Contributed paper

OPTO-ELECTRONICS REVIEW **13**(1), 1–8

Review of drop analysis technology for liquid property study

Q. SONG*, G.X. ZHANG, and Z.R. QIU

State Key Laboratory of Precision Measuring Technology and Instruments, College of Precision Instrument and Opto-electronics Engineering, Tianjin University, Tianjin, 300072, P.R. China

Drop analysis takes a multidisciplinary and integrated approach to monitor the drop growth in the process of liquid forming into the drop, so as to measure the physical and chemical parameters of the tested liquids and to discriminate different liquids qualitatively and quantitatively. In this paper, fiber drop analysis (FDA), capacitive drop analysis (CDA), image drop analysis (IDA,) and spectral drop analysis (SDA) are summarized in review. Main features and application fields of each method are introduced. The combination of various drop analysis technologies and its significance are presented.

Keywords: drop analysis, liquid drop fingerprint, fiber, capacitive, image, spectral.

1. Introduction

Liquid property study has been long a concern for industrial, agricultural and environmental science. Many theories and methods have been constructed and applied for measuring various natural parameters of liquids. As we know, a great deal of information on liquid properties is contained intrinsically, or can be encoded, in the process of liquid forming into the drop. This makes it possible to analyse a liquid by monitoring its drop growth. Drop analysis technology (DAT) is recently developing with the growing modern optoelectronic technology and computer technology. It takes a multidisciplinary and integrated approach including optical fiber, electrical, spectral and image methods. All these drop analysis methods will be introduced in this paper in summarization and review.

Drop analysis has some remarkable features compared with other instrumental methods. For example, a variety of physical and chemical parameters of tested liquids can be potentially obtained directly or indirectly during a measuring cycle, including surface tension, concentration, refractive index, turbidity, and chemical constitution. Besides, a unique and definite liquid drop fingerprint (LDF) can be obtained through drop analysis, just like the fingerprint of a certain person. LDF is suitable for fine discrimination among different liquids and it can be used for distinguish quality goods from counterfeits, such as fake beverage, fake medicine, and fake wine. What is more, drop analysis is a pollution-free method to study liquid properties because there is no chemical reagent and reaction. And also, drop analyser is favourable for real-time online measurement, which makes it particularly useful for monitoring the manufacturing process of liquids. The above advantages make drop analysis of extensive prospect in the fields of environmental quality monitoring, pharmaceutical technology, food, beverage, and other liquid-related fields.

2. Drop analysis methods

2.1. Fiber drop analysis (FDA)

The fiber drop analysis method (FDA) was first introduced by McMillan *et al*. in 1992 [1]. It is based on the light intensity study passing through the liquid drop through a special drop head positioned with two optical fibers. This novel technology extends the liquid analysis based on drop weight/volume study into a whole new field.

Figure 1 shows the fiber drop head in two forms of a flat cylindrical design in (a) and a reverse cone angle design in (b). A pendant drop is formed at the end of the drop head through a delivery capillary. Experiments prove that the concave design in (b) can ensure the liquid fully wet the end surface of the drop head. The modulated light from an IR LED is injected into the liquid drop by a source fiber positioned in the drop head. A detector fiber, on the opposite side of the drop head, couples some of this injected radiation after various reflection, refraction, and absorption of the optical signal inside the drop, and transmits it to a photoelectric transducer.

Figure 2(a) shows propagation of the light inside the drop during its growth. The salient end face on the fibers indicates the effective domain within the emergence or acceptance angle. The ray paths drawn in this selection of video recording are the ones that lead to light coupling from the source fiber to the detector fiber via total internal reflections (TIR) inside the drop. The radiation, which enters the detector fiber within its acceptance angle is propagated in the fiber with low loss and received by the transducer. During drop growth, the amount of coupled radiation varies reproducibly to produce a fiber drop trace

*e-mail: sunny512@eyou.com

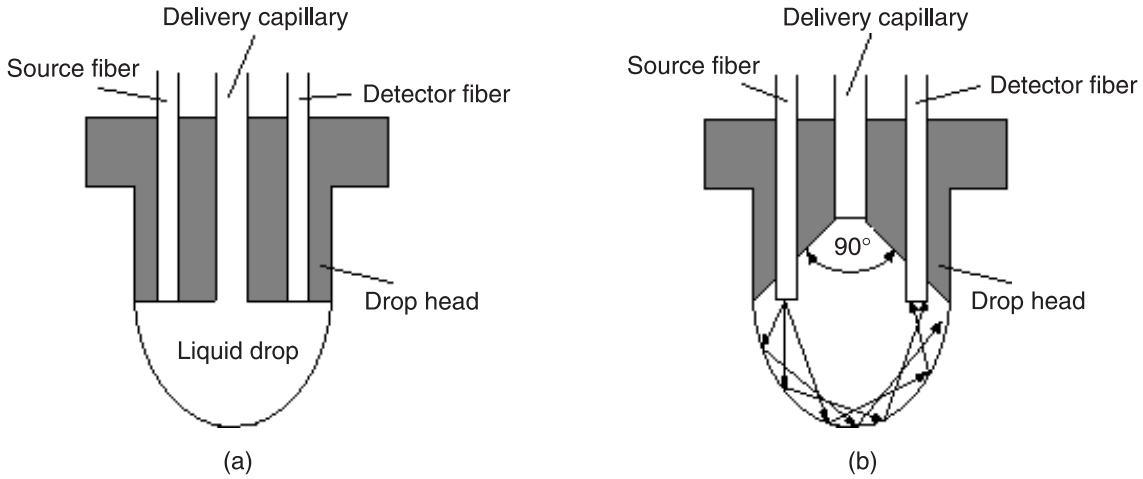

Fig. 1. Fiber drop head: (a) flat cylindrical head and (b) drop head with a 90° reverse cone angle.

