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Determination of low-level water content in ethanol by fiber-optic evanescent absorption sensor

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ABSTRACT

Evanescent field absorption spectroscopy in the infrared range of coiled fiber-optic sensor has been applied to determine the low-level water content in ethanol. Principal component regression and classical least square models have been utilized to build the calibration model and predict the water concentrations. The standard errors of predictions of water concentrations in ethanol were 3.16% and 0.42% respectively. Some methods to improve the accuracy of predicted water concentration in ethanol were suggested. The predicted concentration of water is acceptably accurate and cost-effective. The study demonstrates that the coiled fiber-optic sensor based on evanescent absorption spectroscopy is a feasible technology for prediction of the low-level water content in bio-ethanol and other industries in both on-line and remote situation.

1. Introduction

Ethanol is a popular biofuel used as an effective alternative to fossil fuel such as gasoline or diesel and has been paid much attention because of the limited quantity of fossil fuel, the pollution concern and the ever-increasing cost [1]. Current interest in ethanol used as biofuel lies in the product derived from the starch or sugar in a wide variety of crops. During the production of ethanol from corns, one basic but important step is the distillation by which the water can be removed because only the ethanol with concentration of 93% or higher is appropriate to be used as biofuel [2]. Therefore, one remote, effective, reliable and *in situ* analysis technology to determine the percentage of water in bio-ethanol is important for its usage as biofuel. Recently, encoded photometric near infrared (NIR) spectroscopy [1], dual-beam NIR spectrometers based on acousto-optic tunable [3] and Hadamard transformation [4], combined with chemometrics have been utilized for the determination of water in bio-ethanol. Ethanol also is one of the most popular organic solvents in pharmaceutical industry and needs to be purified and regenerated due to its high demand. The major impurities in the ethanol are water and methanol, so continuous on-line monitoring of water content during ethanol recycling process is very significant. However, Karl Fisher titration employed largely for the propose is slow, destructive and easily subject to human errors [5]. NIR spectroscopy applied to the analysis has been tried as a substitute for the wet analytical method [5–7].

Fiber-optic evanescent field absorption sensor is the most important, widely-acclaimed and accepted one in available today [8–10]. Comparing to the conventional counterpart, the evanescent sensor's advantages are its multiplexing capability, immunity to electromagnetic interference, high sensitivity and remote on-line measurement. Fiber-optic evanescent sensor has been successfully used in chemical sensing in which the study of absorption spectra of gases and fluid samples were performed [8,11,12]. Those sensors have important applications in detection of atmospheric hazards [13], contaminated soil and drainage water contaminated by organic solvents [14]. To increase sensitivity of sensors, the use of selective ray launching in fiber [8], tapering the sensing region [15], bending fiber in U-shape [16,17], flexible tubular waveguide sensor [18] and coiled fiber sensors [19] have been suggested. Compared with other sensors, the advantages of a coiled fiber sensor are its simple-design, compactness and sturdiness, and high sensitivity. It has been demonstrated experimentally that the coiling results in conversion from low order modes to high order modes [19] and there will be an improvement in sensitivity due to having long sensing region and farther penetration length of high order modes. Therefore, Fiber-optic evanescent absorption coiled sensor has been demonstrated to be more practical in industrial applications [13,20].

The miniaturized near-infrared spectrometer has been utilized to determinate water content in ethanol [5]. Infrared fiber evanescent-wave spectroscopy spectra of water–ethanol mixtures have been recorded and calculated based on a causal dispersion analysis

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technique [21]. Photonic crystal fiber based on evanescent-wave sensor has also been used to detect the biomolecules in aqueous solution positioned in the air holes of microstructured part of a photonic crystal fiber [22]. A long-period fiber grating based transducers in the analysis of ethanol fuel has investigated by measuring the concentration of ethanol in ethanol–water mixtures and the resolution up to 0.23% can be obtained [23]. However, the use of fiber-optic evanescent absorption sensors to predict the water content in ethanol has not been reported up to date. Compared with the technologies which used to investigate the ethanol–water mixtures reported in previous publications [5,21–23], the technology based on fiber-optic evanescent absorption sensors is more simple-designed, compact and sturdy. In this paper, evanescent field spectra of a coiled fiber-optic sensor in ethanol with different concentration (0.5–10% water content) have been recorded and quantitative analysis was performed by using principal component regression (PCR) and classical least square methods. Overall results demonstrate that fiber-optic evanescent field absorption sensor combined with classical least square method can predict relative exactly water content in ethanol.

