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Ultrasonic characterization of aqueous mixture comprising insoluble and soluble substances with temperature compensation

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ABSTRACT

This paper presents an ultrasonic technique for simultaneously determining the concentrations of insoluble and soluble substances in aqueous mixtures at different temperatures. First of all, the phase velocity spectra and the attenuation spectra of aqueous mixtures which are sensitive to the concentrations of substances are analyzed. Then, a synergy interval partial least squares (Si-PLS) model is applied to build the sub-models for the concentrations of substances at different temperature points. Finally, the overall model is constructed to build the relations among the sub-models by linear interpolation, in which the temperature effects are taken into account. The experimental and analytical results show that the overall model has the potential to simultaneously determine the concentrations of substances in aqueous mixtures at different temperatures. The proposed technique is time-saving in analyzing online signals, and thus will find wide applications in laboratory and industry for investigating aqueous mixtures and monitoring online processes.

1. Introduction

In food, chemical and pharmaceutical industries, aqueous mixtures comprising insoluble and soluble substances have been widely used in such processes as mixing, suspension, crystallization, etc. It is of great industrial interest to develop a rapid and reliable analytical method for quantifying the concentrations of substances in aqueous mixtures [1]. To this end, many techniques have been proposed. Conventional methods, e.g., manual timed sampling and titration analysis, are time-consuming and difficult to be implemented online [2]. Optical and electrical techniques require the presence of specific properties of media, like transparency or electrical conductivity [3]. In comparison with the aforementioned techniques, the ultrasonic technique is quite applicable to the optically opaque, conductive and non-conductive, highly-concentrated dispersed systems [4].

Since the ultrasonic spectra are affected by the concentrations of insoluble and soluble substances in aqueous mixtures, the ultrasonic technique has been widely used for the measurement of substance concentrations [5–8]. Krause et al. [5] combined the multivariate regression method and the ultrasonic spectra to simultaneously detect the concentrations of sugar and ethanol in aqueous solutions. Rodriguez-Molares et al. [6] proposed an empirical model based on ultrasonic attenuation, temperature, and frequency to estimate the biomass concentration of a biological suspension. Zhan et al. [7] developed an ultrasonic measurement system based on least squares support vector machines and ultrasonic spectrum for online measurement of particle concentrations in multi-component suspensions. These studies suggest that the ultrasonic technique can be successfully applied to analyze the concentrations of substances in some solutions or suspensions, but the measurement of the concentrations of substances in aqueous mixtures comprising insoluble and soluble substances using the ultrasonic technique has been scarcely reported. Geier et al. [8] combined the measurements of ultrasonic velocity and attenuation coefficient to simultaneously determine the concentrations of yeast (insoluble substance) and maltose (soluble substance). Goodenough et al. [2] measured the concentration of particulate matter in a fluctuating high-temperature liquid system which included soluble substance through the attenuation coefficient. In their studies, the attenuation coefficient was proportional to the concentration of insoluble particles, but independent to that of soluble substance because the concentration of soluble substance was small. However, the concentrations of soluble substances in many mixtures are high so that the attenuation cannot be ignored, and those methods will result in the measurement inaccuracy.

The use of ultrasonic technique may be limited by the complexity of mixtures, which may give rise to unmanageable or inaccurate physical models for describing the relation between ultrasonic features and substance concentrations [9]. Being fast and easy to perform, the

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multivariate methods are alternatives to traditional ones and used to correlate target variables (***Y***) with descriptor variables (***X***) [10]. The partial least squares (PLS) model is capable of modeling the complex system in high-dimensional feature spaces and with fewer training data [11]. Although the entire PLS modeling process including sample preparation, signal processing, feature extraction, parameter optimization and model evaluation is time-consuming, the analysis can be completed in a short time once the PLS model is established [12]. Therefore, the PLS model is a promising technique for online measurement of the concentrations of substances in aqueous mixtures.

The full spectrum often contains hundreds or thousands of variables, but some variables may contain useless or irrelevant information like noise and background [13]. Thus, the selection of specific spectral interval is of great importance to simplify model, reduce the computational efforts and improve the accuracy and robustness of model [14].

In industrial processes, it is crucial to take the temperature effects into consideration. Temperature affects the physical parameters of substances and further the ultrasonic signals. Some researchers [15,16] have detected the concentrations of ternary mixtures at constant temperature. The accurate temperature control is needed to get a good estimation of concentration. Krause et al. [17] combined the sub-models for different temperature points by linear approximation of each coefficient over temperature to build a unified model which was used to detect the concentrations of substances in ternary solutions at different temperatures. However, the method required the sub-models to have the same framework about regression coefficients and predictor variables. Huang et al. [18] designed an ultrasonic device to measure solid suspension concentrations at different temperatures using the linear functions of attenuation and temperature for concentration, but this method was suitable for the binary mixture only.