(FDT), as shown in Fig. 2(b), where the horizontal axis refers to the time series according to the acquisition interval determined by the program, the vertical axis refers to the uncalibrated output voltage signal corresponding to the light intensity.

At point 1 and 2, the rays that first couple via TIR reflections in the remnant drop are not within the acceptance angle, and they are consequently heavily attenuated once they get into the detector fiber. From point 3 to 8, the light intensity signal appears to be a curve from peak to hollow, since the reflection angle and optical path vary with the drop profile. At point 9, the light path direction changes suddenly and the path-length shortens, which produce a strong separation peak when the drop falls off. It is obvious that the coupled light signal between the source fiber and the detector fiber is determined fundamentally by the shape of the liquid on the drop head for low absorbance liquids, since the numerical aperture (NA) of fiber and the fiber positions are fixed.

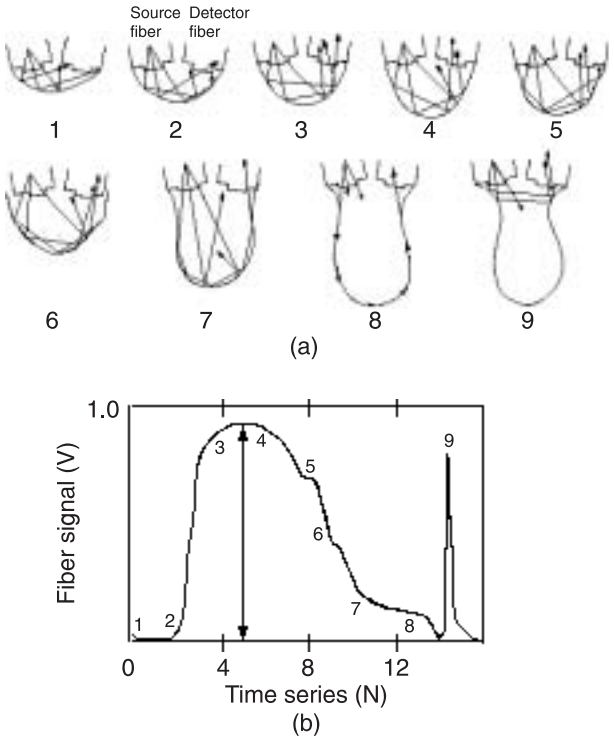

Fig. 2. Coupled optical signals in fiber drop analysis (after Ref. 1): (a) propagation of light inside the drop during its growth and (b) fiber drop trace.

Large quantities of experiments for different samples prove that, the FDT is unique for a certain liquid under certain conditions, including mechanical structure of the drop head, the position of fibers inside the liquid drop, the electrical parameters in the processing circuit and the circumstance temperature, humidity and pressure. Therefore FDT can be used for fine discrimination among different liquids. Moreover, the optical signal is in fact a very fruitful source of information on the bulk properties of the liquid. Preliminary investigations by McMillan *et al.* [2] have show that the drop period is related to the surface tension and density of liquids, the main peak of FDT is corresponding to the refractive index and the separation peak can give a measurement of viscosity.

However, because the FDT is related to time, the speed of drop growth should be quite small and stable so that the drop is under quasi-equilibrium condition, on which the drop analysis is based. Since the speed of drop growth essentially depends on the flow control of the feeding pump, it inevitably leads to a heavy demand on the pump in practice. If the speed cannot be controlled precisely, the repeatability of measurement and the uniqueness of FDT cannot be ensured. This problem is even more serious when a volatile liquid is measured.

2.2. Capacitive drop analysis (CDA)

Drop volume measurement is an agelong subject in surface science. Various methods have been developed specifically for this purpose. The capacitive drop analysis (CDT) introduced by Wang *et al.* [3] in 1999 provides another choice, through a specially designed capacitive sensor, as shown in Fig. 3(b). The capacitive drop sensor uses the drop head as

