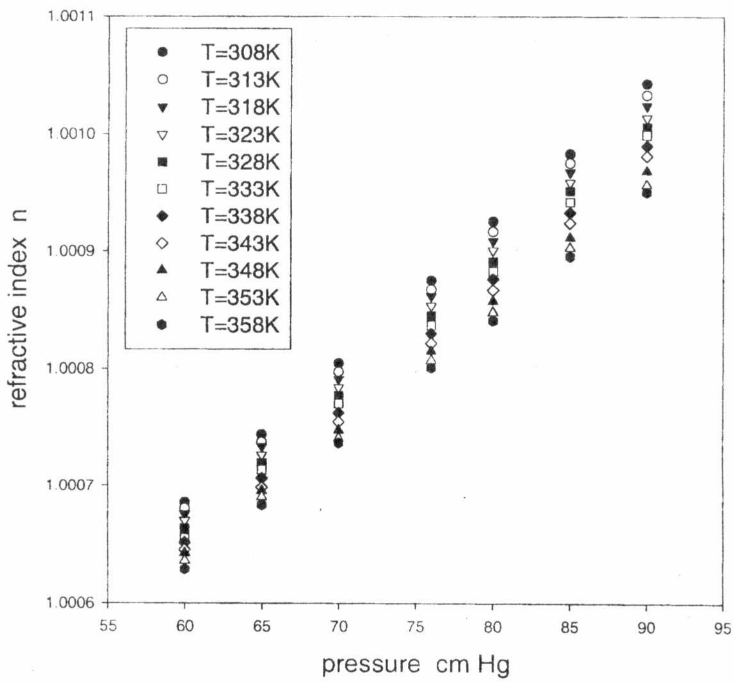

Fig. 4b. An example of pressure dependence of refractive index at constant temperature and laser wavelength, for $Freon_{12}$, $(dn/dp)_{T,\lambda}$.

One can write the relation between the refractive index and the pressure at constant temperature as follow:

$$n_T(p) = ap + c$$

where

n: is the refractive index;
p: is the pressure in cm Hg;
a: is the slope $=(dn/dp)_T$; and
c: is constant depends on the temperature of the gas .

The values of the rate of change of the refractive index with respect to the pressure at constant temperature $(dn/dp)_T$ which was known as pressure coefficient were listed in Table 1 for Carbon dioxide and $Freon_{12}$ gases. These values decrease by increasing the temperature.

TABLE 1. The rate of change of refractive index n with respect to gas's temperature T, at constant pressure and wavelength,λ $(dn/dT)_{p,\lambda}$,

Temp K	308	313	318	323	328	333	338	343	348	353	358
$(dn/dp)_T$ $CO_2 x10^{-6}$	5.44	5.43	5.37	5.25	5.22	5.20	5.06	4.90	4.83	4.81	4.79
$(dn/dp)_T$ $R_{12}x10^{-5}$	1.19	1.18	1.17	1.15	1.15	1.14	1.13	1.12	1.09	1.07	1.07

Temperature dependence of refractive index $n_p(T)$

We are interested here to precisely represent the values of the refractive index and their behavior with respect to the temperature at constant pressure.

Figure (5 a,b) shows an example of the refractive index n of Carbon dioxide gas(CO_2) and $Freon_{12}$ (R_{12}) gas as a function of the temperature T ranging from 308 up to 358 K at constant pressure P at the values from 60 up to 90 cm Hg at λ=488 nm.

From that Figure the refractive index n decreases by increasing the temperature T at constant pressure p. This was reasonable because when the temperature of the gas increases, the density of the gas decreases, which leads to decrease the refractive index. The values of $(dn./dT)_p$ for Carbon dioxide and $Freon_{12}$ gases at 488 nm wavelength of argon laser were listed in Table 2.

The values of the thermo-optical coefficient $(dn/dT)_p$ determine how the gas can converge or diverge the incident laser beam according to the sign of (dn/dT). If the sign of the thermo-optical coefficient $(dn/dT)_p$ was positive, the gas converges the incident laser beam. If negative, the gas diverges the incident light. In our case the two gases diverge the incident light beam.

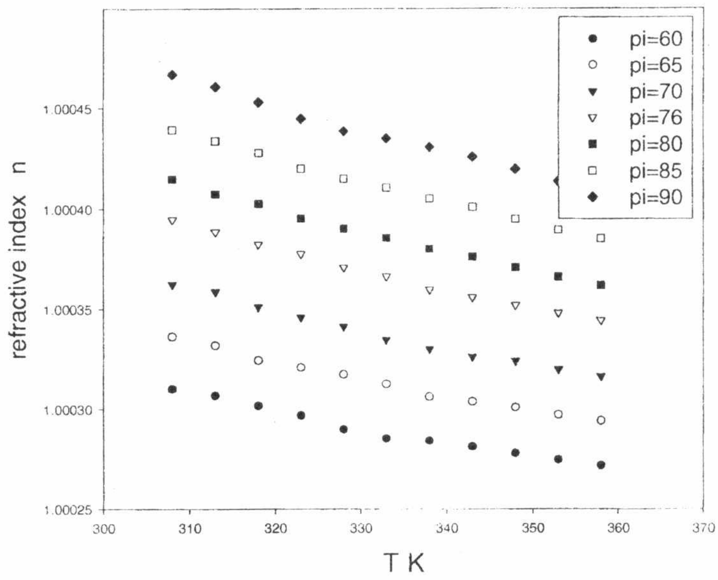

Fig. 5a. **An example of temperature dependence of refractive index at constant pressure and laser wavelength, for Carbon dioxide, $(dn/dT)_{p,\lambda}$.**

