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MEASUREMENTS OF CONCENTRATION DIFFERENCES BETWEEN LIQUID MIXTURES USING DIGITAL HOLOGRAPHIC INTERFEROMETRY

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Abstract

We present an alternative method to detect and measure the concentration changes in liquid solutions. The method uses *Digital Holographic Interferometry* (DHI) and is based on measuring refractive index variations. The first hologram is recorded when a wavefront from light comes across an ordinary cylindrical glass container filled with a liquid solution. The second hologram is recorded after slight changing the liquid's concentration. Differences in phase obtained from the correlation of the first hologram with the second one provide information about the refractive index variation, which is directly related to the changes in physical properties related to the concentration. The method can be used – with high sensitivity, accuracy, and speed – either to detect adulterations or to measure a slight change of concentration in the order of 0.001 moles which is equivalent to a difference of 0.003 g of sodium chloride in solutions. The method also enables to measure and calculate the phase difference among each pixel of two samples. This makes it possible to generate a global measurement of the phase difference of the entire sensed region.

Keywords: Digital Holographic Interferometry, refractive index measurements, phase difference, full-field measurements.

1. Introduction

Liquid mixtures can be classified based on their physical properties such as concentration, weight, colour, and boiling temperature, among others [1]. The concentration of a liquid solution refers to the amount of solute (in moles or mass) dissolved in a certain quantity of solvent [2]. Methods and tools for accurate measurements that can detect slight concentration variations are greatly important for science, regulatory agencies, food processors, and consumers. Expensive liquids , including olive oil, fruit juices, honey, alcoholic drinks, and gasoline, are especially vulnerable to adulteration. For this reason, a fast and accurate technique is required to validate the concentrations of products or liquid mixtures. Optical techniques are non-destructive and are generally preferred for this purpose.

The index of refraction is one of the most important optical properties of an object [3]. In liquid solutions, this parameter is unique and proportional to the concentration of a substance [4]. Commonly, the refractive index is determined using Snell's law, which involves the displacement of the angle of an incident beam with respect to a refracted beam by a phase object. Some methods based on this law use prisms [5–8], squares [9, 10], and special containers [11]. However, these methods require a good estimation of the angles, which reduces their accuracy. Other disadvantages are that they use only a small region (scarcely a point) to obtain

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the refractive index of a sample, and the systems are difficult to calibrate and apply in real environments.

New full-field optical techniques have been developed that are more precise, accurate, non-destructive, and non-invasive. These methods have high resolution and stability, and they can measure profiles of physical variations in mixtures [12–14]. The traditional techniques that have been used to measure and visualize refractive index variations are the Schlieren, shadowgraph, and interferometry techniques, from which *Digital Holographic Interferometry* (DHI) has been developed [15]. Important efforts have been made to establish refractive index values using DHI [16]. They are related to concentration variations in liquid samples [17–18]. However, these methods use a special container and require knowledge of the dimensions of the container in advance. Also, they provide point measurements and are not able to take global measurements of a sample.

We present a fast, simple, high-precision, non-destructive, full-field optical technique for measuring concentration differences between liquid mixtures. The proposed method can obtain information from every small region of the wavefront coming from each sample being analyzed. All the regions are then used to calculate the global variation using the concentration variations of the samples. The process of phase retrieval is carried out digitally using the Fourier method [19]. This method uses an ordinary cylindrical container, which makes its implementation easier for industrial processes. Commonly, tubes are used to transport liquid products, and the proposed method makes it possible to monitor the concentration of liquid products during transport.

The remaining of the paper is organized as follows: in Section 2, we explain operation of the proposed optical system. Section 3 presents the numerical principles, the phase estimation method and the relation between a phase difference and a concentration variation of two liquid solutions. The experimental results are reported in Section 4. Finally, in Section 5, we summarize the conclusions of our work.

2. Experimental setup

A schematic diagram for detecting and measuring the concentration changes using DHI is shown in Fig. 1.