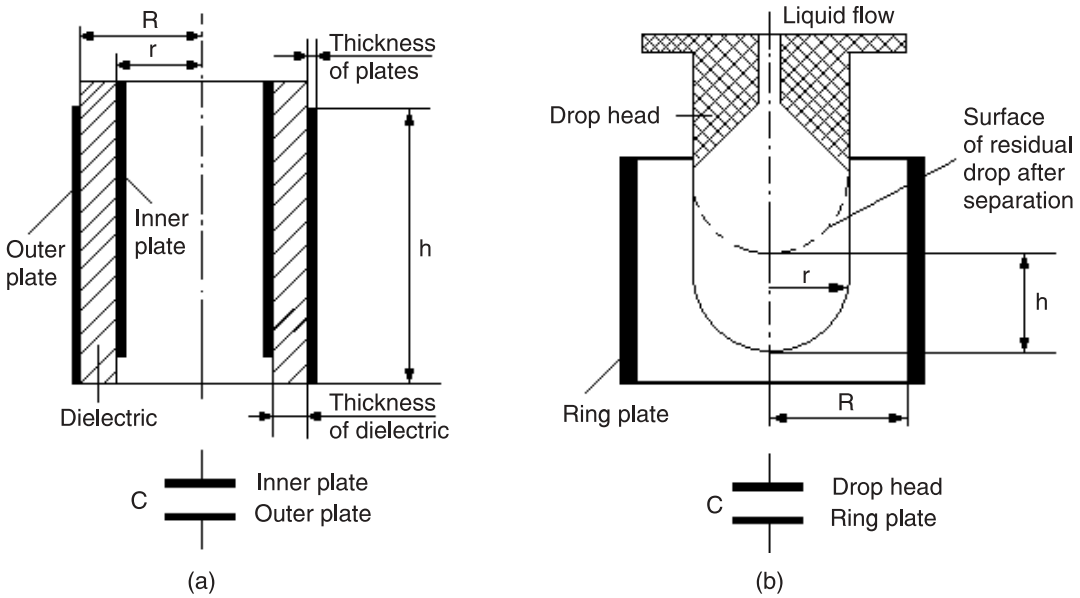

Fig. 3. Construction of the capacitive drop sensor from a common cylindrical capacitive sensor: (a) cylindrical capacitive sensor, (b) capacitive drop sensor.

one of its plate and a cylindrical ring plate, which surrounds the drop head and the space occupied by the formed drop, as another. The drop, which can be seen either as an extension of the drop head plate if the liquid is highly conductive, or as a dielectric material if it is less conductive, changes the capacitance value along with drop growth.

To simplify the mathematical model of the capacitive drop sensor, we assume that:

- the drop is highly conductive,
- the drop, during formation, only extends its length in the axis direction without changing its diameter,
- edge effects are ignored.

So, the capacitance variation during drop growth from a residual drop can be expressed approximately as

$$\Delta C = \frac{2\varepsilon_0 \varepsilon_a \pi h}{\ln \dfrac{R}{r}}, \tag{1}$$

where ε_0 and ε_a are the absolute dielectric constant of vacuum and the relative dielectric constant of the atmosphere, respectively, h is the length of drop growth from a residual drop, R is the inner radius of the ring plate and r is the end radius of the drop head.

After simplification, the drop volume is given by

$$V = \pi r^2 h. \tag{2}$$

Then, the relation between the variation of capacitance ΔC and the drop volume V is obtained as the following

$$V = \frac{k_0}{2\varepsilon_0 \varepsilon_a} \Delta C, \tag{3}$$

where $k_0 = r^2 \ln(R/r)$.

Calculations show that variation of k_0 can be kept within 1% when r varies from 2.78 mm to 3.22 mm and within 5% when r varies from 2.52 mm to 4.36 mm. Therefore k_0 can be regarded as constant when the drops do not change very much in a diameter. In this case, the drop volume is linearly related to the capacitance.

Since many liquids are not good conductors, errors will arise when using Eq. (3) in this case. By consideration of the effect of dielectric constant variations, Eq. (3) can be rewritten empirically as

$$V = \frac{k_1(k_2 \varepsilon_l + \varepsilon_a)}{\varepsilon_0 \varepsilon_a (\varepsilon_l - \varepsilon_a)} \Delta C, \tag{4}$$

where k_1, k_2 are the correction coefficients related to the structural parameters of the drop head, ε_l is the relative dielectric constant of the tested liquid in the real-time environment. When $r = 3$ mm, $k_1 = 11.23 \times 10^{-6}$ m^2 and $k_2 = 0.185$.

CDA converts the change of drop volume during drop growth to the change of capacitance of a capacitive drop sensor. It has proved to be capable of measuring drop volume with an accuracy of approximately 2 µl. The ability of CDA to measure surface tension based on Eq. (5) of Harkins and Brown was also explored

$$\sigma = \frac{dV_e gF}{r}, \tag{5}$$

where σ is the surface tension (mN/m), d is the density of the liquid (kg/m^3), g is the local acceleration of gravity (m/s^2), r is the outer radius of the capillary tube (mm), and V_e is the drop volume for slow dynamic equilibrium conditions (mm^3). F is the empirically derived correction factor as the following

$$F = 0.14782 + 0.27896X - 0.166X^2, \tag{6}$$

where $X = r/(V_e)^{1/3}$.

The experiments prove that the maximum differences between the measured values of surface tension and the reference values are never more than 1 mN/m. The remaining differences might be caused by the inaccuracy of the empirical factor F, as well as the conical concave design at the end of the drop head since Eq. (6) was derived for a drop head with a flat end surface.

CDA is suitable for measuring both drops in equilibrium and those in the process of formation. It is particularly useful for volatile liquids, in which case the measurement of drop volumes using flowmeters and pump may be superseded. Furthermore, CDA can also be used to study liquid concentration and it was found out that the capacitive variation for the aqueous glycerol solution is linearly dependent on concentration.

The main disadvantage of CDA results from the dielectric constant of the tested liquid. As mentioned above in Eq. (4), the drop volume (V) can be got from measured variation of the capacitance (ΔC) only if the dielectric constant of the tested liquid (ε_l) is known. Because ε_l is largely influenced by the environmental temperature, the measurement result is relatively inaccurate if ε_l is decided from handbooks. Thus, there must be a real-time device for measuring ε_l.

