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Construction of a precision capacitance sensing apparatus consisting of interdigital electrode and capacitance-to-digital converter for determination of trace water contents in organic solvents

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This paper presents a detailed description of the precision of capacitance sensing apparatus constructed using interdigital electrode(IDE) and micro-capacitive technique and application of it for determination of trace water contents in almost all organic solvents having permittivities in the range of 2-8. In order to choose appropriate IDE gap so as to achieve the high sensitivity for water detection, by changing the gap of IDE, we measured capacitance versus water content in various organic solvents with different permittivities. As a result of experiments, the IDE with 20 μm gap had the excellent linear correlation and large slope in the water content−capacitance curve of selected organic solvents. The developed precision capacitance sensing apparatus exhibits high sensitivity with a detection limit as 0.003, 0.003, 0.004, 0.004, 0.005, 0.006, 0.007, 0.009 v/v% for water in 1,4-dioxane (1,4-Diox), diethyl carbonate (DCE), diethylamine (DEA), methyl tert butyl ether (MTBE), piperidine, methyl acetate (MA), 1,2-dimethoxyethane(1,2-DME), tetrahydrofuran(THF), respectively and the linear relationships with water content within the range 0.01~0.40v/v%. The measuring results of trace water in organic solvents with permittivity below 8 using developed equipment a well consistent with those of the Karl Fischer method. Consequently, it can be employed to real-time monitor trace water during the drying process for almost all organic solvents with low permittivity conveniently.

Keywords: Capacitance-to-digital converter, Interdigital electrode, Karl Fischer titration, Organic solvents, Water content

Organic solvents play important role in scientific research and industrial manufacture. Owing to continuous expansion of applications of organic solvents, higher demands are now being placed on the analysis of trace impurity content, especially water. Water is one of the common difficult-to-remove impurities in organic solvents and in the synthetic chemistry, the water in organic solvent is fatal for the water-sensitive reagent or catalyst. Therefore, determination and control of trace water of organic solvents are crucial in laboratory and industry applications.

To date, several methods have been reported and employed to detect the trace water of organic solvents. Well-known methods for the determination of water content, the Karl Fischer titration and its modification are the methods most often used for water determination in laboratory scale[1-4]. In spite of its reliability and accuracy, Karl Fischer titration has many disadvantages. It is time-consuming, harmful to operate due to the contact with toxic reagents and incapacity for real-time measurement. Other methods which allow the determine the water in liquid and solid samples include gas chromatography[5,6], near infrared spectroscopy[6-8], refractometric method[3], microwave accelerated Dean-Stark method[9, 10], electrochemical method[11], as well as absorption and fluorescence spectroscopy[12, 13].

Above-mentioned methods yield accurate information and low detection limits, but are time-consuming and require a laboratory because of employment the analytical instruments. In addition to exact laboratory methods, rapid, cheap and real-time measurement methods without special working procedures are also required in a wide range of organic solvents entering or leaving various technical processes.

Another type of rapid cheap methods is based on the measurement of electrical properties such as conductivity and permittivity of organic solvents which change with water content[14-19]. The capacitance technique is suitable to evaluate water content in medium with relative low permittivity (2~8) because of the high relative permittivity of water ($\varepsilon_r \approx 80$).

Besides, the method based on measurement of capacitance offers several advantages, including low cost and miniature equipment, simple procedure, no requiring addition reagents, possibility of real-time measurement and good repeatability; these advantages make this method appealing for its application towards the determination of water concentration in large scale producing and drying processes of organic solvents.

Many articles for study and application of interdigital electrode (IDE) and capacitive technique have been reported[23-26]. However, in many case, this method is applied to assess the relative humidity in atmosphere[20-22] or solid such as rubber wood etc.[28]. Some papers described the results of determination of water concentration, but analyses were performed at high contents[27].

Herein, we describe the construction and development of sensitive, precision, miniature capacitance sensing apparatus which consists of IDE and capacitance-to-digital converter (CDC) using micro-capacitive technique and propose rapid, cheap, accuracy method for trace water content measurement during large scale drying and storage processes of low permittivity organic solvents, applying it to various organic solvents.

