Lapeira, E., Mialdun, A., Yasnou, V. *et al.* Digital Interferometry Applied to Thermogravitational Technique. *Microgravity Sci. Technol.* **30**, 635–641 (2018). https://doi.org/10.1007/s12217-018-9632-7

DIGITAL INTERFERMETRY APPLIED TO THERMOGRAVITATIONAL TECHNIQUE

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Abstract

In this work, we have applied Optical Digital Interferometry approach to thermogravitational micro-column technique.

By the new analysis, we examine the entire height of the micro-column and determine the complete concentration profile inside. The measurements were carried out by two lasers with different wavelength $\lambda = 633nm$ and $\lambda = 470nm$. The system was validated with binary subsystems of the THN-IBB-C12 ternary mixture at equal mass fractions. The results were compared with values of Benchmark Fontainebleau and they showed an excellent agreement.

Keywords: Thermodiffusion, binary mixtures, Thermogravitational micro-column, Optical Digital Interferometry.

1. Introduction

Since over last decades, optical methods have been widely used in the determination of transport properties as the thermodiffusion, molecular diffusion and Soret coefficients of binary mixtures. For example, Optical Beam Deflection (Kolodner et al. 1988; Zhang et al. 1996), Optical Digital Interferometry (Mialdun and Shevtsova 2008) and Thermal Diffusion Forced Rayleigh Scattering (Wiegand et al. 2007; Wittko and Köhler 2003) have been used to analyse several binary mixtures. All these optical methods have demonstrated good sensitivity in measurements.

Now the challenge is focused on ternary mixtures, so many of these techniques have been modified in order to analyse more complex systems. As a result, nowadays several instruments such as (Gebhardt et al. 2013) and (Mialdun et al. 2015) are able to determine the transport properties of different ternary mixtures using optical analysis methods or by samples extraction (Larrañaga et al. 2015).

Optical methods allow to work with small sample volume because the measurements are usually carried out in situ. In the case of biological substances, for instance, it is not always easy or possible to obtain big samples. The conventional thermogravitational parallelepiped and cylindrical columns (Larrañaga et al. 2015b; Urteaga et al. 2012) need at least 30 ml of sample, so it is not viable to analyse biological samples using those techniques. For this reason, a new thermogravitational micro-column was designed, constructed and validated in Mondragon University (Naumann et al. 2012) in order to determine the thermodiffusion coefficient purely by optical method. The sample volume of this micro-column is less than 50 µl so it makes feasible the investigation of expensive substances, which cannot be obtained in large quantities. The optical approach applied to the micro-column, made possible to analyse the continuous concentration profile in binary mixtures between two points. Nevertheless, by this analysis method (Naumann et al. 2012), the accuracy of determining the vertical concentration gradient was not so good because it analysed only two points of the height of micro-column.

Thus, in this work we have changed the configuration of the ~~installation~~ instrument by applying the Digital Interferometry. The new configuration enables the analysis of the concentration profile over the height of the micro-column. The system was validated using binary mixtures of Benchmark Fontainebleau (Platten et al. 2003).

One of the benefits of this configuration is that it measures the stationary separation in situ without perturbing the mixture. Therefore, it is going to be possible to analyse the transitory theory of the thermogravitational effect. In addition, it will allow the convective stability analysis of binary and ternary mixtures.

This article is organized as follows: in section "Experimental setup", a brief description of the micro-column and the design of new configuration of the optical arrangement and image processing are explained. In section "Results and discussion", the results of thermodiffusion coefficient of binary mixtures are shown. Finally, section "Conclusions" outlines the results.

2. Experimental setup

Thermogravitational micro-column

The thermogravitational micro-column used in this work is the same as in (Naumann et al. 2012) with a slight difference. Only the core part of the cell, shaping the gap of the micro-column, was replaced for the reason that the inlet and outlet were clogged up after multiple uses. Therefore, we improved the design to solve the problem. The new core part was made with the same material *Ketron PEEK* and was manufactured in *Denatek Engineering and Manufacturing Technologies* company with the greatest accuracy possible. After the manufacturing process, the gap size was verified in Mondragon University by MITUTOYO CRYSTA APEX S-7106 precision coordinate measuring machine see Fig.1.

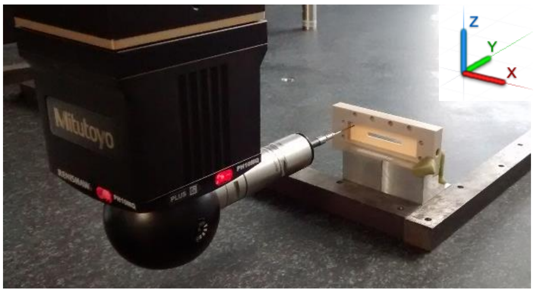


Fig.1 Measurement of the gap with MITUTOYO CRYSTA APEX S-7106 machine.

~~The measurements with this machine consists on selecting several points near the gap Fig.2a on surface 1 and then changing Y axis, selecting other points in surface 2, Fig.2b. Finally, the distances between selected points are calculated.~~ The new gap thickness is Lx=0.51±0.025 mm, the height of Lz=30 mm and width of Ly=3 mm.

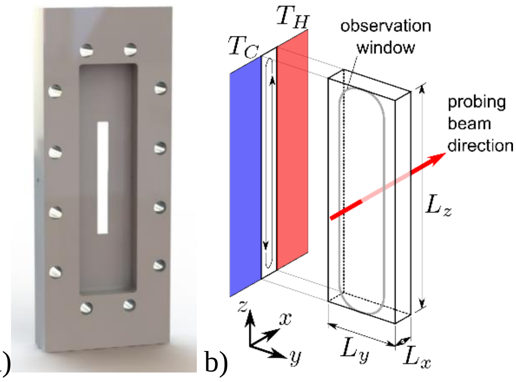
a) b)


Fig.2 Core part of the micro-column, a) Shape of the gap of the micro-column, b) Configuration of the gap.

Design of the new configuration of optical diagnostics

The new configuration of the installation is based on Digital Interferometer (Mialdun and Shevtsova 2011). The two main contributions of this configuration are: On the one hand, all the height of the column is analysed as the laser beam was expanded to cover all the window of micro-column. On the other hand, we introduced two lasers with different wavelengths, a Diode-Pumped one with $\lambda = 470\,nm$ wavelength (Spectra-Physics) Fig.3 (1) and a He-Ne laser with $\lambda = 633\,nm$ wavelength (Research Electro-Optics) to be able to analyse also ternary mixtures in the future; below in this section the all notations refer to Fig.3. In order to work with both lasers at the same time without mixing their interference patterns, we have designed a special shutter system that is installed at the exit aperture of each laser. This shutter system consists of a shaft moving up and down (3) allowing or denying the pass of laser beam. The movements of interrupter's shaft and the acquisition of images are synchronized by program implemented in LabView (8).