2.3. Fiber-capacitive drop analysis (FCDA) and the liquid drop fingerprint (LDF)

The variation of the drop growth speed or liquid-feeding speed will produce a problem that the fiber drop trace (FDT) in FDA is irreproducible for a certain liquid and is incomparable for different liquids. It is an essential trouble of the drop analysis based on FDT in measuring property parameters and in discriminating liquids. Therefore a new representation of volume-based fiber drop trace (VFDT) is developed by Qiu *et al*. [4] in 2000 to solve this problem, by merging FDA and CDA into fiber-capacitive drop analysis (FCDA). Figure 4 shows the principle of FCDA [5].

Figures 5(a) and 5(b) show the time-based FDT and the drop volume variation of the pure water on the condition that the feeding speed becomes slower gradually. There are

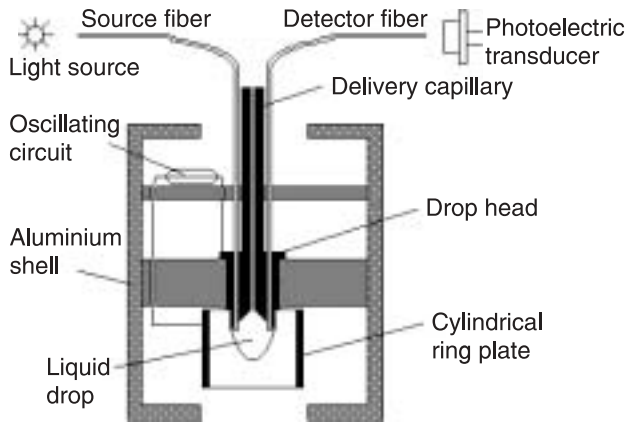

Fig. 4. Principle of fiber-capacitive drop analysis.

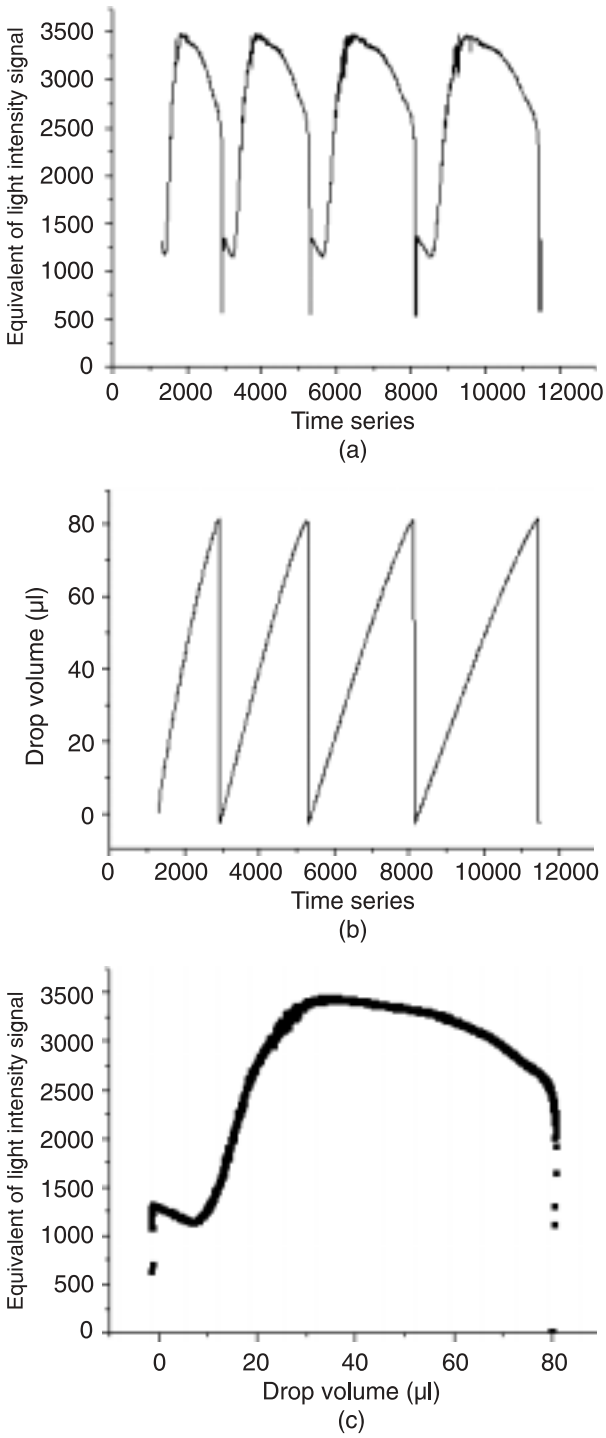

Fig. 5. Experimental results of the pure water under non-constant delivery speed: (a) the light intensity signal or time-based fiber drop trace, (b) the drop volume signal, and (c) the volume-based fiber drop trace.

obviously some differences in the four continuous FDTs. Figure 5(c) shows the volume-based fiber drop trace (VFDT), which uses the instant drop volume as the horizontal axis instead of time.

VFDT is actually an overlapping curve of time-based FDT in some successive periods of drop growth based on the drop volume. It can be found that the VFDT is of excel-

lent repeatability, which proves the VFDF is no longer influenced by the variation of feeding speed. This can be explained by the following qualitative explanation. The light intensity detected by the fiber after TIR (total internal reflection) inside the drop depends on the instant shape or volume of the drop, which determines the optical path, no matter how long to form this instant shape.