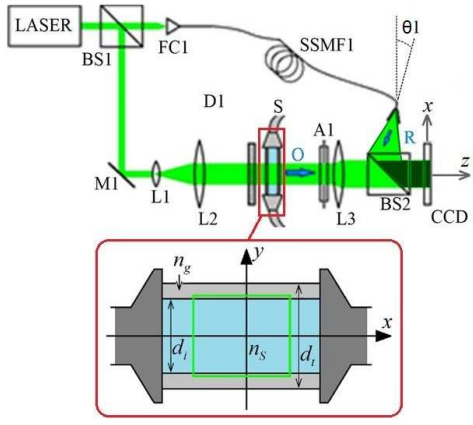

Fig. 1. A schematic diagram of the experimental setup using DHI. BS1, BS2: cubic beam splitters; FC1– a fibre collimator; M1 – a mirror; L1, L2, L3 – lenses; SSMF1 – a single-mode fibre; S – a liquid sample; D1 – a diffuser; A1 – an aperture; O – an object beam; R – a reference beam; $\theta 1$ represents the carrier spatial frequency along the direction x of the sensor plane. The wavefront comes from the green region in the glass view; x' and $y'$are the rectangular coordinates of the container with the liquid inside.

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Monochromatic He-Ne laser light with $\lambda = 543$ nm and a maximum output power of 15 mW is split into two beams by a beam splitter BS1. The reflected beam (the "object beam") from mirror M1 is reflected towards lenses L1 and L2 (expanded and collimated ones, respectively) and a diffuser D1. The beam passes through an ordinary glass tube with unknown inner dimensions d_i and containing a liquid sample S. This object beam enters through a rectangular aperture A1 and is collected by a positive lens L3, which creates on a CCD sensor an image of the tube containing the sample. The transmitted beam (the "reference beam") travels through a single-mode optical fibre SSMF1. It is sent into a cubic beam splitter BS2, which is placed in front of the CCD in such a way that it interferes with the object beam. Thus, a hologram (H_S) is recorded from the aqueous sample. The liquid solutions to be analysed are injected into the tube at a constant rate (~36 ml/s), and the interference patterns are recorded using a CCD, which is a monochromatic sensor with 1280 × 1024 pixels (1.3 MP) and a pixel size of 6.7 µm × 6.7 µm. All digital processing is done using Matlab. When recording the holograms, the temperature was stabilized at 20°C.

3. Method

The holographic technique can record the amplitude and phase (complete information) of a wave-front scattered by an object. The holographic interferometry setup uses the holography method to interferometrically compare two or more wave-fronts recorded at different moments or states [14]. The results of the comparison are used to obtain the phase difference map, which shows the physical variations between two liquids.

In order to measure the concentration difference between two liquid mixtures, we recorded two holograms that describe the substance coming from each liquid sample. By using the DHI double exposure method and an ordinary glass tube as an object, we obtained a hologram H_{S_1} from a wave-front coming from the tube filled with a certain liquid solution S_1 in the optical system (see Fig. 1). This can be represented using:

$$U_{S_1} = u_{S_1}(x,y)\ \exp[i\phi_{S_1}(x,y)], \tag{1}$$

where: u_{S_1} represents the amplitude; φ_{S_1} is the phase of the wavefront; and x and y are rectangular coordinates of the recording sensor plane. A second hologram H_{S_2} is then recorded either using another liquid solution or after slightly modifying the concentration of the liquid sample (creating S_2). The new phase is φ_{S_2}, which indicates a change in the optical path length. $\varphi_{S_2} = \varphi_{S_1} + \Delta\varphi_{S_2-S_1}$, which creates a wavefront that can be expressed as:

$$U_{S_2} = u_{S_2}(x,y)\ \exp\{i[\phi_{S_1}(x,y) + \Delta\phi_{S_2\text{-}S_1}(x,y)]\}, \tag{2}$$

or simply:

$$U_{S_2} = u_{S_2}(x,y)\ \exp[i\phi_{S_2}(x,y)]. \tag{3}$$

The two wave-fronts scattered by the tube have a phase distribution due to the morphological and physical properties of the object phase (see the red part of Fig. 1). The phase of the wave-fronts can be represented as:

$$\phi_m = k\{[d_t(x,y) - d_i(x,y)]n_g(x,y) + d_i(x,y)n_{S_m}(x,y)\}, \quad m = 1,2, \tag{4}$$

where $k = 2\pi/\lambda$; d_i and d_t are the inner and outer transversal distances of the glass tube; n_{S_m} and n_g are the refractive indices of the mixture and the glass walls, respectively.