Experimental Section

Reagents and preparation of a series of standard solutions

The solvents 1,4-dioxane(2.21), diethyl carbonate(2.82), diethylamine(3.78), methyl tert butyl ether(4.5), piperidine(5.8), methyl acetate(6.68), 1,2-dimethoxyethane(7.2), tetrahydrofuran(7.58), dichloromethane(8.93), and phenol(9.3) were selected for basis experiments; the brackets contain the relative permittivities according to literatures[29,30]. All organic solvents were purified using standard methods and dried with molecular sieves Type 5A (pore size 5Å°C) as desiccants to 0.01 v/v% (100 ppm) or even lower water concentrations. Triple-distilled water produced in SZ-97A system was used in all experiments. All experiments were performed at the ambient temperature of 20°C and the relative humidity of 65%.

The solvent/water mixtures with different water fractions were prepared by slowly adding distilled water into the above dried organic solvents under ultrasound at room temperature. The water contents of a series of 16 working standard solutions increase with an interval of 0.026 v/v% from 0.01 v/v% to 0.40 v/v%. All standard solutions were protected by molecular sieves to minimize absorption of surrounding moisture.

The water content was also determined by the Karl Fischer titration method using a Mettler Toledo DL 39 system for comparison analysis.

Fabrication of IDE

Fig. 1 shows the schematic diagram of the fabricated IDE. 60 nm Cr and 400 nm Au as the electrode layers were deposited on quartz glass and a thin layer of photo resist was spun on the surface of Cr/Au layer. Then the photo resist was patterned by photolithography to form IDE structure through reactive ion etching method. Finally, the photo resist was removed to get the IDE.

The parameter that has the biggest effect on electrical properties of the IDE is gap size (d). In order to investigate the effect of the IDE gap(d) on water determination in organic solvents, seven kinds of gap(d) were designed and fabricated, namely 5, 10, 15, 20, 25, 30 and 35 μm. Here, all of the IDEs have the electrode line length (L) of 15 mm, width (w) of 100 μm and the number of electrode pairs (N) of 50 as major parameters of the IDE.

Apparatus and measurement

The variation of water content contained in organic solvents has a crucial effect on the permittivity change of system. In other words, if the micro-capacitance variation is measured highly precisely, the water content in organic solvents can be determined. From this, capacitance sensing apparatus for detection of water was designed and fabricated based on technique using IDE and CDC. The rapid development of microelectronic technology has resulted the appearance of integrated CDC[31] with precise capacitance measurement functions on a single chip and it was allowed to measure the capacitance with high precision.

In capacitance-digital conversion technique, in general, a square wave of tens to hundreds of kHz is applied to the purposed condenser and the capacitance is measured using the charge-discharge effect. We have studied to construct the capacitance sensing

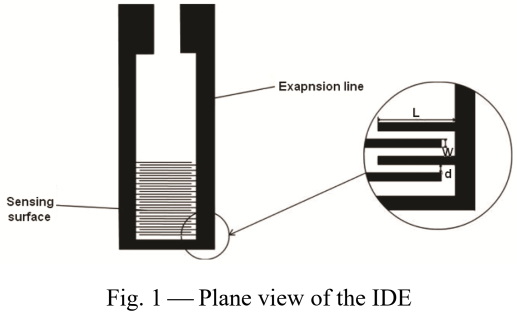

Fig. 1 — Plane view of the IDE

apparatus using this principle of micro-capacitance measurement. We used AD7746[31] provided by Analog Device Company as a CDC and 8-bits microchip of 8051 series, STC15W202 as communication and control element.

The apparatus was constructed as in Fig. 2 using the same series of STC12LE5412AD for data processing and measurement value displaying.

The reason why AD7746 was employed as a CDC was that it could reduce the error due to the capacitance between the sensing electrode and ground. Regarding the brief features of AD7746, these are full-scale capacitance range of ±4pF, accuracy of 4fF, 24-bit resolution, 21-bit effective resolution and communication with an external device through the I^{2}C serial interface.