This paper is aimed to establish a reliable method for simultaneous measurement of the concentrations of insoluble and soluble substances in aqueous mixture at different temperatures. Titanium dioxide (TiO_2) and glucose are taken as insoluble and soluble substances in the experiments respectively. At first, the phase velocity spectra and the attenuation spectra of aqueous mixtures are analyzed. Then, the sub-models for predicting the concentrations of substances at different temperature points are built. Finally, the overall model is built to establish the relations among sub-models by linear interpolation, and the temperature effects are taken into consideration. The proposed method is less time-consuming in analyzing online signals and thus will find wide applications in laboratory and industry for investigating aqueous mixture and monitoring online processes.

2. Materials and methods

2.1. Sample preparation

The samples are aqueous mixtures composed of pure water, TiO_2 (as the insoluble substance) and glucose (as the soluble substance). The substance concentration refers to the fraction of the mass of one substance to that of the mixture. The samples are prepared as shown in Fig. 1.

At every temperature point, TiO_2 is prepared in 8 groups from 0 g to 210 g, with an interval of 30 g, and glucose is prepared in 13 groups from 0 g to 180 g, with an interval of 15 g, respectively. 600 g pure water is added into the possible combinations of TiO_2 and glucose to obtain 104 samples (including the sample of pure water). These samples make up the calibration subset which is used to build the calibration model. The temperature points for calibration are selected in the range from 16 to 40 °C and with an interval of 2 °C.

Similarly, at every temperature point, TiO_2 is prepared in 5 groups from 0 g to 210 g, with an interval of 27 g between the first and second groups and 54 g from the second to fifth groups, and glucose is prepared in 7 groups from 0 g to 180 g, with an interval of 28 g,

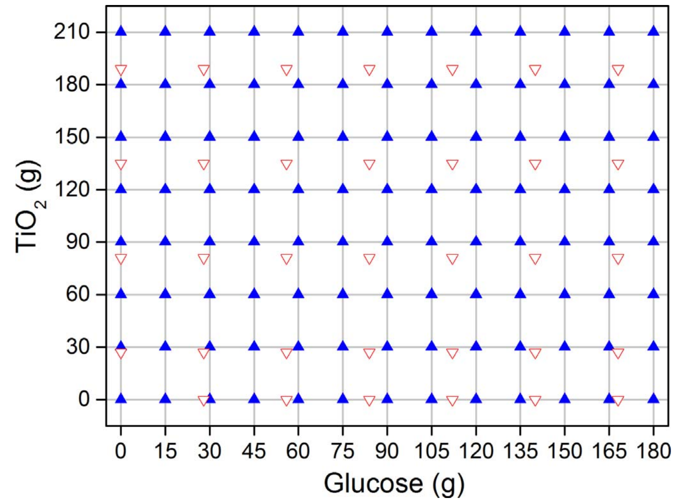

Fig. 1. The distributions of samples at each temperature point. (The solid up triangles represent the calibration subset, and the hollow down triangles stand for the prediction subset.).

respectively. 600 g pure water is added into the possible combinations of TiO_2 and glucose to obtain 35 samples. These samples (the sample of pure water is excluded) constitute the prediction subset which is used to evaluate the model performance only. The temperature points for prediction are selected in the range from 16 to 40 °C and with an interval of 1 °C.

2.2. Experimental setup

The measurement cell as well as the measuring principles are explained schematically in Fig. 2 The wave is transmitted into the samples by an ultrasonic sensor (Olympus V306-SU, with the center frequency of 2.25 MHz), which is excited via an ultrasonic pulser/receiver (Olympus Models 5072 PR) at 100 Hz. The ultrasonic sensor has direct contact with the samples in order to reduce the arbitrary influences of coupling agent and so on, enhance the signal strength of reflected echoes and improve the stability and repeatability of system. The incident wave which traverses the samples is reverberated from the front face of reflector. The reflected echoes are received by the same ultrasonic sensor (pulse-echo method) and detected with an oscilloscope (Tektronix DPO7254) at the sampling rate of 500 MHz.

The samples and the measurement cell are contained in a transparent flat-bottomed cylindrical tank, while the tank is immersed in a circulating thermostatic water bath to control the sample temperature with the accuracy of ± 0.1 °C. The temperatures of the samples are measured by Pt 100 temperature sensors. To ensure the homogeneity of samples, the samples are constantly stirred with a four-bladed pitched blade turbine impeller.

The experiments are carried out for each sample at all temperature

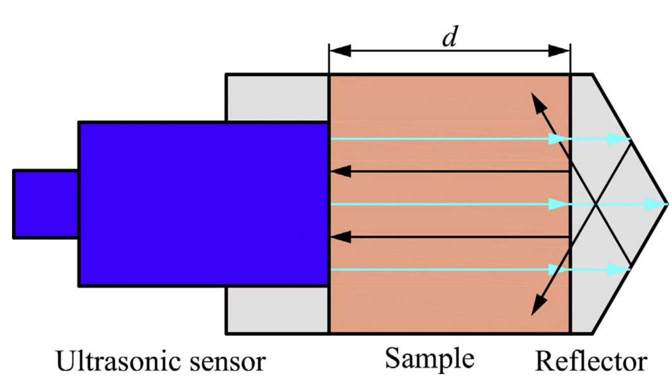

Fig. 2. The measurement cell.