2. Theoretical fundamentals

The theory of internal reflection and evanescent field absorption has been described in detail [24], and a brief description will be discussed in this paper. When a beam of light propagates along an optical fiber, the electromagnetic field does not fall abruptly to zero at the core/cladding interface. Instead, the light transmitted in optical fiber by total reflection at the interface causes a standing wave whose evanescent field penetrates in the fiber cladding over some distance. The intensity of evanescent field $E(x)$ decays exponentially with the distance x perpendicular to the interface by following equation:

$$E(x) = E_0 \exp\left(-\frac{x}{d_p}\right) \tag{1}$$

in which E_0 is the intensity of the incident radiation, the depth of penetration d_p of the evanescent field is related to the angle of incident θ, refractive indexes of core n_1 and cladding n_2 and the wavelength λ as follow [16]:

$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2\theta - n_2^2}}. \tag{2}$$

When the analyte exists in the cladding or surrounding medium of the core, the analyte can absorb energy from the fraction of the light in the evanescent field at its absorbing wavelength. Therefore, the transmitted intensity loss in a fiber-optic evanescent field can be described by using a Beer–Lamber's law relationship

$$I_1 = I_0 \exp(-\alpha l) \tag{3}$$

in which l is the length of fiber in an absorbing medium, I_1 is the transmitted intensity in the presence of an analyte and I_0 is the incident intensity. In our experiment, each spectrum was referenced to the background spectrum of a coiled fiber in-air, so I_0 is the transmitted intensity of the coiled fiber in-air. The bulk absorption coefficient α is given by

$$\alpha = \frac{c\varepsilon}{\log_{10} e} \tag{4}$$

in which ε is the molar absorptivity and c is the molar concentration. So, the absorbance signal A obtained from an evanescent field measurement at absorbing wavelength can be approximated by the following equation:

$$A = \lg\frac{I_0}{I_1} = cl\varepsilon. \tag{5}$$

The absorbance A is linearly dependent on the fiber length and analyte concentration. However, it has been pointed out this law overestimates fiber absorbance, especially, at higher analyte concentration, the absorbance displays non-linear dependent on the concentration. More accurate description taken into the varying amounts of evanescent absorption suffered by different modes at higher concentration has been developed [25]. For our samples, the maximum analyte concentration is about 10% and Eq. (5) is accurate enough for the analysis of water concentration though a multi-mode fiber was used in our experiment.

3. Experiment

The layout for the evanescent field absorption spectra measurement was shown schematically in Fig. 1. A infrared source (silicon carbide source, Newport Co.) was chopped at 150 Hz, collimated with a planoconvex lens, then focused into a monochromator (Oriel Co., Model 77250) by using a biconvex lens of focal length 2.45 cm. The light from the output slit of the monochromator was 1:1 focused ($d_i = d_o = 2f$) with a one-inch focal length biconvex lens. Before focusing the light into the fiber, a sapphire ball lens (focal length 3.6 mm) was used to couple more high-order-mode signals into the fiber. The input and output ends of the fiber were mounted on a 3D transition stage to maximize the light coupled into and from the fiber. A cryogenically-cooled InSb detector (Infrared Associates Inc. Model Is1.0) was used to detect the signals from the fiber. Another sapphire ball lens was used at the output end of fiber to increase to the light detected by the InSb detector. The InSb detector was connected to a pre-amplifier, then a lock-in amplifier (Stanford Research, Model 510). A PC which was connected the lock-in amplifier via a serial port was used to collect and analyze the data by using a home-made program that sampled the output voltage of the lock-in amplifier at approximate 5 Hz frequency. The wavelength of the monochromator was calibrated using a standard calibration curve.

Sapphire is known for its chemical resistance, high transmittance in the infrared region and high melting point making it an ideal material for chemical sensing in extreme environments. The sapphire fibers using in our experiment were grown using the laser heated pedestal growth (LHPG) method (obtained from the Micromaterials Incorporation, USA). The LHPG method prohibits an effective way of applying a cladding layer on sapphire fiber, this

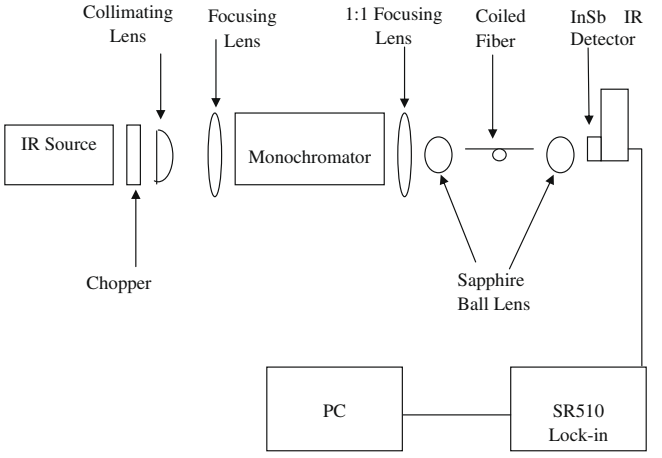

Fig. 1. Schematic block diagram of experimental set-up for measurement of evanescent field absorption spectrum.