3.1. Phase measurement

The total intensity recorded on the electronic sensor using any liquid sample in the tube is expressed by:

$$I(x,y) = |R(x,y)|^2 + |U(x,y)|^2 + U(x,y)R^*(x,y) + R(x,y)U^*(x,y), \tag{5}$$

where $U(x,y) = u(x,y)\exp[i\varphi(x,y)]$ and $R(x,y) = r(x,y)\exp[-i2\pi(f_x x + f_y y)]$, which are the complex amplitudes of the liquid mixture and the reference beam, respectively. $f_x = (\sin\theta 1)/\lambda$ and $f_y = (\sin\theta 2)/\lambda$ create a spatial frequency along the x and y directions caused by a small inclination $\theta 1$ and $\theta 2$ of the reference beam, since only the phase of the reference beam changes according to the register media, and "$*$" denotes the complex conjugate.

Equation (5) can be written as:

$$I(x,y) = a(x,y) + c(x,y)\exp[i2\pi(f_x x + f_y y)] + c^*(x,y)\exp[-i2\pi(f_x x + f_y y)], \tag{6}$$

where $a(x,y) = u^2(x,y) + r^2(x,y)$ and $c(x,y) = r(x,y)u(x,y)\exp[i\varphi(x,y)]$.

The size of the aperture was chosen in order to obtain a greater amount of high frequencies in the Fourier spectrum. In order to obtain the phase term in every hologram, a Fourier transform must be performed on (6), which is expressed as:

$$FT\{I(x,y)\} = A(\mu,\nu) + C(\mu - f_x, \nu - f_y) + C^*(\mu + f_x, \nu - f_y), \tag{7}$$

where capital letters represent the Fourier transform (see Fig. 2), while (μ,ν) are the spatial frequencies in the x and y directions, respectively.

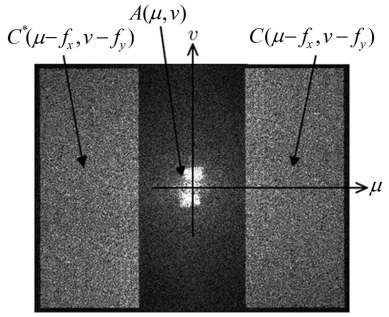

Fig. 2. A Fourier spectrum with the aperture.

The complex conjugate terms C or C^* are used to obtain the required phase term of the reconstructed wave-fronts. From this, only one of the three terms is filtered. Its inverse Fourier transform is then calculated to obtain the phase distribution:

$$\varphi(x,y) + 2\pi(f_x x + f_y y) = \arctan\frac{\mathrm{Im}[c(x,y)]}{\mathrm{Re}[c(x,y)]}. \tag{8}$$

The complete phase recovery process is visualized in Fig. 3 and can also be seen in previous studies [19, 21].

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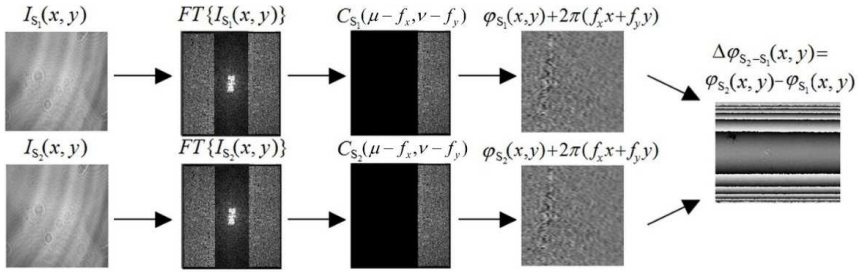

Fig. 3. The phase recovery process.

3.2. Concentration difference in liquid

With the individual phase terms H_{S_1} and H_{S_2}, the procedure continues with the calculation of the phase difference $\Delta\varphi_{S_2-S_1} = \varphi_{S_2} - \varphi_{S_1}$. A phase term depends on the transverse distances and the refractive index of the liquid mixture inside a glass tube. Thus, we can represent this phase difference as:

$$\Delta\phi_{S_2-S_1}(x,y) = k\{d_i(x,y)[\Delta n_{S_2-S_1}(x,y)]\}, \tag{9}$$

where $\Delta n_{S_2-S_1}(x,y)$ is the refractive index difference between substances S_2 and S_1.