After the shutting system, both laser beams are passed ~~from~~ through neutral density filters in order to adjust the intensityFig.**3** (4). Then, to expand the beams, we used two spatial filter systems (Thorlab, KT310) with an aspheric lens, a pinhole and a collimator in order to obtain a good quality beam (5). Taking into account that the height of the micro-column is 30 mm, the final beam diameters were expanded to approximately 40 mm. Afterwards, both ~~laser~~ beams are directed into a Mach-Zehnder interferometer (6), where each beam is divided into two equal beams. One passes through the micro-column (7) (object beam) and the other one is the reference beam. At the end of the interferometer, divided beams are joined creating an interference patterns that are acquired by CCD camera (QImaging QIClick-CCD Camera) (9).

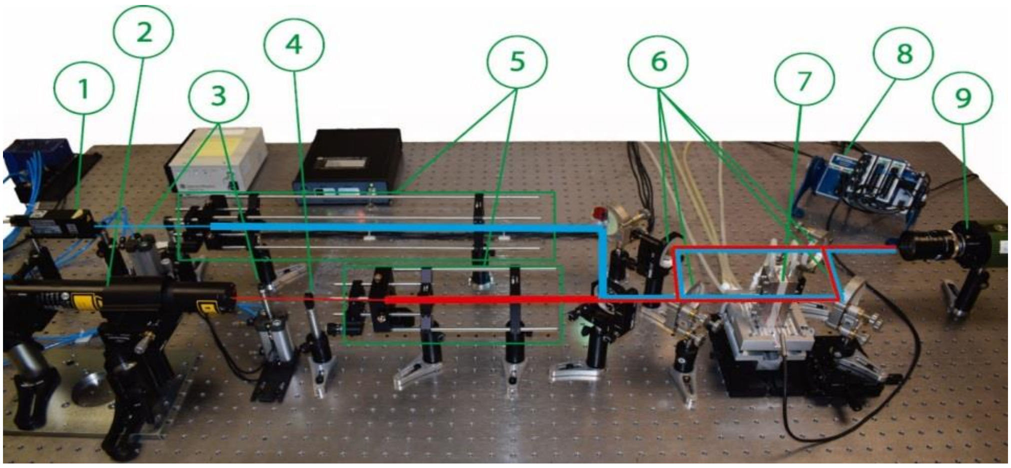
Digital interferometry is a trusted technique that can be used to determine the concentration of a mixture by analysing the refractive index. The refractive index varies because of a temperature and concentration variations,

$$\Delta n(y,z)=\left(\frac{\partial n}{\partial T}\right)_{T_o,c_o,\lambda}\Delta T(y,z)+\left(\frac{\partial n}{\partial c}\right)_{T_o,c_o,\lambda}\Delta c(y,z), \qquad (1)$$

Where, $(\partial n/\partial T)$ and $(\partial n/\partial c)$ are the contrast factors and $\Delta T(y,z)$ and $\Delta c(y,z)$ are the spatial temperature and concentration variation~~s in vertical direction~~. In our system, the temperature gradient is applied in the same direction as the laser beam, so we can omit the temperature variation $\Delta T(y,z)$ influence. Thus, the total variation of the refractive index is due to the concentration variation (2). In turn, Δn is obtained from the phase difference $\Delta\varphi$, which is measured by the interferometry (3), where L_x is the geometric path in liquid.

$$\Delta n(y,z)=\left(\frac{\partial n}{\partial c}\right)_{T_O,c_O,\lambda}\Delta c(y,z), \qquad (2)$$

$$\Delta n(y,z)=\frac{\lambda}{2\pi L}\Delta\varphi(y,z) \qquad (3)$$

a) 

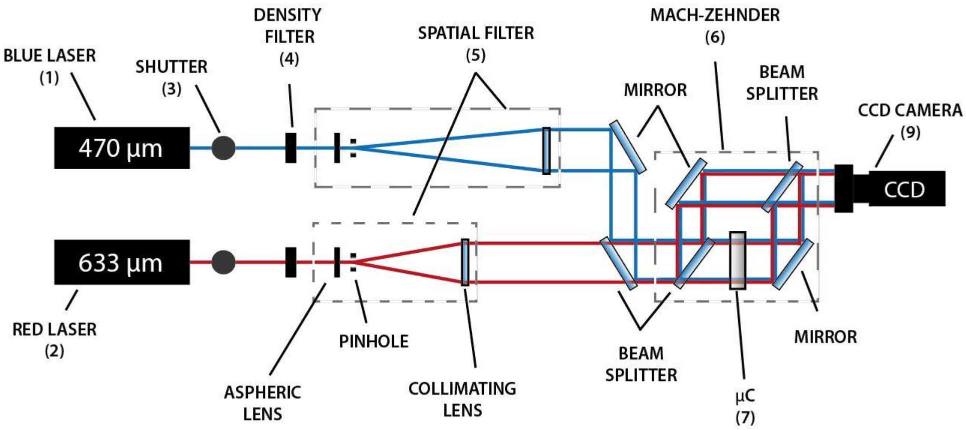
b) 

Fig.3 Digital Interferometry applied to thermogravitational micro-column installation. a) ~~Complete installation~~ General view; b) Scheme of the installation.

Experimental scenario and Image processing

Both the interferometer configuration and image processing are based on Optical Digital Interferometry technique. Before starting the measurements, we stabilize the system at 25ºC for 4 hours and acquire the images every 10 minutes in order to check the stability of the system. At the end of the measurement, one of the last acquired images in the stabilization step is taken as the reference image ~~Fig.4~~. After applying the temperature gradient of $\Delta T = 8^{o}C$, the image acquisition rate is increased in order to see the evolution of phase variation in time. As the initial concentration change is bigger than near the stationary state, the acquisition of images is divided in three stages. For these binary mixtures, the image acquisition rate of first stage is 2 minutes during 36 minutes, in the second stage every 6 minutes during 72 minutes and finally every 12 minutes until the mixture reach the stationary state.

To extract the phase information from each acquired image, we use the 2D Fourier Transform technique described in literature (Mialdun and Shevtsova 2011). The Fig.4 outlines the image analysis steps. The phase information enables the determination of the refractive index of the sample. As a result, knowing the concentration derivative of the refractive index $(\partial n/\partial c)$ is possible to determine the entire concentration profile along the micro-column for each instant (for each acquired image). Once the mixture reach the stationary stage, the slope of the concentration along the height of the micro-column $(\partial c/\partial z)$ is used in order to determine the thermodiffusion coefficient.

This concentration profile correspond to the midline of y scale of the column in y-z plane (bounded by white dashed lines in Fig.**4**).