AD7746 and STC15W202, as capacitance measurement circuits, were assembled close to the capacitive sensor so that wiring capacity and stray capacitance didn't exceed 1pF. STC12LE5412AD, as a circuit for processing and displaying functions of measurement, calibration curve and temperature compensation data, calculates water contents based on measured capacitance values and outputs it to the liquid crystal display. As shown in Fig. 2, the output terminal of the IDE was connected in series through the reference condenser 1 to the first channel of AD7746 and the reference condenser 2 with the same capacitance as condenser 1 was connected to the second channel. The capacitance values of two channels were matched by employing three condensers for precise measurement with capacitance of 12pF as reference condensers and connecting them in series so that the deviation in the capacitance values of them was not different from the capacitance variation with environmental parameters such as temperature or humidity. To reduce the error in the measurement, the capacitance of the second measurement channel (condenser 2) of AD7746 was measured by a microprocessor prior to each measurement, and the capacitance value of standard condenser 1 was estimated based on it. The series connection of three 12 pF condensers to the measurement channel of the CDC is intended to place the capacitance range of the organic solvent samples within the measurement range of AD7746. From this, electrical capacitance ranges of all the target samples was measured by compressing between 0 and 4 pF, the entire measuring band of AD7746, and the capacitances of the organic solvent samples were determined by the method of recalculating.

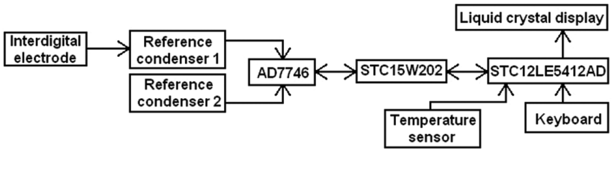

Fig. 2 — The block diagram of the apparatus.

Using the fabricated apparatus, the water contents of the organic solvents were determined as follows. First, the calibration curves were obtained between the electrical capacitance variations and water content of organic solvent series samples. Then, the calibration curve was employed to determine the water content corresponding to the small variation of electrical capacitance of unknown sample by least squares method. In the fabricated device, calibration curve and temperature compensation data are inputted by keyboard and through drawing of calibration curve and temperature compensation, water content is calculated automatically and displayed on liquid crystal screen. Care must be taken in measuring the samples to ensure that the entire electrode is fully immersed in sample solutions.

Result and Discussion

Effect of IDE gap

A series of 16 working standard solutions of 1,4-Diox, MTBE, MA were prepared using the standard procedures and the capacitance versus water content were measured using the IDEs with various gap sizes of 5 μm, 10 μm, 15 μm, 20 μm, 25 μm, 30 μm and 35 μm. Fig. 3 plots the capacitance as the function of water content, capacitance is the mean value from 3 measurements. As shown in Fig. 3 (a) and (b), the change in the capacitance against water fraction reduces along with the increase of electrode gap (15 μm~25 μm) in 1,4-Diox, MTBE and good linear relationships were obtained in working solutions containing below 0.4 v/v% H_2O. However, for the IDEs with less than 10 μm gap, the slope in the curve of capacitance versus water content reduces than former and exhibited poor level of linearity in both kinds of organic solvents.

The same tendency was observed in MA. (Fig. 3c). For the gap in the range 20 μm ~ 35 μm, decrease of capacitance and good linear coefficient along with the increment of water proportion from 0.01 v/v% to 0.4v/v%, small slope and bad linearities for gap below 15 μm were observed.

The experiments revealed that in case of small gap, sensitivity of IDE is affected by the properties of organic solvents, thus sufficient movement of solution. So, due to high sensitivity and good linearity the appropriate gap of the IDE for determination of water content was 20 µm which was used for all other experiments.

Characterization of apparatus

Measurement of errors corresponding to the temperature and humidity

We also investigated the influence of temperature on the measurement using measurements data from1,4-Diox, containing different water fraction at various temperature.(Fig. 4) The ambient temperature varied from 5 to 40 °C and all measurements were done four times in every solution. When the temperature was in the range of 5 to 30 °C, the relative standard deviations for all solutions were between 0.1 and 0.647%. So, we confirmed good precision of measurements. In other temperatures, measurement errors from the change of permittivity caused by variation of temperature were existed and the RSDs were under 1.462%.