The refractive index difference is related to the change of concentration CON and the temperature T between substances. Then, $\Delta n_{S_2-S_1}$ in (9) can be expressed as:

$$\Delta n_{S_2-S_1}(x,y) = \left[\frac{\partial n_S}{\partial CON}\right]_T [CON_{S_2}(x,y) - CON_{S_1}(x,y)] + \left[\frac{\partial n_S}{\partial T}\right]_{CON} [T_{S_2}(x,y) - T_{S_1}(x,y)], \tag{10}$$

where $\left[\frac{\partial n_S}{\partial CON}\right]_T$ and $\left[\frac{\partial n_S}{\partial T}\right]_{CON}$ are values that represent the dependence of the refractive index on CON and T, respectively. CON_{S_2} and T_{S_2} are the concentration and the temperature of S_2, whereas CON_{S_1} and T_{S_1} are those of S_1.

Aqueous salt mixtures (NaCl + H_2O) have a linear relationship between n and CON $\left(\left[\frac{\partial n_S}{\partial CON}\right]_T\right)$, which is considered to be constant at 1.71×10^{-3} at a temperature of 20°C. Then, (9) can be written as:

$$\Delta\phi_{S_2-S_1}(x,y) = k\{d_i(x,y)[1.71\times10^{-3}][CON_{S_2}(x,y) - CON_{S_1}(x,y)]\}, \tag{11}$$

Using (11), we can calculate the concentration difference between S_1 and S_2, but d_i is not known because we used an ordinary glass cylinder whose walls are optically imperfect. To solve this issue, we used a reference solution S_{H_2O} and another liquid mixture ($S_{H_2O+NaCl}$) with known parameters to create an independent expression that eliminates the dependence on d_i. Then, we need to create another phase difference $\Delta\varphi_{ref}$ using these two solutions. We employed it to obtain d_i as:

$$d_i(x,y)=\frac{\Delta\phi_{ref}(x,y)}{[1.71\times10^{-3}][\Delta CON_{S_{ref}}(x,y)]}k^{-1}, \tag{12}$$

where $\Delta\varphi_{ref}=\varphi_{H_2O+NaCl}-\varphi_{H_2O}$ and $\Delta CON_{ref}=CON_{H_2O+NaCl}-CON_{H_2O}$.

Using (11) and (12), we can calculate the concentration difference between two substances as:

$$\Delta CON_{S_2-S_1}(x,y)=\frac{\Delta\phi_{S_2-S_1}(x,y)}{\Delta\phi_{ref}(x,y)}\left[\Delta CON_{ref}(x,y)\right]. \tag{13}$$

By employing (13), the full-field distribution of the concentration difference in a glass tube can be calculated and visualized.

4. Results

In order to verify operation of the experimental setup, we calculated and visualized the global concentration difference distribution between saline mixtures. The liquid samples were prepared by mixing distilled water (S_{H_2O}) (50 ml) and definite quantities of NaCl (0.25, 0.5, 0.75, 1, 1.25 and 1.5 g) to create each mixed solution (NaCl + H_2O) with specific molarities of $S_{mol_1}=0.086$, $S_{mol_2}=0.172$, $S_{mol_3}=0.258$, $S_{mol_4}=0.344$, $S_{mol_5}=0.43$, and $S_{mol_6}=0.516$ moles. A set of $\Delta\varphi_{S_2-S_1}$ was calculated for solutions with concentration differences of 0.086 mol between them. The first solution with a lower concentration is taken as S_1, and the next liquid solution with a higher concentration – as S_2 (see Figs. 4a–4f).