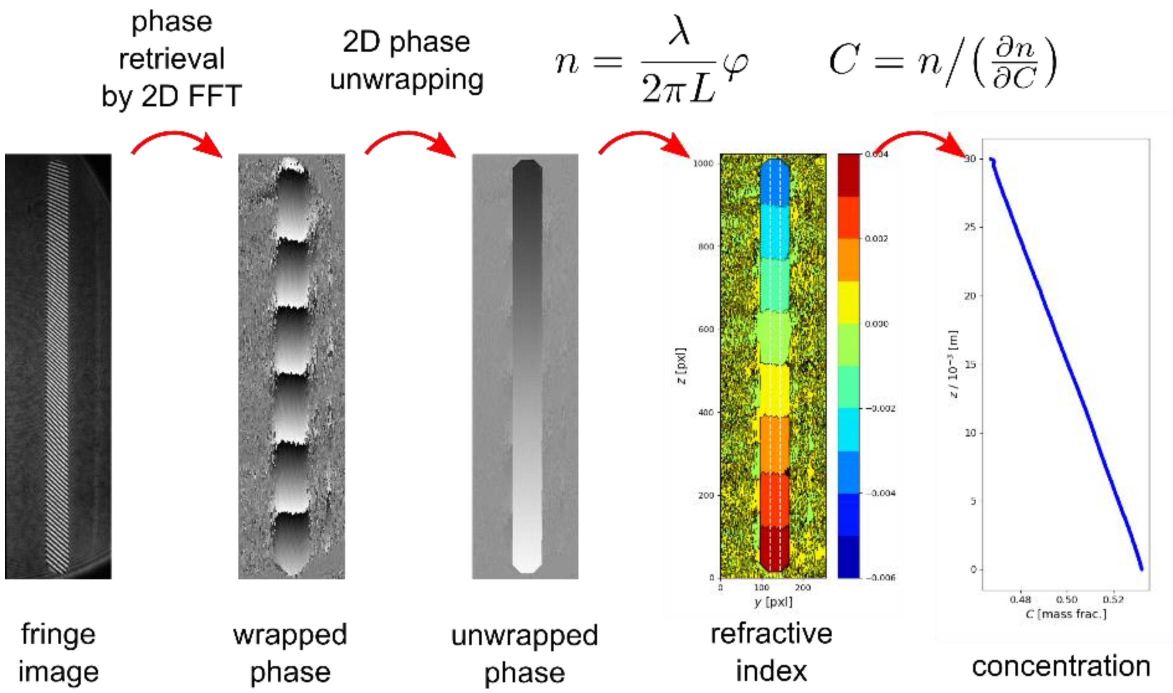


Fig.4 Steps for the phase information extraction of each acquired image.

The concentration variation during the all experiment is shown in Fig.5. There it can be appreciate the stabilization process at 25ºC for approximately 3-4 hours. Then, the temperature gradient is applied so concentration in the sample start changing until mixture reach the stationary state. Negative concentration variation means that the reference component is enriched at the bottom part of the micro-column.

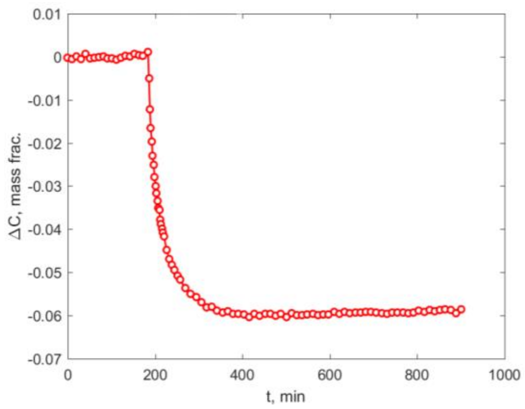


Fig.5 ~~Separation of the concentration in time for measurement~~ Time evolution of the concentration separation of THN-C12 binary mixture at 50% of mass fraction with $\Delta T = 8^{o}C$, monitored by ~~and using~~ 470nm wavelength.

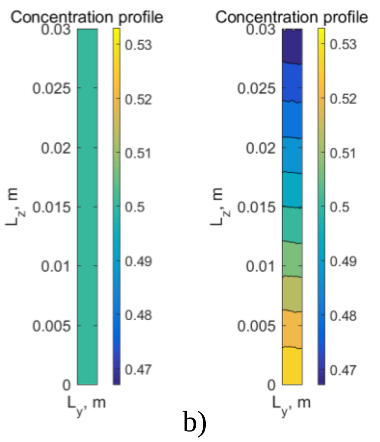
3. Results and discussion

For the validation of the new analysis method, we have measured the thermodiffusion coefficients of three binary mixtures at equal mass fraction of THN (purity, 98+%), IBB (purity, 99%) and C12 (purity, 99%). All measurements have been carried out at mean temperature of 25ºC. The thermophysical properties as density, thermal expansion and dynamic viscosity were taken from (Alonso de Mezquia et al. 2015) and the contrast factor $(\partial n/\partial c)$ at 633 nm wavelength of three binary mixtures ~~were~~ was taken from (Gebhardt et al. 2013). To calculate the $(\partial n/\partial c)$ at 470 nm, Cauchy dispersion relation has been used as it is detailed in (Mialdun, A. and Shevtsova 2017). In Table 1, all the optical and thermophysical properties taken from literature are shown.

Table 1. Optical and thermophysical properties of THN-IBB-C12 binary mixtures at equal mass fraction at 25ºC. Density, thermal expansion and dynamic viscosity are taken from (Alonso de Mezquia et al. 2015) and $(\partial n/\partial c)$ from (Gebhardt et al. 2013).

	THN-C12	THN-IBB	IBB-C12
ρ (kg/m^3)	841.248	904.514	792.355
$\alpha \times 10^{-3}$ (K^{-1})	0.895	0.888	0.961
$\mu \times 10^{-3}$ $(Pa\,s)$	1.523	1.374	1.133
$(\partial n/\partial c)$ $(\lambda = 633nm)$	0.1155	0.0547	0.0625
$(\partial n/\partial c)$ $(\lambda = 470nm)$	0.1258	0.0577	0.0700

During the image processing, the concentration in the entire cross-section of the cell is determined ~~in~~ from each image. The Fig.6a shows the initial concentration profile when the micro-column is stabilized at 25ºC and in Fig.6b when it reaches the stationary state with $\Delta T = 8^oC$.



a) b)

Fig.6 Concentration profiles inside the micro-column ~~of~~ filled with THN-C12 at 50 % mass fraction; a) when mixtures is stabilized at 25^oC, b) when the mixtures reaches the stationary state after applying $\Delta T = 8^oC$.

Afterwards, the vertical concentration profile is represented in function of the height of the micro-column and is fitted with the polynomial of the first order obtaining $(\partial c/\partial z)$ as shown in Fig.7.

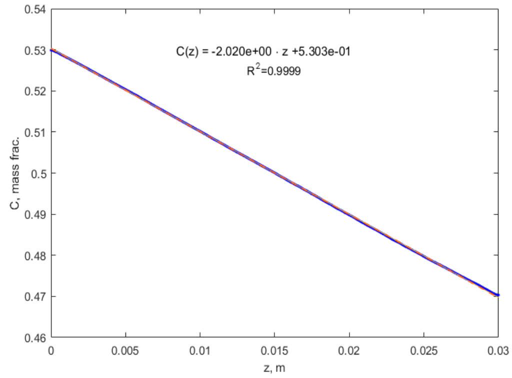


Fig.7 Concentration gradient at stationary state along the height of the micro-column of THN-C12 at 50% mass fraction with $\Delta T = 8^oC$.

Finally, the thermodiffusion coefficient of binary mixtures is determined (4) (Larrañaga et al. 2014),

$$D_T = -\frac{L_x^{\,4}}{504}\frac{g\,\alpha}{\nu\, C_0\,(1-C_0)}\frac{\partial c}{\partial z} \qquad (4)$$

where, L_x is the gap of the micro-column, g is the gravity, α is the thermal expansion coefficient, ν is the kinematic viscosity and C_0 is the initial concentration of the reference component.