The new representation of VFDT makes the FDT independent from the speed of drop growth and the volatility of liquid, and accordingly ensures the reproducibility of measurement against the variation of the feeding speed of the pump. In addition, the VFDT is more favourable for fine discrimination of liquids since it improves the comparability of the FDT of different liquids. VFDT can be called the liquid drop fingerprint (LDF) directly.

As it has been mentioned above in CDA, the drop volume lies on the dielectric constant of the tested liquid measured real-timely. Because the capacitance variation ΔC is linearly related to time during drop growth and also ΔC is linearly related to the drop volume V for a certain liquid, it is appropriate to construct the capacitance-based fiber drop trace to exclude the influence of feeding speed. The capacitance can be regarded as the equivalent drop volume. Thus, the liquid drop fingerprint is free from the dielectric constant of the tested liquid with special reference to applications of liquid discrimination.

Figure 6 shows LDFs of some kinds of liquids, including pure water, LanTian beer, mature vinegar, LaoChou soy and JianLian rice wine. The horizontal and vertical axes are expressed in voltage signals, which is obtained from A/D card after the processing circuits of fiber signal and capacitive signal. Visual features and qualitative differences can be observed in LDF. The equivalent drop volume and the light intensities of different liquids are different. The peak heights and the peak shapes, and the areas surrounded by the LDF curves and the horizontal axis are different too. In general, LDF is powerful for fine discrimination among different liquids by using the information extracted from the LDF of samples and constructing a mathematical model or database for identification.

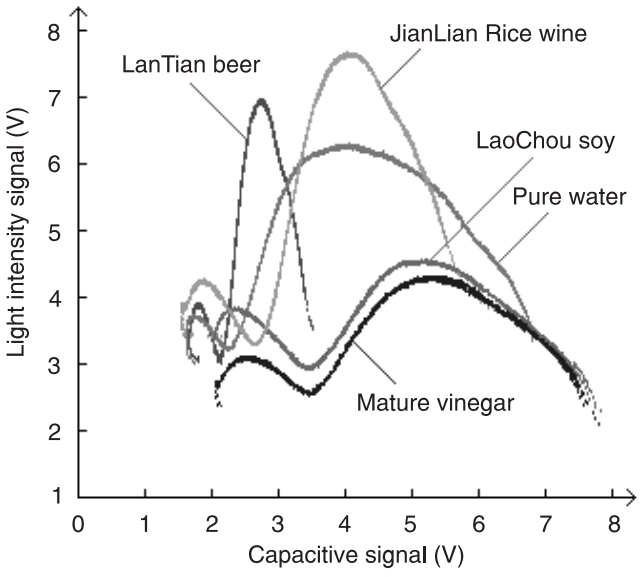

Fig. 6. Liquid drop fingerprints of different liquids.

2.4. Image drop analysis (IDA) and fiber-image drop analysis (FIDA)

Along with the recent developments in image technology, it is possible to record the liquid drop shape to study the liquid properties. Colleagues in university of Toronto develop a computer software package named axisymmetric drop shape analysis (ADSA) [6,7] to determine liquid-fluid interfacial tension and contact angle by fitting the Laplace equation of capillary to an arbitrary array of coordinate points selected from the drop profile. Image drop analysis (IDA) introduced by Qiu *et al*. [8] is devoted to the dynamic measurement of a growing drop during the drop formation based on ICCD. The technique combines recent advances in digital image acquisition and processing to monitor the drop growth real-timely and to make analysis of the characteristics of drop shape in various stages.

Figures 7(a) and 7(b) are the profile records of pure water and 100% ethanol taken by a CCD camera during their drop growth under quasi-equilibrium condition. It is obvious that the drop shapes of two different liquids are different, which suggests that the drop shape determined by the liquid property may be used for discriminating liquids and for property measurement.

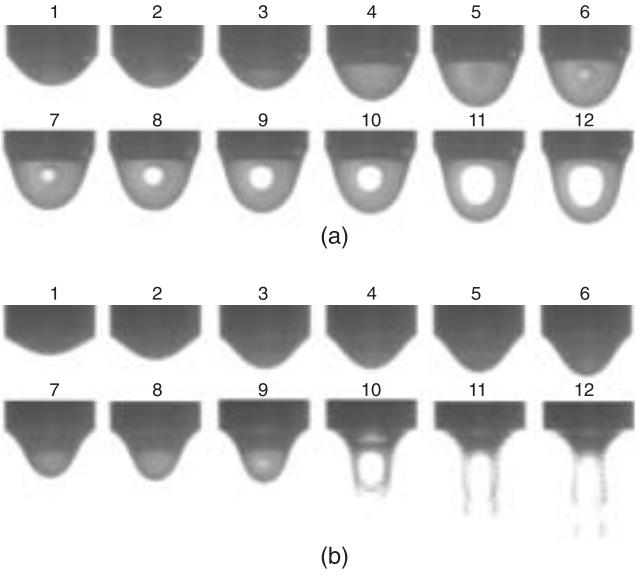

Fig. 7. ICCD profile records of liquids during their drop growth: (a) pure water and (b) 100% ethanol.