The results at the relative humidity from 40 to 80% of above solutions indicated no changes of capacitance under 67% and only slight deviations were existed above 67%. For the relative humidity of 40~67% and 67~80%, the RSDs were within the range 0.1-0.589%, 0.5~1.283%, respectively (Fig. 5).

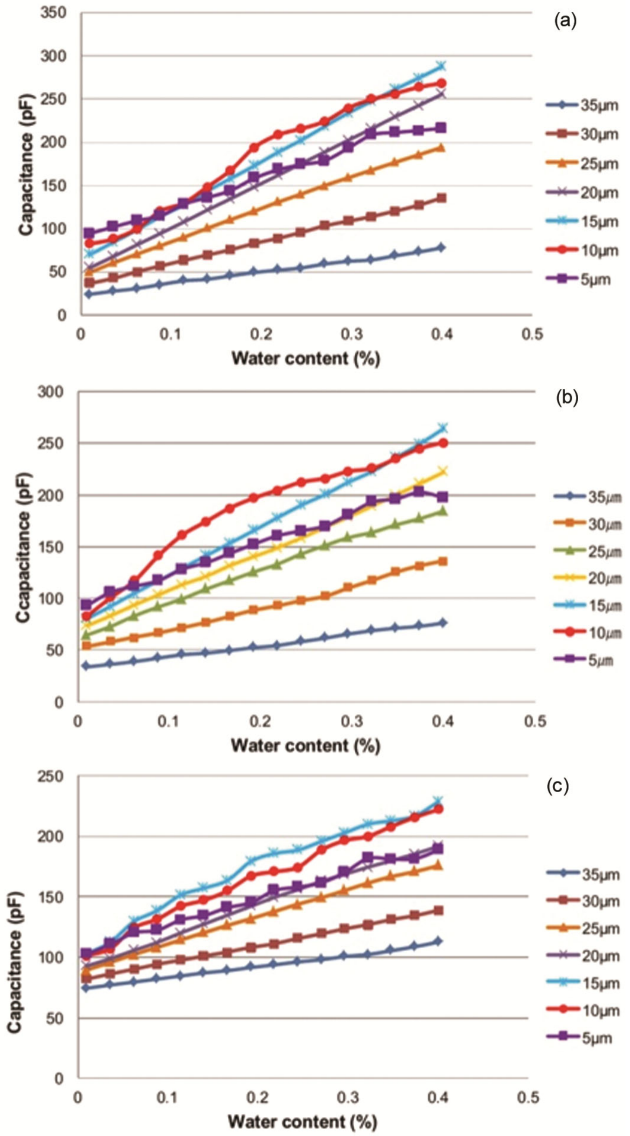

Fig. 3 — Capacitance versus water content under various IDE gaps for (a) 1,4-dioxane, (b) methyl tert butyl ether and (c) methyl acetate

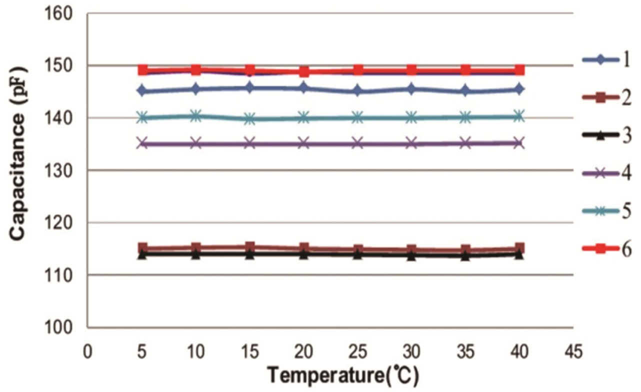

Fig. 4 — Capacitance as a function of temperature in some organic solvent samples (RH: 65%). 1: methylacetate(0.213%), 2: diethylamine carbonate (0.124 v/v%), 3: methyl tert butyl ether(0.116%),4: piperidine (0.142%), : 1,4-dioxane(0.182 v/v%), 6: dichloromethane (0.388%) The brackets contain the water contents