The Table 2, Table 3 and Table 4 show the thermodiffusion coefficients of THN-C12, THN-IBB and IBB-C12 binary mixtures and the mean values with the respective deviations.

The obtained results show a good agreement with Benchmark Fontainebleau values (Platten et al. 2003) ~~so we have seen that the new configuration provides reliable results~~ that makes us confident in reliability of the new configuration.

For the first time, with the new configuration, we have analysed all the height of the column and we have seen the entire concentration profile inside the thermogravitational column.

Table 2. Thermodiffusion coefficients of THN-C12 binary mixtures at 50% mass fraction.

THN-C12	633 nm $(\partial c/\partial z)$	633 nm $D_T \times 10^{-12}$ (m^2/sK)	470 nm $(\partial c/\partial z)$	470 nm $D_T \times 10^{-12}$ (m^2/sK)	Benchmark (Platten et al. 2003)
1	-2.124	5.53	-2.070	5.39	
2	-2.264	5.90	-2.177	5.66	
3	-2.304	5.99	-2.275	5.92	
4	-2.260	5.88	-2.180	5.68	
5	-2.299	5.99	-2.212	5.76	
Average	**-2.250**	**5.86±0.33**	**-2.183**	**5.68±0.29**	**5.9±0.3**

Table 3. Thermodiffusion coefficients of THN-IBB binary mixtures at 50% mass fraction.

THN-IBB	633 nm $(\partial c/\partial z)$	633 nm $D_T \times 10^{-12}$ (m^2/sK)	470 nm $(\partial c/\partial z)$	470 nm $D_T \times 10^{-12}$ (m^2/sK)	Benchmark (Platten et al. 2003)
1	-1.062	3.27	-1.010	3.11	
2	-0.801	2.46	-0.794	2.44	
3	-0.844	2.60	-0.804	2.68	
4	-1.062	3.27	-0.983	3.03	
5	-0.937	3.03	-0.984	2.89	
6	-0.902	2.78	-0.877	2.70	
Average	**-0.935**	**2.90±0.44**	**-0.909**	**2.81±0.37**	**2.8±0.1**

Table 4. Thermodiffusion coefficients of IBB-C12 binary mixtures at 50% mass fraction.

IBB-C12	633 nm $(\partial c/\partial z)$	633 nm $D_T \times 10^{-12}$ (m^2/sK)	470 nm $(\partial c/\partial z)$	470 nm $D_T \times 10^{-12}$ (m^2/sK)	Benchmark (Platten et al. 2003)
1	-1.079	3.82	-1.022	3.61	
2	-0.994	3.52	-0.987	3.49	
3	-1.209	4.28	-1.094	3.87	
4	-1.123	3.98	-1.074	3.80	
5	-1.146	4.06	-1.112	3.94	
6	-1.071	3.79	-0.988	3.49	
Average	**-1.104**	**3.91±0.39**	**-1.046**	**3.70±0.24**	**3.7±0.2**

4. Conclusions

In this work, we have changed the configuration of the previously reported optical analysis method applied to thermogravitational micro-column. The new configuration of the interferometer and the image processing is based on Optical Digital Interferometry analysis method. With the new configuration, we are able to analyse the entire window of micro-column instead of analysing only two points. Thanks to this improvement, we are able to see the entire concentration profile inside the micro-column during the measurements.

To validate the new system, we have determined the thermodiffusion coefficients of three binary mixtures at equal mass fractions. Results have been compared with Benchmark Fontainebleau

~~By t~~The new analysis method ~~in future it is going to be possible~~ can be readily extended to analyse ternary mixtures. The analysis of the entire concentration profile will allow to study the thermogravitational effect in the transitory state of binary and ternary mixtures.

Acknowledgements

Authors would like to thank the support of Research Groups (IT1009-16) and Research Fellowship (Pre_2014_1_283) of Basque Government, TERDISOMEZ (FIS2014-58950-C2-1-P) and MEZNAFLU (ESP2017-83544-C3-1-P) of the MINECO and DCMIX (DCMIX-NCR-00022-QS) from the European Space Agency. Also would like to thank Denatek engineering and manufacturing technology company for manufacturing the gap.

References

Alonso de Mezquia, D., Larrañaga, M., Bou-Ali, M.M., Madariaga, J.A., Santamaría, C., Platten, J.K.: Contribution to thermodiffusion coefficient measurements in DCMIX project. Int. J. Therm. Sci. 92, 14–16 (2015). doi:10.1016/j.ijthermalsci.2015.01.013

Gebhardt, M., Köhler, W., Mialdun, A., Yasnou, V., Shevtsova, V.: Diffusion, thermal diffusion, and Soret coefficients and optical contrast factors of the binary mixtures of dodecane, isobutylbenzene, and 1,2,3,4-tetrahydronaphthalene. J. Chem. Phys. 138, 114503 (2013). doi:10.1063/1.4795432

Kolodner, P., Williams, H., Moe, C.: Optical measurement of the Soret coefficient of ethanol/water solutions. J. Chem. Phys. 88, 6512–6524 (1988)

Larrañaga, M., Bou-Ali, M.M., Lapeira, E., Santamaría, C., Madariaga, J.A.: Effect of Thermophyisical Properties and Morphology of the Molecules on Thermodiffusion Coefficient of Binary Mixtures. Microgravity Sci. Technol. 26, 29–35 (2014). doi:10.1007/s12217-014-9368-y

Larrañaga, M., Bou-Ali, M.M., Lizarraga, I., Madariaga, J.A., Santamaría, C.: Soret coefficients of the ternary mixture 1,2,3,4-tetrahydronaphthalene + isobutylbenzene + n-dodecane. J. Chem. Phys. 143, 24202 (2015)(a). doi:10.1063/1.4926654

Larrañaga, M., Bou-Ali, M.M., Lizarraga, I., Madariaga, J.A., Santamaría, C.: Soret coefficients of the ternary mixture 1,2,3,4-tetrahydronaphthalene + isobutylbenzene + n-dodecane. J. Chem. Phys. 143, 24202 (2015)(b). doi:10.1063/1.4926654

Mialdun, A. and Shevtsova, V.: Analysis of multi-wavelength measurements of diffusive properties via dispersion dependence of optical properties. Appl. Opt. 56, 572–581 (2017)

Mialdun, A., Legros, J.-C., Yasnou, V., Sechenyh, V., Shevtsova, V.: Contribution to the benchmark for ternary mixtures: Measurement of the Soret, diffusion and thermodiffusion coefficients in the ternary mixture THN/IBB/nC12 with 0.8/0.1/0.1 mass fractions in ground and orbital laboratories. Eur. Phys. J. E. 38, 27 (2015). doi:10.1140/epje/i2015-15027-2

Mialdun, A., Shevtsova, V.: Measurement of the Soret and diffusion coefficients for benchmark binary mixtures by means of digital interferometry. J. Chem. Phys. 134, 44524 (2011). doi:10.1063/1.3546036

Mialdun, A., Shevtsova, V.M.: Development of optical digital interferometry technique for measurement of thermodiffusion coefficients. Int. J. Heat Mass Transf. 51, 3164–3178 (2008). doi:10.1016/j.ijheatmasstransfer.2007.08.020