After the instant shape in the process of drop formation are captured and stored real-timely by the CCD image acquisition system, then the image processing system plays the role of edge detection and profile reproduction. If there is a radical change of the image grey in the edge area, the

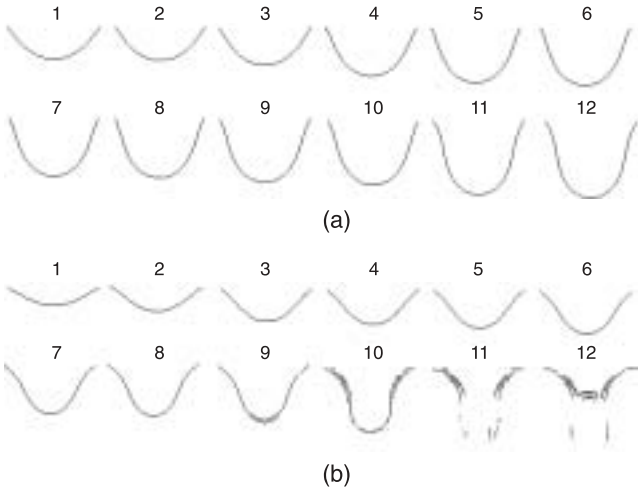

Fig. 8. The edge curves of drop profile: (a) pure water and (b) 100% ethanol.

gradient operator is favourable for detection because a narrowest edge line can be got in this case. But in fact, the image usually becomes ambiguous because of the noise caused by the sensitive components and transmission channels, although the original image itself may be a step change. In this case, Sobel operator or Laplacian operator combined with certain threshold is useful for edge detection. Figures 8(a) and 8(b) are the detected edge curves of pure water and 100% ethanol in one drop formation period through Laplacian operator edge extraction.

Besides drop shape analysis, IDA provides a choice for drop volume measurement. Because the drop shape is relatively simple and fixed, a rectangular image processing region, which includes the tested drop and part of the drop head, is defined for edge detection as shown in Fig. 9. The drop volume is the difference between the volume of the growing drop and that of the remnant drop, calculated from the profiles combined by the drop and the drop head inside the rectangular region.

After the pixel positions of the edges X are determined by using Laplacian operator, the drop volume is calculated from

$$V_t = D\left[\int_{y_1}^{y_t'} \frac{(X_{\max} - X_{\min})^2 \pi}{4} dy - \int_{y_1}^{y_{\min}'} \frac{(X_{\max} - X_{\min})^2 \pi}{4} dy\right], \quad (7)$$

where X_{max} and X_{min} refer to the pixel positions of two boundary points of a drop in the same section $y_1, y_t', y_{\min}'$, are shown in Fig. 9, D is the coefficient of volume equivalent, which converts the pixel unit to the volume unit (mm^3). D is defined as

$$D = \left[\frac{L(\text{mm})}{d}\right]^3, \quad (8)$$

where L is the actual width of the drop head inside the rectangular image processing region (mm) and d is the difference in the pixel positions $X_{max} - X_{min}$ of the drop head inside the region.

Since L is determined after manufacturing and d is measured based on data collected real-timely, the volume will be independent from errors of optical parameters, such as focus length of the CCD camera and light intensity.

The remarkable advantage of IDA is that there is no need to determine the dielectric constant of the tested liquid and it can be used for measuring unknown liquids. IDA is favourable for volatile liquids since it is a non-contact measurement. IDA is insensitive to the electrical parameters of liquids. IDA provides not only the volume, but also the shape information of the drop during its growth. Studies on the drop shape are turned into digital process, which provides a potential prospect for further analysis.

The liquid drop fingerprint (LDF) can also be obtained by merging IDA and FDA into the fiber-image drop analysis (FIDA). Because both of these two methods are based on photoelectric conversion principle, mutual coupling influence must be eliminated. The ultraviolet light source is specially selected for fiber drop sensor to avoid the possible effects on the drop profile captured by CCD.

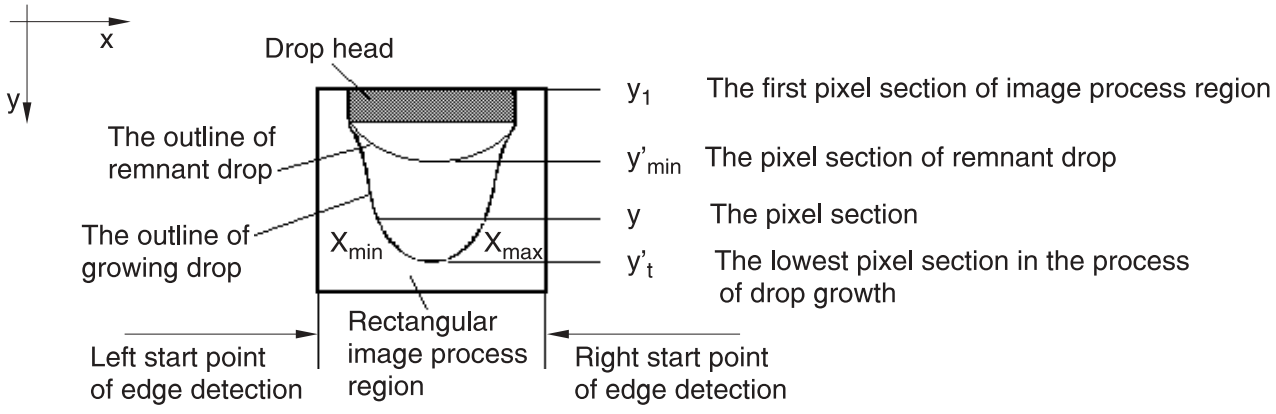

Fig. 9. Drop volume measurement inside the rectangular image processing region.