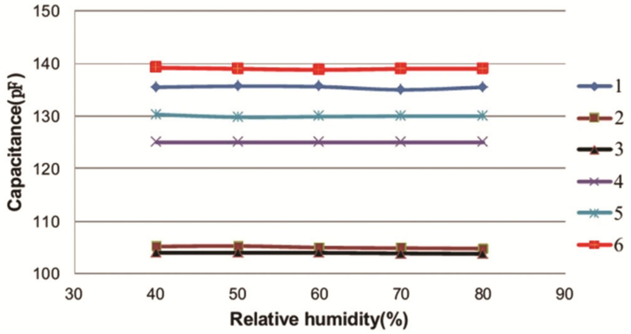

Fig. 5 — Capacitance as a function of relative humidity in some organic solvent samples (temperature 20°C). 1:methyl acetate(0.213%), 2: diethylamine carbonate(0.124v/v%), 3: methyl tertbutyl ether(0.116%), 4: piperidine(0.142%), 5: 1,4-dioxane(0.182v/v%), 6: dichloromethane(0.388%) The brackets contain the water contents

Linear range, limit of detection limit of quantitation in some organic solvents

The H_2O calibration curve (Fig. 6) was plotted using the water concentration between 0.01 v/v% and 0.4 v/v% and regression analysis was done. As shown Fig. 6(a), the correlation coefficient(R2) for 1,4-Diox(2.21), DEC(2.82), DEA(3.78), MTBE(4.5), piperidine(5.8),MA(6.68), 1,2-DME(7.2), THF(7.58) were 0.9998, 0.9996, 0.9994, 0.9992, 0.999, 0.9985, 0.9982, 0.9977, respectively, so good linearity appeared. However, Fig. 6 (b) illustrates that low sensitive and bad linearity with R2 value of 0.9814, 0.98 in dichloromethane(8.93) and phenol(9.3), respectively. The results show that the sensitive and precision of developed apparatus were high in organic solvents with permittivity less than 8.

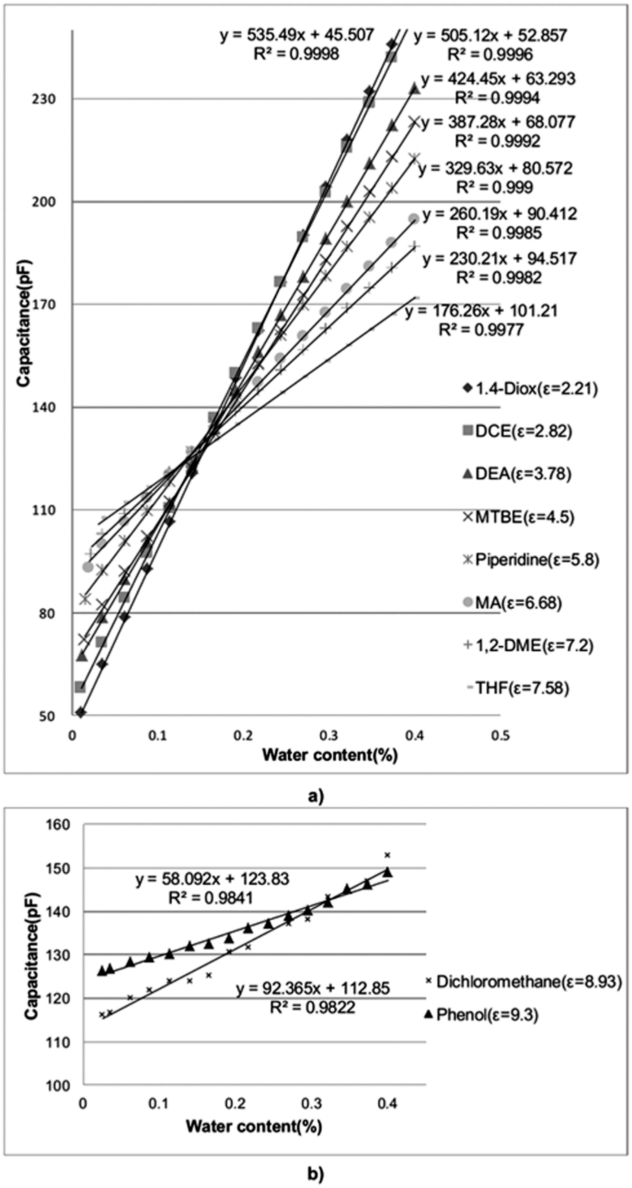

Fig. 6 — H_2O calibration curve in (a) organic solvents with ε:2-8, (b) organic solvent with ε:8-10