Naumann, P., Martin, A., Kriegs, H., Larrañaga, M., Bou-Ali, M.M., Wiegand, S.: Development of a thermogravitational microcolumn with an interferometric contactless detection system. J. Phys. Chem. B. 116, 13889–97 (2012). doi:10.1021/jp3098473

Platten, J.K., Bou-Ali, M.M., Costesèque, P., Dutrieux, J.F., Köhler, W., Leppla, C., Wiegand, S., Wittko, G.: Benchmark values for the Soret, thermal diffusion and diffusion coefficients of three binary organic liquid mixtures. Philos. Mag. 83, 1965–1971 (2003). doi:10.1080/0141861031000108204

Urteaga, P., Bou-Ali, M.M., Alonso De Mezquia, D., Santamaría, J., Santamaría, C., Madariaga, J.A., Bataller, H.: Measurement of thermodiffusion coefficient of hydrocarbon binary mixtures under pressure with the thermogravitational technique. Rev. Sci. Instrum. 83, (2012). doi:10.1063/1.4737628

Wiegand, S., Ning, H., Kriegs, H.: Thermal diffusion forced Rayleigh scattering Setup optimized for aqueous mixtures. J. Phys. Chem. B. 111, 14169–14174 (2007). doi:10.1021/jp076913y

Wittko, G., Köhler, W.: Precise determination of the Soret, thermal diffusion and mass diffusion coefficients of binary mixtures of dodecane, isobutylbenzene and 1,2,3,4-tetrahydronaphthalene by a holographic grating technique. Philos. Mag. 83, 1973–1987 (2003). doi:10.1080/0141861031000108213

Zhang, K.J., Briggs, M.E., Gammon, R.W., Sengers, J. V.: Optical measurement of the Soret coefficient and the diffusion coefficient of liquid mixtures. J. Chem. Phys. 104, 6881 (1996). doi:10.1063/1.471355

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Thermogravitational micro-column

The thermogravitational micro-column used in this work is the same as in (Naumann et al. 2012) with a slight difference. Only the core part of the cell, shaping the gap of the micro-column, was replaced for the reason that the inlet and outlet were clogged up after multiple uses. Therefore, we improved the design to solve the problem. The new core part was made with the same material *Ketron PEEK* and was manufactured in *Denatek Engineering and Manufacturing Technologies* company with the greatest accuracy possible. After the manufacturing process, the gap size was verified in Mondragon University by MITUTOYO CRYSTA APEX S-7106 precision coordinate measuring machine see Fig.1.

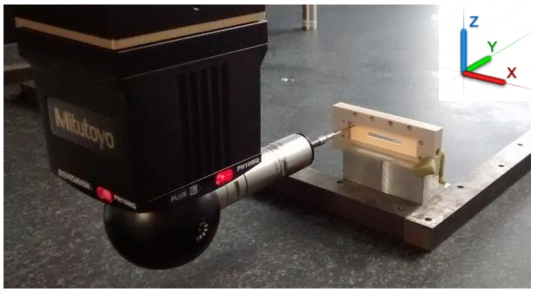


Fig.1 Measurement of the gap with MITUTOYO CRYSTA APEX S-7106 machine.

The new gap thickness is Lx=0.51±0.025 mm, the height of Lz=30 mm and width of Ly=3 mm.

a) b)

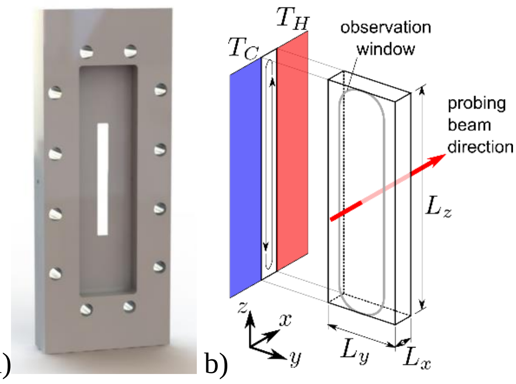


Fig.2 Core part of the micro-column, a) Shape of the gap of the micro-column, b) Configuration of the gap.

Design of the new configuration of optical diagnostics

The new configuration of the installation is based on Digital Interferometer (Mialdun and Shevtsova 2011). The two main contributions of this configuration are: On the one hand, all the height of the column is analysed as the laser beam was expanded to cover all the window of micro-column. On the other hand, we introduced two lasers with different wavelengths, a Diode-Pumped one with $\lambda = 470\,nm$ wavelength (Spectra-Physics) Fig.3 (1) and a He-Ne laser with $\lambda = 633\,nm$ wavelength (Research Electro-Optics) to be able to analyse also ternary mixtures in the future; below in this section the all notations refer to Fig.3. In order to work with both lasers at the same time without mixing their interference patterns, we have designed a special shutter system that is installed at the exit aperture of each laser. This shutter system consists of a shaft moving up and down (3) allowing or denying the pass of laser beam. The movements of interrupter's shaft and the acquisition of images are synchronized by program implemented in LabView (8).

After the shutting system, both laser beams are passed through neutral density filters in order to adjust the intensityFig.**3** (4). Then, to expand the beams, we used two spatial filter systems (Thorlab, KT310) with an aspheric lens, a pinhole and a collimator in order to obtain a good quality beam (5). Taking into account that the height of the micro-column is 30 mm, the final beam diameters were expanded to approximately 40 mm. Afterwards, both beams are directed into a Mach-Zehnder interferometer (6), where each beam is divided into two equal beams. One passes through the micro-column (7) (object beam) and the other one is the reference beam. At the end of the interferometer, divided beams are joined creating an interference patterns that are acquired by CCD camera (QImaging QIClick-CCD Camera) (9).

Digital interferometry is a trusted technique that can be used to determine the concentration of a mixture by analysing the refractive index. The refractive index varies because of a temperature and concentration variations,

$$\Delta n(y,z) = \left(\frac{\partial n}{\partial T}\right)_{T_o,c_o,\lambda} \Delta T(y,z) + \left(\frac{\partial n}{\partial c}\right)_{T_o,c_o,\lambda} \Delta c(y,z), \qquad (1)$$

Where, $(\partial n/\partial T)$ and $(\partial n/\partial c)$ are the contrast factors and $\Delta T(y,z)$ and $\Delta c(y,z)$ are the spatial temperature and concentration variations. In our system, the temperature gradient is applied in the same direction as the laser beam, so we can omit the temperature variation $\Delta T(y,z)$ influence. Thus, the total variation of the refractive index is due to the concentration variation (2). In turn, Δn is obtained from the phase difference $\Delta\varphi$, which is measured by the interferometry (3), where Lx is the geometric path in liquid.

$$\Delta n(y,z) = \left(\frac{\partial n}{\partial c}\right)_{T_O,c_O,\lambda} \Delta c(y,z), \qquad (2)$$

$$\Delta n(y,z) = \frac{\lambda}{2\pi L}\Delta\varphi(y,z) \qquad (3)$$

a) b)