2.5. Spectral drop analysis (SDA) and 3D liquid drop fingerprint

Fiber drop analysis reveals the variation regularity of the light signal passing through the liquid drop during the drop growth. Generally the monochromatic light source is used. Even though the white light is employed, it is considered as an intensity source but not a spectrum source with some wavelength width. The coupled light intensity is affected by mechanical and optical properties of the tested liquids and it is different for different liquids because the profile and volume of the drop during its growth are different. However in fact, the collected light intensity is not only dependent on the drop itself and resulted differences in total internal reflection and optical paths inside the drop, but also dependent on the composition of the liquid, because various liquids consist of various substances which have different absorption in the light signal of different wavelength. Therefore the spectral drop analysis [9] is developed to study the liquid composition by studying the absorption spectrum of the multi-wavelength light signal passing through the liquid.

Figure 10 is the schematic diagram of fiber-capacitive-image-spectral (FCIS) drop analysis. The fluid with stabilized flow rate and minute flow flux is supplied by a computer-controlled micro-flow feeding pump and forms into a satiated and uniform liquid drop through the liquid drop sensor. The light signal emitted from the light source is injected into the liquid drop sensor through the input optical path. The light intensity signal passing through the drop is collected and transmitted by the output optical path and is sent to the computer in two ways. One is transformed to the electrical signal by a photoelectric transducer and is sent to an A/D converter via an amplifier and filter circuit. The other is transferred to a FFT spectrum analyser, which changes the light intensity signal to the absorption spectrum of the liquid.

After introducing the spectral analysis into the liquid drop analyser, a 3D liquid drop fingerprint can be obtained by merging the light intensity signal from the fiber drop sensor, the drop volume signal from the capacitive drop sensor or CCD image processing and the absorption spectrum signal from the FFT infrared spectrum analyser. Figure 11 is the 3D liquid drop fingerprints of ethanol and propanol, in which the spectrum signal is express in form of relative spectral curve. Relative spectral curve is got by the light intensity percentage relative to the maximum one in all wavelengths in the same drop volume, and it makes 3D LDF unrelated to the instant drop profile or volume. It can be seen that 3D LDF covers a more extensive range of physical and chemical properties on liquids, and it enhances the capability of drop analysis in fine discrimination among different liquids because it is nearly impossible to get the same 3D LDF for two different liquids under the same testing system.

3. Conclusions

Drop analysis technology is devoted to reveal the intrinsic characteristics of liquids based on monitoring the drop formation process. Fiber drop analysis (FDA) makes use of the special light-transmission ability of optical fibers, to detect the liquid properties inside the liquid drop. Capacitive drop analysis (CDA) converts the change of drop volume during drop growth to the change of capacitance, through a specially designed capacitive sensor composed of the drop head and a cylindrical ring plate. Image drop analysis (IDA) makes the profile record of the growing drop directly by using CCD camera, and the collected image can be stored for edge detection and drop volume calculation by using digital image processing technology. Spectral drop analysis (SDA) is to study the liquid composition by studying the absorption spectrum of the multi-wavelength light signal passing through the liquid.

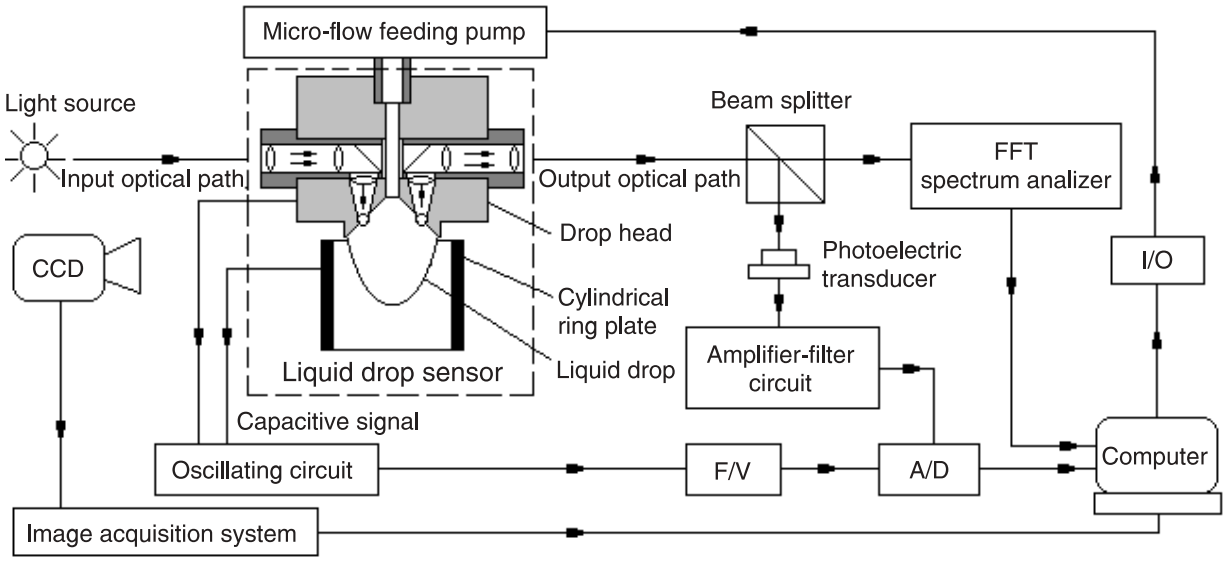

Fig. 10. Principle of fiber-capacitive-image-spectral (FCIS) drop analysis.