To determine the limit of detection (LOD) and limit of quantitation (LOQ), using dried organic solvent as blank solution for every solvent, 20 measurements were performed in parallel. The LOD and LOQ were estimated based on the following equations: LOD=3σ/a and LOQ=10σ/a (σ=standard deviation of blank solution and a=the slope of the calibration curve) The LOD and LOQ are, respectively, 0.003 and 0.01v/v% for 1,4-Diox(2.21), 0.003 and 0.01v/v% for DEC(2.82), 0.004 and 0.012v/v% for DEA(3.78), 0.004 and 0.012v/v% for MTBE(4.5), 0.005 and 0.015v/v% for piperidine(5.8), 0.006 and 0.018v/v% for MA(6.68), 0.007 and 0.021v/v% for 1,2-DME(7.2), 0.009 and 0.027v/v% for THF(7.58).

We focused on the alterations of slopes and intercepts along with the permittivity(20°C) of organic solvents. The tendency between slope and permittivities are decreased in Fig. 6(a). In contrast to, intercepts represented background are increased with the increase of permittivity. Fig. 7 and Fig. 8 depict the third polynomial functions of slopes

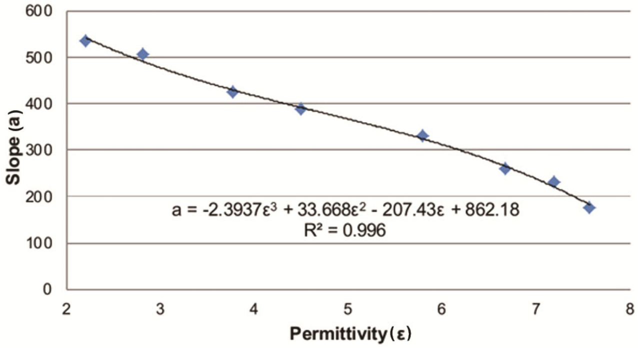

Fig. 7 — The interpolative curve of slope versus permittivity of organic solvents

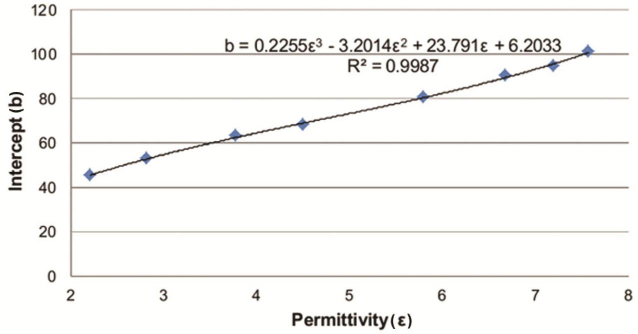

Fig. 8 — The interpolative curve of intercept versus permittivity of organic solvents

Table 1 — H_2O contents of various organic solvents, as determined by the developed IDE-CDC method and Karl Fischer method (n=6)

Organic solvents	Permittivity at 20°C	IDE-CDC		Karl Fischer	
		Mean value (v/v%)	RSD (%)	Mean value (v/v%)	RSD (%)
1,4-Diox	2.21	0.37	2.7	0.36	2.5
DEC	2.82	0.21	3.2	0.22	2.3
DEA	3.93	0.35	2.2	0.37	1.9
MTBE	4.5	0.18	3.8	0.19	4.7
Piperidine	5.8	0.37	2.2	0.37	1.5
MA	6.68	0.27	3.5	0.26	2.3
1,2-DME	7.35	0.36	2.7	0.35	1.3
THF	7.43	0.27	2.2	0.25	2.3
TEA	2.42	0.15	4.1	0.18	4.6
DPE	3.56	0.21	2.9	0.22	2.2
DEE	4.3	0.15	4.2	0.18	3.8
EGEE	5.3	0.33	2.8	0.34	2.5
EA	6.02	0.25	3.6	0.22	3.1
AN	7.24	0.14	4.7	0.16	4.8
Morpholine	7.4	0.29	2.6	0.27	2.9

and intercepts against the permittivity: $a=-2.3937\varepsilon^3+33.668\varepsilon^2-207.43\varepsilon+862.18$, $b=0.2253\varepsilon^3-3.2014\varepsilon^2+23.791\varepsilon+6.2033$.