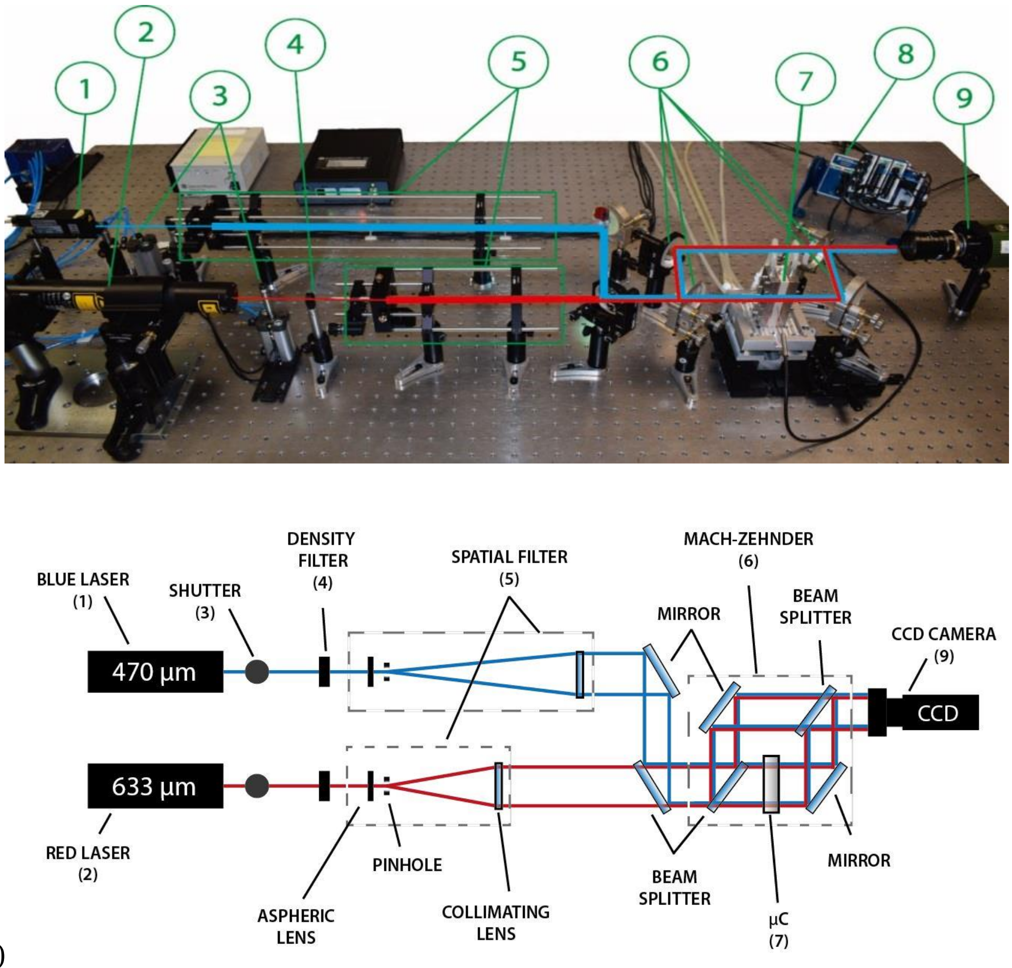


Fig.3 Digital Interferometry applied to thermogravitational micro-column installation. a) General view; b) Scheme of the installation.

Experimental scenario and Image processing

Both the interferometer configuration and image processing are based on Optical Digital Interferometry technique. Before starting the measurements, we stabilize the system at 25ºC for 4 hours and acquire the images every 10 minutes in order to check the stability of the system. At the end of the measurement, one of the last acquired images in the stabilization step is taken as the reference image. After applying the temperature gradient of $\Delta T = 8^{o}C$, the image acquisition rate is increased in order to see the evolution of phase variation in time. As the initial concentration change is bigger than near the stationary state, the acquisition of images is divided in three stages. For these binary mixtures, the image acquisition rate of first stage is 2 minutes during 36 minutes, in the second stage every 6 minutes during 72 minutes and finally every 12 minutes until the mixture reach the stationary state.

To extract the phase information from each acquired image, we use the 2D Fourier Transform technique described in literature (Mialdun and Shevtsova 2011). The Fig.4 outlines the image analysis steps. The phase information enables the determination of the refractive index of the sample. As a result, knowing the concentration derivative of the refractive index $\left(\partial n/\partial c\right)$ is possible to determine the entire concentration profile along the micro-column for each instant (for each acquired image). Once the mixture reach the stationary stage, the slope of the concentration along the height of the micro-column $\left(\partial c/\partial z\right)$ is used in order to determine the thermodiffusion coefficient.

This concentration profile correspond to the midline of y scale of the column in y-z plane (bounded by white dashed lines in Fig.**4**).

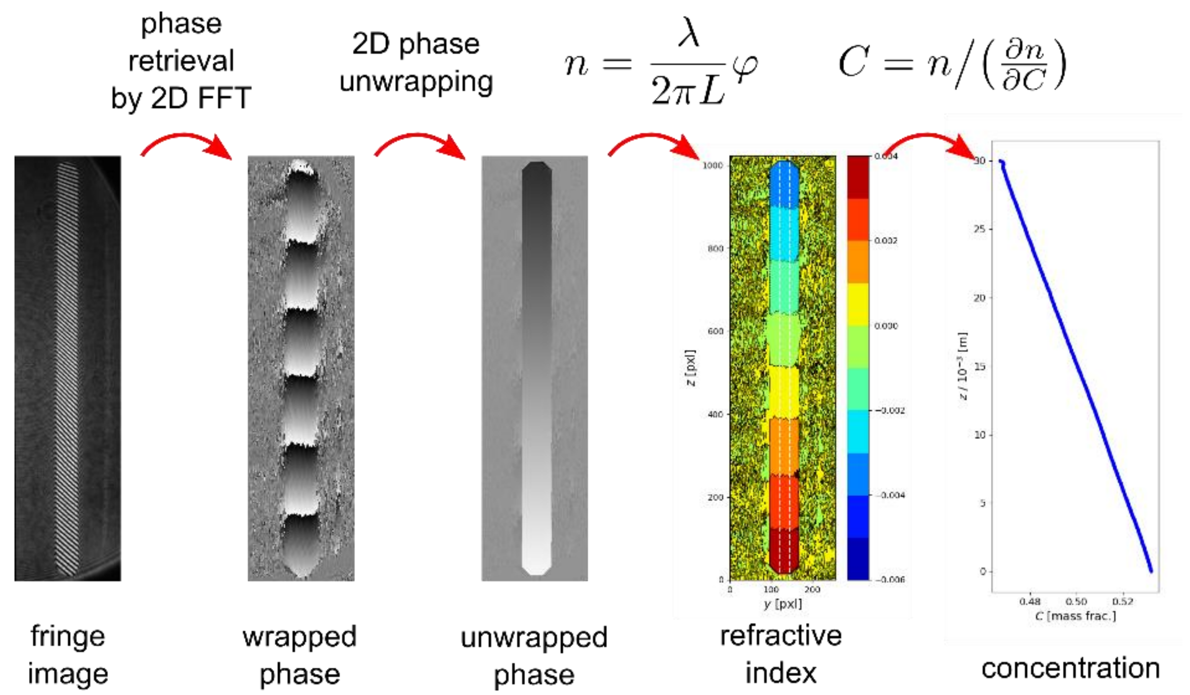


Fig.4 Steps for the phase information extraction of each acquired image.