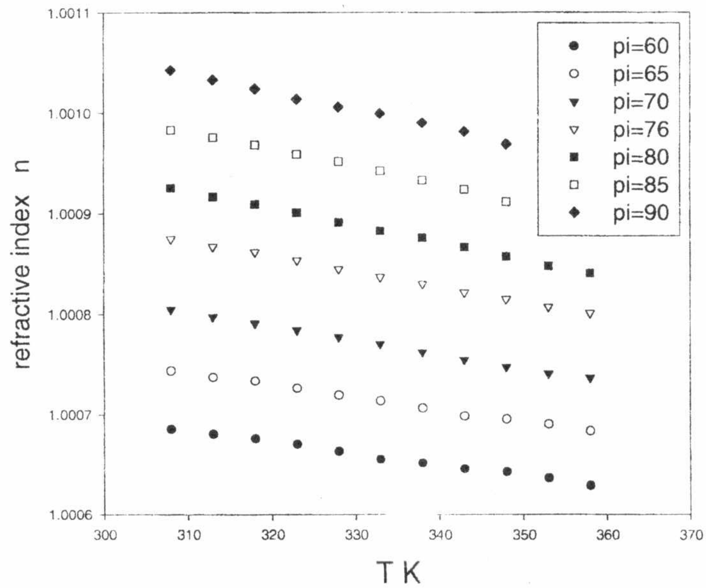

Fig. 5b. **An example of temperature dependence of refractive index at constant pressure and laser wavelength, for Freon$_{12}$, $(dn/dT)_{p,\lambda}$.**

TABLE 2. The rate of change of refractive index n with respect to gas's pressure P, at constant temperature T and wavelength,λ $(dn/dP)_{T,\lambda}$,

Pressure cm Hg	60	65	70	75	80	85	90
$-(dn/dT)_p$ $CO_2 x10^{-7}$	7.25	7.79	8.50	9.34	9.84	11.1	11.5
$(dn/dT)_p$ $R_{12} x10^{-6}$	1.13	1.22	1.40	1.51	1.70	1.79	1.84

Wavelength dependence of refractive index $n_{T,P}(\lambda)$

By using the measured values of refractive index of Carbon dioxide (CO_2) and $Freon_{12}$ (R_{12}) gases at two different wavelengths of Argon ion laser. The dispersion curves of the two investigated samples (Carbon dioxide and $Freon_{12}$ gases) at the visible region (from 400 to 750 nm) were estimated.

Eq.(5) was used to fit the data, from which the values of A and B were obtained.

The values of dispersion constants A and B of the two gases were determined with listed values in Table 3.

TABLE 3. Dispersion constants of Carbon dioxide and $Freon_{12}$ gases and the rate of change of their refractive index with respect to wavelength, $(dn/d\lambda)_{p,T}$.

Gas	A	B	$-(dn/d\lambda)x10^{-7}$
CO_2	1.000249308	37.315291	4.74048
R_{12}	1.000698721	41.579791	5.07857

These values were used to get the dispersion curves for Carbon dioxide and $freon_{12}$ gases. By substituting these values in the preceding Cauchy's equation, the refractive index of the two gases at any wavelength in the visible region were obtained.

Figure 3a,b show the dependence of the refractive index of Carbon dioxide (CO_2) and $Freon_{12}$ (R_{12}) gases on the wavelength at temperature 308 K respectively, from which $(dn/d\lambda)_{T,P}$ was calculated.

Discussion

In the past, it was belived that the preferred method to determine the refractive indecies of gases is the using of the Fabry- Periot interferometer and Jamin interferometer. In this paper we used MZIS for the same purpose with a employment with a high degree of accuracy. A comparison was made with a literature [21] using a white light with difference 43 x 10^{-6} to 44 x 10^{-6} at T = 308 K and 1 atm. Pressure value. This leads to the same degree of accuracy of other calculated physical parameters related to the refractive index.

Conclusion

In this new employment of MZIS to measure the refractive index of CO_2 and R12 we constructed a new arrangement of the system to meet this measurements. A multimode Argon Ion Laser(MAIL) with six different wavelengths was used as a light source with the aid of a high-resolution monochromator the wavelength was selected. The refractive index, $n_p(T)$ and $n_T(P)$ of the investigated gases were measured with a high degree of accuracy. In addition the other physical parameters such as $(dn/dT)_p$ and $(dn/dp)_T$ were calculated with the same degree of accuracy. The Cauchy's equation was fitted to determine the constants A and B during the calculation of $(dn/d\lambda)_T$.