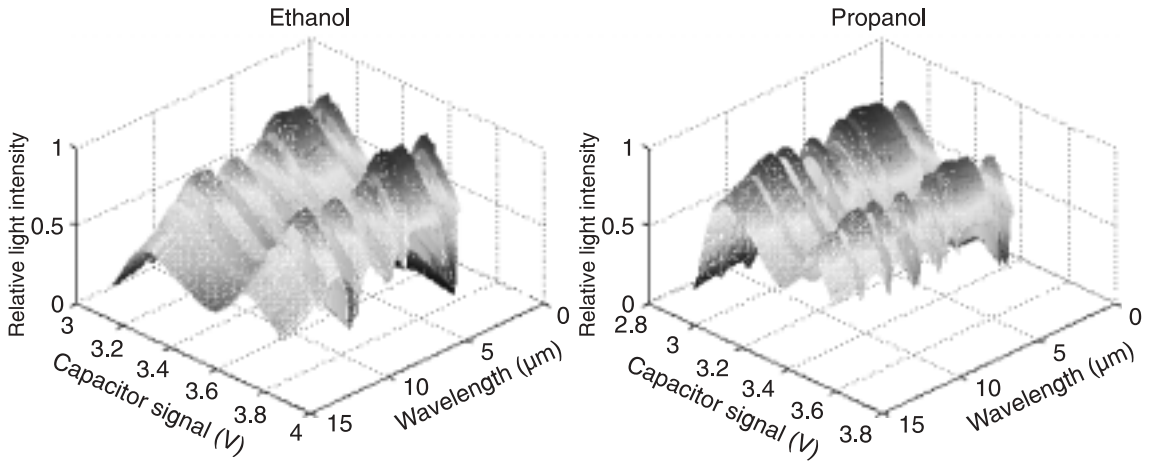

Fig. 11. 3D liquid drop fingerprints of ethanol and propanol.

By means of technology combination and signal amalgamation, the unique liquid drop fingerprint (LDF) can be obtained. Sampling tests show that different liquids have different LDFs, different brands of the same kind of liquid have different LDFs, too. Another conclusion is that the same liquid with different concentrations will also produce different LDFs. Experimental results prove that LDF is the overall database on the liquid property and it is feasible to discriminate liquids based on LDF.

Future development of the drop analysis will include calibration of the instrumentation, characterization of the liquid drop fingerprint and construction of liquids database, in order to quantitate fine discrimination and measurement of liquid properties.

Acknowledgements

The authors would like to express their sincere thanks to Dr N.D. McMillon, Dr A.T. Augousti, Dr J. Mason, Dr C.H. Wang, and Dr D.F. Zhang and some other colleagues in the Kingston University for their material assistance and technical support, because a large number of the preliminary researches and experiments were carried out in Kingston University with their enthusiastic help.

References

1. N.D. McMillan, O. Finlayson, F. Fortune, M. Fingleton, D. Dely, D. Townsend, D.D.G. McMillan, and M.J. Dalton, "The fibre drop analyser: a new multianalyser analytical instrument with applications in sugar processing and for the analysis of pure liquids", *Meas. Sci. Technol.* 3, 746–764 (1992).
2. N.D. McMillan, P. Davern, V. Lawlor, M. Baker, K. Thompson, J. Hanrahan, M. Davis, J. Harkin, M. Bree, P. Goossens, S. Smith, D. Barratt, R. Corden, D.G. E. McMillan, and D Lane, "Instrumental engineering of a polymer fibre drop analyser for both quantitative and qualitative analysis with special reference to fingerprinting liquids", *Colloid. Surf.* **A114**, 75–97 (1996).
3. C.H. Wang, A.T. Augousti, J. Mason, and N.D. McMillan, "The capacitive drop tensiometer-a novel multianalysing technique for measuring the properties of liquids", *Meas. Sci. Technol.* **10**, 19–24 (1999).
4. Z.R. Qiu, "A study on the technology of drop analysis", (doctorial dissertation), Tianjin University of China (2000).
5. Q. Song, G.X. Zhang, Z.R. Qiu, A.P. Zhang, and Q.W. Shi, "Liquid signature analyser based on fiber-capacitive drop analysis", *Instrum. Sci. Technol.* **32**, 43–59 (2004).
6. J.K. Spelt, Y. Rotenberg, D.R. Absolom, and A.W. Neumann, "Sessile-drop contact angle measurements using axisymmetric drop shape analysis", *Colloid. Surf.* **24**, 127–137 (1987).
7. P. Cheng, D. Li, L. Boruvka, Y. Rotenberg, and A.W. Neumann, "Automation of axisymmetric drop shape analysis for measurements of interfacial tensions and contact angles", *Colloid. Surf.* **43**, 151–167 (1990).
8. Q. Song, G.X. Zhang, and Z.R. Qiu, "Drop growth monitoring and drop volume measurement based on image drop analysis with CCD", *Instrum. Sci. Technol.* **31**, 1–13 (2003).
9. Q. Song, G.X. Zhang, and Z.R. Qiu, "Spectral drop analysis and 3D liquid drop fingerprint", *Instrum. Sci. Technol.* **32**, 153–165 (2004).