The concentration variation during the all experiment is shown in Fig.5. There it can be appreciate the stabilization process at 25ºC for approximately 3-4 hours. Then, the temperature gradient is applied so concentration in the sample start changing until mixture reach the stationary state. Negative concentration variation means that the reference component is enriched at the bottom part of the micro-column.

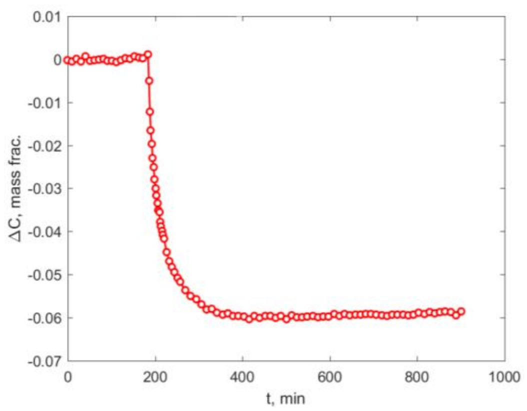


Fig.5 Time evolution of the concentration separation of THN-C12 binary mixture at 50% of mass fraction with $\Delta T = 8^{o}\,C$, monitored by 470nm wavelength.

3. Results and discussion

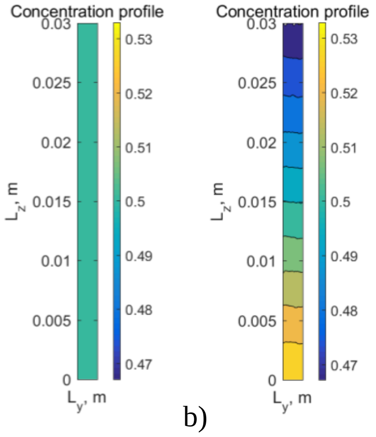
For the validation of the new analysis method, we have measured the thermodiffusion coefficients of three binary mixtures at equal mass fraction of THN (purity, 98+%), IBB (purity, 99%) and C12 (purity, 99%). All measurements have been carried out at mean temperature of 25ºC. The thermophysical properties as density, thermal expansion and dynamic viscosity were taken from (Alonso de Mezquia et al. 2015) and the contrast factor $(\partial n/\partial c)$ at 633 nm wavelength of three binary mixtures was taken from (Gebhardt et al. 2013). To calculate the $(\partial n/\partial c)$ at 470 nm, Cauchy dispersion relation has been used as it is detailed in (Mialdun, A. and Shevtsova 2017). In Table 1, all the optical and thermophysical properties taken from literature are shown.

Table 1. Optical and thermophysical properties of THN-IBB-C12 binary mixtures at equal mass fraction at 25ºC. Density, thermal expansion and dynamic

viscosity are taken from (Alonso de Mezquia et al. 2015) and $(\partial n/\partial c)$ from (Gebhardt et al. 2013).

	THN-C12	THN-IBB	IBB-C12
ρ (kg/m^3)	841.248	904.514	792.355
$\alpha \times 10^{-3}$ (K^{-1})	0.895	0.888	0.961
$\mu \times 10^{-3}$ $(Pa\,s)$	1.523	1.374	1.133
$(\partial n/\partial c)$ $(\lambda = 633nm)$	0.1155	0.0547	0.0625
$(\partial n/\partial c)$ $(\lambda = 470nm)$	0.1258	0.0577	0.0700

During the image processing, the concentration in the entire cross-section of the cell is determined from each image. The Fig.6a shows the initial concentration profile when the micro-column is stabilized at 25ºC and in Fig.6b when it reaches the stationary state with $\Delta T = 8^o C$.



a) b)

Fig.6 Concentration profiles inside the micro-column filled with THN-C12 at 50 % mass fraction; a) when mixtures is stabilized at $25^o C$, b) when the mixture reaches the stationary state after applying $\Delta T = 8^o C$.

Afterwards, the vertical concentration profile is represented in function of the height of the micro-column and is fitted with the polynomial of the first order obtaining $(\partial c/\partial z)$ as shown in Fig.7.

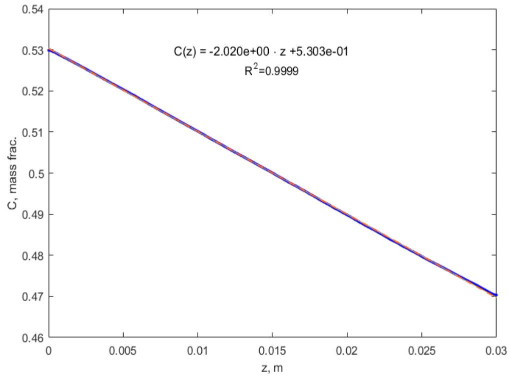


Fig.7 Concentration gradient at stationary state along the height of the micro-column of THN-C12 at 50% mass fraction with $\Delta T = 8^o C$.

Finally, the thermodiffusion coefficient of binary mixtures is determined (4) (Larrañaga et al. 2014),

$$D_T = -\frac{L_x^{\,4}}{504}\frac{g\,\alpha}{\nu\, C_0\,(1-C_0)}\frac{\partial c}{\partial z} \qquad (4)$$

where, L_x is the gap of the micro-column, g is the gravity, α is the thermal expansion coefficient, ν is the kinematic viscosity and C_0 is the initial concentration of the reference component.

The Table 2, Table 3 and Table 4 show the thermodiffusion coefficients of THN-C12, THN-IBB and IBB-C12 binary mixtures and the mean values with the respective deviations.

The obtained results show a good agreement with Benchmark Fontainebleau values (Platten et al. 2003) that makes us confident in reliability of the new configuration.

For the first time, with the new configuration, we have analysed all the height of the column and we have seen the entire concentration profile inside the thermogravitational column.

Table 2. Thermodiffusion coefficients of THN-C12 binary mixtures at 50% mass fraction.

THN-C12	633 nm		470 nm		Benchmark (Platten et al. 2003)
	$(\partial c/\partial z)$	$D_T \times 10^{-12}$ (m^2/sK)	$(\partial c/\partial z)$	$D_T \times 10^{-12}$ (m^2/sK)	
1	-2.124	5.53	-2.070	5.39	
2	-2.264	5.90	-2.177	5.66	
3	-2.304	5.99	-2.275	5.92	
4	-2.260	5.88	-2.180	5.68	
5	-2.299	5.99	-2.212	5.76	
Average	**-2.250**	**5.86±0.33**	**-2.183**	**5.68±0.29**	**5.9±0.3**

Table 3. Thermodiffusion coefficients of THN-IBB binary mixtures at 50% mass fraction.

THN-IBB	633 nm		470 nm		Benchmark (Platten et al. 2003)
	$(\partial c/\partial z)$	$D_T \times 10^{-12}$ (m^2/sK)	$(\partial c/\partial z)$	$D_T \times 10^{-12}$ (m^2/sK)	
1	-1.062	3.27	-1.010	3.11	
2	-0.801	2.46	-0.794	2.44	
3	-0.844	2.60	-0.804	2.68	
4	-1.062	3.27	-0.983	3.03	
5	-0.937	3.03	-0.984	2.89	
6	-0.902	2.78	-0.877	2.70	
Average	**-0.935**	**2.90±0.44**	**-0.909**	**2.81±0.37**	**2.8±0.1**

Table 4. Thermodiffusion coefficients of IBB-C12 binary mixtures at 50% mass fraction.