Using above polynominal functions, the linear calibration curves of organic solvents with permittivity below 8 can be easily obtained by calculating. Proposed method can be used for the organic solvents with low permittivity containing water under 0.4 v/v%.

Water detection in real samples

The water detection in organic solvents using developed apparatus (IDE-CDC) and polynomical functions was further validated through the real samples. Karl Fischer method is widely recognized as a standard method for the determination of water content in solvents, therefore we made a comparison between the two methods for water detection in organic samples. All measurements were done at the ambient temperature 20±5°C, the relative humidity 67±10%.

The samples were collected from product and stock tanks for all selected organic solvents. Table 1 lists the concentration of the water found in these samples using IDE-CDC method and Karl Fischer method

The water contents in triethylamine(TEA), di-n-propyl ether(DPE), diethylether(DEE), ethylene glycol ethyl ether(EGEE), ethyl acetate(EA), aniline(AN), morpholine were determined by obtained calibration curve from third polynominal functions. These results indicated that yielded similar concentrations of different two methods reinforced the good accuracy of the method proposed in the present study.

Conclusion

In conclusion, a precision capacitance sensing apparatus with IDE and CDC has been constructed and applied to detection of trace water and the method which determines the water content in organic solvents readily has been suggested. Developed apparatus using microcapacitive technique is capable to detect trace water in organic solvents with linearly respond to a change of water content in organic solvents with low permittivity(2-8) over range of 0.01-0.40 v/v%. The LODs in some organic solvents such as 1,4-Diox, DEC, DEA, MTBE, Piperidine, MA, 1,2-DME, THF are 0.003, 0.003, 0.004, 0.004, 0.005, 0.006, 0.007, 0.009v/v%, respectively. According to the results of IDE-CDC and Karl Fischer for real samples herein presented, proposed method can be employed to real-time monitor trace water in the drying and storage processes for organic solvents approximately.

References

1 Dantan N, Frenzel W & Küppers S, Determination of water traces in various organic solvents using Karl Fischer method under FIA conditions, *Talanta*, 52 (2000) 101.

2 De-Aquino E V, Rohwedder J J R & Pasquini C, A monosegmented-flow Karl Fischer titrator, *Talanta*, 71 (2007) 1288.

3 Sanchez V, Baeza R, Ciappini C, Zamora M C & Chirife J, Comparison between Karl Fischer and refractometric method for determination of water content in honey, *Food Control*, 21 (2010) 339. Scholz E, Karl Fisher titration (Springer, New York), (1984).

4 Xu B Q, Rao C Q, Cui S F, Wang J, Wang J L & Liu L P, Determination of trace water contents of organic solvents by gas chromatography-mass spectrometry-selected ion monitoring, *J Chromatogr A*, 1570 (2018) 109.

5 Bampi M, Scheer A P & Castilhos F, Application of near infrared spectroscopy to predict the average droplet size and water content in biodiesel emulsions, *Fuel*, 113 (2013) 546.

6 Watanabe A, Furukawa H, Miyamoto S & Minagawa H, Non-destructive chemical analysis of water and chlorine content in cement paste using near-infrared spectroscopy, *Constr Build Mater*, 196 (2019) 95.

7 Van de Wort F R, Sedman J, Cocciardi R & Juneau S, An automated FTIR method for the routine quantitative determination of moisture in lubricants: Analternative to Karl Fischer titration, *Talanta*, 72 (2007) 289.

8 Villet S, Tomao V, Visinoni F & Chemat F, New and rapid analytical procedure for water content determination: Microwave accelerated dean–stark, *Anal Chim Acta*, 632 (2009) 203.

9 Sadjia B, Valérie T, Karine R, Amina H, Chahrazed B & Farid C, First approach on moisture determination in food products using alpha-pinene an alternative solvent for dean-stark distillation, *Food Chem*, 134 (2012) 602.