References

1. **Jamin,** *J. Ann. Chem. Phys.*, **49**, 282 (1857).

2. **Hohm, U. and Kerl, K.,** *Meas. Sci. Technol.*, **1**, 329 (1990).

3. **Holmes, A.J.T. and Cozens, J.R.,** *J. Phys. D: App. Phys.*, **8**, 4004 (1975).

4. **Webb, B. and Viskanta, R.,** *J. Heat Transfer*, **109**, 427 (1987).

5. **Betzler, K.,** ***et al.*,** *Rev. Sci. Instrum.*, **59**, 652 (1988).

6. **Tianchuli and Xiaadi Tan,** *Appl. Opt.* **32**, 2274 (1993).

7. **Chandra S. Vikram, William Witherow, K. and Jams D.** *Trolinger, Appl. Opt.*, **30**, 733 (1991).

8. **Richard E., Gaskin and Colin Lewise,** *Optical Acta*, **27**, 1287 (1980).

9. **Ghazy, R., El-Baradie, B., Elshaer, A. and El-Mekawy, F.M., Optics and** *Laser Technology*, **31**, 335 (1999).

10. **Olbright, G.R. and Peyghambarian, N.,** *Appl. Phys. Lett.*, **48**, 1184 (1986).

11. **Kristian, O., Sylverster. Hvid** *"Theoretical Studies of Linear and Nonlinear Optical Properties of Pure Liquids and Solutions" Ph. D.,* Aarhus University, Denamark (1998).

12. **Mark, D. Hopler and John, R. Rogers.,** *Appl. Opt.*, **30**, 733 (1991).

13. **Daniel, D. Young, Kenneth, C., Jungling, Toml., Williamson and Elgenen, R.,** *Nichols, IEEE*, 720 (1972).

14. **Hawkes, J.B. and Astheimer, R.W.,** *J. Opt. Soc. Am.*, **38**, 617 (1948).

15. **Vedam, K. and Limuswan, Pichet,** *Rev. Sci. Instrum.*, **48**, 245 (1977).

16. **Shama, S.A. M.** *Sc., Thesis,* Tanta University (2002).

17. **Ghazy, R.,** *Acta Physica, Pol. A,* **57**, 939 (1999).

18. **Martin Schroedter**, *Mathematica for Student*, England (2000).

19. **Francis A. Jenkins and Harvey, E., White** "*Fundamentals of Optics* " 4th ed. Mc Graw Hill (1984).

20. **Subrahmanyam, N. and Lal, B.,** "*A Text Book of Optics*" S. Chandl Co. Ltd, Ram Nagar, New Delhi (1983).

21. **West, R.C. and Astle, M.G.** (Ed.) "*CRC Handbook of Chemistry and Physics*" F-58, E-2, E-357 (1979).

(*Received* 5/4/2006;
accepted 27/8/2007)

التعيين الدقيق لمعامل انكسار الغازات الأكثر شيوعا تلوثا للبيئة

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فى هذا البحث تم بناء مقياس تداخل من النوع ماخ – زندر لقياس معامل انكسار الغازات بشكل عام . تم استخدام ليزر الأرجون متعدد الأطوال الموجية كمصدر ضوئى . وقد تم تصميم نظام انسياب الغاز محل الدراسة بشكل دقيق والذى تم ربطه بمقياس التداخل . تم التحكم فى انسياب الغاز بواسطة مانومتر زئبقى بمدى يتراوح بين 60-90cm-Hg بدقة قياس تقع فى حدود ± 0.5 cm-Hg أيضا تم تزويد التجربة بنظام تسخين تتراوح درجة حراراته ما بين 308-358K بدقة قياس فى حدود 1.0 ± درجة مئوية . وباستخدام هذا النظام تم تعيين معامل انكسار الغازات المقترحة للدراسة والملوثة للبيئة وهى غاز ثانى أكسيد الكربون وغاز الفريون – ١٢ كداله فى كلا من الضغط ودرجة الحرارة . كذلك تم تعيين المعامل الضوء – حرارى لكلا الغازين كداله فى الضغط عند ثبوت درجة الحرارة وأيضا كداله فى درجة الحرارة عند ثبوت الضغط . أيضا تم دراسة سلوك معامل انكسار هذه الغازات كداله فى الطول الموجى عند ثبوت درجة الحرارة وذلك نظرا لوجود هذه الغازات فى الهواء الجوى مما أدى بنا لضرورة دراسة ظاهرة التشتت الضوئى لكلا الغزين حيث تم تعيين قيمة الثوابت A,B باستخدام معادلة كوشى .

#المؤلف الذى ترجع اليه المراسلات