IBB-C12	633 nm		470 nm		Benchmark (Platten et al. 2003)
	$(\partial c/\partial z)$	$D_T \times 10^{-12}$ (m^2/sK)	$(\partial c/\partial z)$	$D_T \times 10^{-12}$ (m^2/sK)	
1	-1.079	3.82	-1.022	3.61	
2	-0.994	3.52	-0.987	3.49	
3	-1.209	4.28	-1.094	3.87	
4	-1.123	3.98	-1.074	3.80	
5	-1.146	4.06	-1.112	3.94	
6	-1.071	3.79	-0.988	3.49	
Average	**-1.104**	**3.91±0.39**	**-1.046**	**3.70±0.24**	**3.7±0.2**

4. Conclusions

In this work, we have changed the configuration of the previously reported optical analysis method applied to thermogravitational micro-column. The new configuration of the interferometer and the image processing is based on Optical Digital Interferometry analysis method. With the new configuration, we are able to analyse the entire window of micro-column instead of analysing only two points. Thanks to this improvement, we are able to see the entire concentration profile inside the micro-column during the measurements.

To validate the new system, we have determined the thermodiffusion coefficients of three binary mixtures at equal mass fractions. Results have been compared with Benchmark Fontainebleau

The new analysis method can be readily extended to analyse ternary mixtures. The analysis of the entire concentration profile will allow to study the thermogravitational effect in the transitory state of binary and ternary mixtures.

Acknowledgements

Authors would like to thank the support of Research Groups (IT1009-16) and Research Fellowship (Pre_2014_1_283) of Basque Government, TERDISOMEZ (FIS2014-58950-C2-1-P) and MEZNAFLU (ESP2017-83544-C3-1-P) of the MINECO and DCMIX (DCMIX-NCR-00022-QS) from the European Space Agency. Also would like to thank Denatek engineering and manufacturing technology company for manufacturing the gap.

References

Alonso de Mezquia, D., Larrañaga, M., Bou-Ali, M.M., Madariaga, J.A., Santamaría, C., Platten, J.K.: Contribution to thermodiffusion coefficient measurements in DCMIX project. Int. J. Therm. Sci. 92, 14–16 (2015). doi:10.1016/j.ijthermalsci.2015.01.013

Gebhardt, M., Köhler, W., Mialdun, A., Yasnou, V., Shevtsova, V.: Diffusion, thermal diffusion, and Soret coefficients and optical contrast factors of the binary mixtures of dodecane, isobutylbenzene, and 1,2,3,4-tetrahydronaphthalene. J. Chem. Phys. 138, 114503 (2013). doi:10.1063/1.4795432

Kolodner, P., Williams, H., Moe, C.: Optical measurement of the Soret coefficient of ethanol/water solutions. J. Chem. Phys. 88, 6512–6524 (1988)

Larrañaga, M., Bou-Ali, M.M., Lapeira, E., Santamaría, C., Madariaga, J.A.: Effect of Thermophyisical Properties and Morphology of the Molecules on Thermodiffusion Coefficient of Binary Mixtures. Microgravity Sci. Technol. 26, 29–35 (2014). doi:10.1007/s12217-014-9368-y

Larrañaga, M., Bou-Ali, M.M., Lizarraga, I., Madariaga, J.A., Santamaría, C.: Soret coefficients of the ternary mixture 1,2,3,4-tetrahydronaphthalene + isobutylbenzene + n-dodecane. J. Chem. Phys. 143, 24202 (2015)(a). doi:10.1063/1.4926654

Larrañaga, M., Bou-Ali, M.M., Lizarraga, I., Madariaga, J.A., Santamaría, C.: Soret coefficients of the ternary mixture 1,2,3,4-tetrahydronaphthalene + isobutylbenzene + n-dodecane. J. Chem. Phys. 143, 24202 (2015)(b). doi:10.1063/1.4926654

Mialdun, A. and Shevtsova, V.: Analysis of multi-wavelength measurements of diffusive properties via dispersion dependence of optical properties. Appl. Opt. 56, 572–581 (2017)

Mialdun, A., Legros, J.-C., Yasnou, V., Sechenyh, V., Shevtsova, V.: Contribution to the benchmark for ternary mixtures: Measurement of the Soret, diffusion and thermodiffusion coefficients in the ternary mixture THN/IBB/nC12 with 0.8/0.1/0.1 mass fractions in ground and orbital laboratories. Eur. Phys. J. E. 38, 27 (2015). doi:10.1140/epje/i2015-15027-2

Mialdun, A., Shevtsova, V.: Measurement of the Soret and diffusion coefficients for benchmark binary mixtures by means of digital interferometry. J. Chem. Phys. 134, 44524 (2011). doi:10.1063/1.3546036

Mialdun, A., Shevtsova, V.M.: Development of optical digital interferometry technique for measurement of thermodiffusion coefficients. Int. J. Heat Mass Transf. 51, 3164–3178 (2008). doi:10.1016/j.ijheatmasstransfer.2007.08.020

Naumann, P., Martin, A., Kriegs, H., Larrañaga, M., Bou-Ali, M.M., Wiegand, S.: Development of a thermogravitational microcolumn with an interferometric contactless detection system. J. Phys. Chem. B. 116, 13889–97 (2012). doi:10.1021/jp3098473

Platten, J.K., Bou-Ali, M.M., Costesèque, P., Dutrieux, J.F., Köhler, W., Leppla, C., Wiegand, S., Wittko, G.: Benchmark values for the Soret, thermal diffusion and diffusion coefficients of three binary organic liquid mixtures. Philos. Mag. 83, 1965–1971 (2003). doi:10.1080/0141861031000108204

Urteaga, P., Bou-Ali, M.M., Alonso De Mezquia, D., Santamaría, J., Santamaría, C., Madariaga, J.A., Bataller, H.: Measurement of thermodiffusion coefficient of hydrocarbon binary mixtures under pressure with the thermogravitational technique. Rev. Sci. Instrum. 83, (2012). doi:10.1063/1.4737628

Wiegand, S., Ning, H., Kriegs, H.: Thermal diffusion forced Rayleigh scattering Setup optimized for aqueous mixtures. J. Phys. Chem. B. 111, 14169–14174 (2007). doi:10.1021/jp076913y

Wittko, G., Köhler, W.: Precise determination of the Soret, thermal diffusion and mass diffusion coefficients of binary mixtures of dodecane, isobutylbenzene and 1,2,3,4-tetrahydronaphthalene by a holographic grating technique. Philos. Mag. 83, 1973–1987 (2003). doi:10.1080/0141861031000108213

Zhang, K.J., Briggs, M.E., Gammon, R.W., Sengers, J. V.: Optical measurement of the Soret coefficient and the diffusion coefficient of liquid mixtures. J. Chem. Phys. 104, 6881 (1996). doi:10.1063/1.471355