10 Gąsiorowska M, Soroka J A, Sawicka Marta J & Wróblewska E K, A new electrochemical method for trace determination in methanol, *Talanta*, 78 (2009) 49.

11 Sun H, Tang X X, Miao B X, Yang Y & Ni Z, A new AIE and TICT-active tetraphenylethene-based thiazole compound: Synthesis, structure, photophysical properties and application for water detection in organic solvents, *Sens Actuat B: Chem*, 267 (2018) 448.

12 Marta J S & Elwira K W, The application of 7H-indolo [1,2-a]quinoliniummerocyanine as a new water sensor in organic solvents, *Chem Pap*, 72 (2018) 741.

13 Ragni L, A capacitive technique to assess water content in extra virgin olive oils, *J Food Eng*, 116 (2013) 246.

14 Mortl A, Muñoz-Carpena R, Kaplan D & Li Y, Calibration of a combined dielectric probe for soil moisture and porewater salinity measurement in organic and mineral coastal wetland soils, *Geoderma*, 161 (2011) 50.

15 Nurge M A & Perusich S A, In-line capacitance sensor for real-time water absorption measurements, *Sens Actuat B: Chem*, 150 (2010) 105.

16 Huang T H, Chou J C, Sun T P & Hsiung S K, A device for skin moisture and environment humidity detection, *Sens Actuat B: Chem*, 134 (2008) 206.

17 Kizito F, Campbell C S, Campbell G S, Cobos D R, Teare B L, Carter B & Hopmans J W, Frequency, electrical conductivity and temperature analysis of a low-cost capacitance soil moisture sensor, *J Hydrol*, 352 (2008) 367.

18 Sekiguchi N, Komeda T, Funakubo H, Chabicovsky R, Nicolics J & Stangl G, Microsensor for the measurement of water content in the human skin, *Sens Actuat B: Chem*, 78 (2001) 326.

19 Zhao Y, Yang B & Liu J, Effect of interdigital electrode gap on the performance of SnO_2-modified MoS_2 capacitive humidity sensor, *Sensors & Actuat B: Chem*, 271 (2018) 256.

20 Alcantara G P, Ribeiro L E B, Alves A F, Andrade C M G & Fruett F, Humidity sensor based on zeolite for application under environmental conditions, *Micropor Mesopor Mater*, 247 (2017) 38.

21 Guo R, Tang W, Shen C & Wang X, High sensitivity and fast response grapheme oxide capacitive humidity sensor with computer-aided design, *Comput Mater Sci*, 111 (2016) 289.

22 Chetpattananondh K, Tapoanoi T, Phukpattaranont P & Jindapetch N, A self-calibration water level measurement using an aninterdigital capacitive sensor, *Sens Actuat A: Phys*, 209 (2014) 175.

23 Kitsara M, Goustouridis D, Chatzandroulis S, Chatzichristidi M, Raptis I, Ganetsos T, Igreja R & Dias C J, Single chip interdigital electrode capacitive chemical sensor arrays, *Sens Actuat B: Chem*, 127 (2007) 186.

24 Xi S, Kang Y, Qu S & Han S, Flexible supercapacitors on chips with interdigital carbon nanotube fiber electrodes, *Mater Lett*, 175 (2016) 126.

25 Igreja R & Dias C J, Extension to the analytical model of the interdigital electrodes capacitance for a multi-layered structure, *Sens Actuat A: Phys*, 172 (2011) 392.

26 Opekar F & Tŭma P, A simple impedance tester for determining the water content in organic solvents, *Sens Actuat B: Chem*, 220 (2015) 485.

27 Chetpattananondh P, Thongpull K & Chetpattananondh K, Interdigital capacitance sensing of moisture content in rubber wood, *Comput Electron Agric*, 142 (2017) 545.

28 Ian M S, Handbook of organic solvent properties, Wiley & Sons, (1996).

29 Christian R, Solvents and solvent Effects in Organic Chemistry, Third, Updated and Enlarged Edn, (2003).

30 Analog devices, 24-bit capacitance-to-digital converter with temperature sensor, AD7745/A.D7746 manual (2005), www. Analog.com