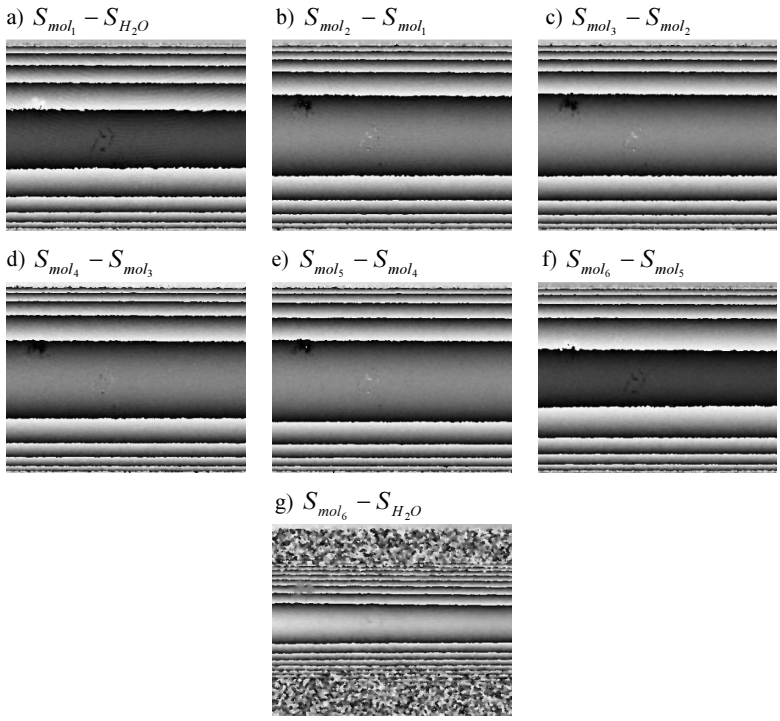

Fig. 4. Wrapped phase difference maps.

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$\Delta\varphi_{ref}$ was calculated in all the experiments using S_{H_2O} and S_{mol_1} as $S_{H_2O+NaCl}$. For example, to calculate the concentration difference between S_{mol_5} and S_{mol_6}, we took the first one as S_1 and the second (with a higher molarity) as S_2 to create $\Delta\phi_{S_2-S_1}$, together with the other values ($\Delta\varphi_{ref}$ and ΔCON_{ref}). Then, the distribution of the concentration difference between the mixtures can be calculated using (13). The values of CON and n of these last two solutions were obtained from [1] and [20]. The concentration difference values obtained with the proposed method are presented in Table 1.

Table 1. Comparisons of concentration values measured by the DHI and those found in [20].

Solutions compared	$\Delta CON_{S_2-S_1}$ (value in Ref. 20) [*mol*]	$\Delta CON_{S_2-S_1}$ (with DHI) [*mol*]	Deviation
$S_{mol_1} - S_{H_2O}$	0.083	0.083	0.0
$S_{mol_2} - S_{mol_1}$	0.086	0.086	0.0
$S_{mol_3} - S_{mol_2}$	0.086	0.088	+0.002
$S_{mol_4} - S_{mol_3}$	0.086	0.081	–0.005
$S_{mol_5} - S_{mol_4}$	0.086	0.082	–0.004
$S_{mol_6} - S_{mol_5}$	0.086	0.085	–0.001

The performance of the CCD sensor employed in this experiment was assessed using liquid substances with concentration differences of 0.086 moles between them. Substances with a higher concentration difference generate a wrapped phase map with a high frequency, which is more difficult to unwrap and does not enable to obtain the concentration differences. For example, if we generate a phase difference between the liquid samples of S_{H_2O} and S_{mol_6}, we obtain the phase difference map shown in Fig. 4g.

5. Conclusions

This work has presented a method of detecting and measuring the global concentration variations in liquid mixtures using DHI. The process measures phase variations between wavefronts scattered by an ordinary glass tube and converts them with a phase change into a concentration variation. The method is non-invasive, simple, fast, and easy to develop in a laboratory and real work environments. The technique can resolve extremely small changes of concentration in the order of –0.001 moles, which is equivalent to a difference of 0.003 g of sodium chloride in saline solutions. In other words, since we used 50 ml of distilled water, the method can distinguish changes in salt concentration of 6×10^{-5} by weight. Additionally, the method does not require a special device to contain the saline sample. The results are in accordance with concentration values published in [20] on aqueous salt solutions ($NaCl + H_2O$). Our method can be used to identify or confirm the identity of a sample, as well as to detect adulterations or fake solutions.

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