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RECENT ADVANCES IN IR SPECTROMETRY TECHNIQUES FOR COMPREHENSIVE CHEMICAL ANALYSIS

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ABSTRACT

The field of chemical engineering relies on advanced analytical techniques to ensure precision and efficiency, with Infrared Spectrometry (IR) emerging as a key tool. In particular, Near-Infrared (NIR) spectroscopy has gained prominence in bioprocess monitoring due to its real-time measurement capabilities for a range of analytes, essential for automatic control, process optimization, and quality assessment. Recent advances in IR spectrometry, particularly Fourier Transform Infrared (FTIR) spectrometry, offer multiplex advantages, high signal-to-noise ratios, precise wavenumber measurements, and data manipulation ease. FTIR spectrometry finds applications in characterizing coals, catalysts, and catalytic reactions. Various experimental methods offer essential insights into heterogeneous catalyst studies, with the choice of probe molecules influencing outcomes significantly. In conclusion, the integration of advanced analytical techniques, such as NIR and FTIR spectroscopy, along with machine learning, has transformed chemical engineering and catalytic research. These methodologies enable precise monitoring, characterization, and optimization, driving advancements in diverse industrial applications and environmental analysis.

Keywords: Chemical Analysis, Infrared Spectrometry, Near-Infrared (NIR) spectroscopy, Fourier transform infrared spectroscopy.

INTRODUCTION

The application of cutting-edge analytical techniques has never been more essential than in the dynamic field of chemical engineering, where precision and efficiency are important. Infrared Spectrometry is one such method that has gained prominence in chemical engineering (IR). The capacity of IR spectrometry to decipher molecular complexity, observe chemical reactions in real-time, and improve industrial operations has made it an essential tool in this constantly changing sector. Over the past decade, a great number of studies have explored the potential of near-infrared (NIR) spectroscopy for monitoring of bioprocesses, where it may provide real-time measurements of a range of different analytes [1,2]. Such measurements can be useful in the frame of several applications, for example within automatic control, process optimization, or on-line quality assessment. However, the successful implementation of NIR spectroscopy for monitoring of bioprocesses is still not routine because the bioprocess poses several challenges. An excellent review on NIR monitoring applied to bioprocesses was elaborated by Scarff et al. In this review, the evolution of NIR monitoring technology is presented based on the type of fermentation process that is run. Here an alternative application-oriented view will be given, focusing on the different practical aspects concerning the implementation of NIR for bioprocess monitoring, with particular emphasis on the on-line configuration. First, a short introduction to the fundamental principles of NIR spectroscopy will be given. Next, the practical aspects when NIR monitoring is applied to fermentation processes [3,4].

Measurement principles

IR spectroscopy is a spectroscopic method using the NIR region of the electromagnetic spectrum (from about 800 nm to 2500 nm). NIR spectroscopy focuses on vibrational energy changes of matter caused by rhythmic variations in the dipole moment of molecules. Vibrational energy changes are related to frequencies of the electromagnetic spectrum lying within the mid-infrared (mid-IR) region between 2500 and 15000 nm [4]. When molecules are irradiated, they can absorb photons that have an amount of energy coincident with the characteristic vibrations of the molecule; absorption then results in the excitation of the molecule to a higher energy level. Although fundamental absorption occurs within the mid-IR region of the spectrum, overtones and combination bands of fundamental absorptions manifest within the NIR region. Photons with twice or three times the amount of energy necessary to elevate a molecule to the energy level corresponding to a fundamental absorption will cause excitation to the second or third energy levels, thereby creating a first and second overtone[5]. However, few molecules manifest overtones, and the higher the overtone, the lower its probability of occurring. Therefore, the first overtone band is generally much weaker in intensity than the fundamental absorption, and the second and higher bands are even weaker. First and second overtones occur at approximately one half and one third of the wavelength of the fundamental absorption, i.e, in the NIR region of the electromagnetic spectrum. Combination bands occur when the absorbed photon excites two or more vibrations simultaneously [6]. For this to happen, the energy of the photon has to equal the sum of the energies of the coupling vibrations[7,8].

Recent Advances in IR Spectrometry

Interferometric infrared spectra measurements have a number of benefits. The first is the multiplex advantage (also known as the Follett advantage), which results from the fact that radiation of all wavelengths strikes the detector concurrently throughout the measurement. All other factors being equal, the Follett advantage allows spectra of the same signal-to noise ratio (SNR) to be measured M times faster on a Fourier spectrometer than on a monochromator, where M is the number of resolution elements in the spectrum [9].

The SNR of spectra measured using a Fourier spectrometer is V times larger for equivalent measurement times. The second benefit is the optical throughput (or Jacquinot) advantage, which states that an interferometer outperforms a monochromator in terms of throughput for spectra obtained at the same resolution when the solid angle and area of the beam at each focus are combined. Interferograms need to be digitized in order to be converted into spectra [10].

The sinusoidal interferogram from a helium neon laser beam that is sent through a separate area of the interferometer's beam splitter is used to sample the optical path difference at equal intervals in virtually all contemporary Fourier transform infrared (FTIR) spectrometers[11]. The laser interferogram's infrared interferogram is normally digitalized once per wavelength (typically at a zero-crossing). The third key benefit of FTIR spectrometry is its extraordinarily high wave number precision, which is a result of this sampling technique[12].

A fourth advantage of FTIR spectra is their simplicity of computer manipulation, which is made possible in part by their high SNR and precise wave number measurements. Numerous FTIR spectrometry applications that will be discussed in this article result from data manipulation techniques just as much as from the high SNR of the spectra themselves.

The organic matter in coal is a heterogeneous collection of elements with different physical and chemical characteristics, some of which are inherited from the organic precursors and others of which are acquired during subsequent diagenesis. The features of the microscopic organic minerals that make up coal are crucial in determining its technological utility, potential for producing petroleum, and a variety of other attributes.

Fourier transform infrared (FT-i.r.) spectroscopy is one of the most widely used and effective methods for characterizing coals and coal products. The majority of FT-i.r. methods used with coal, like the global KBr' or diffuse reflectance methods [13].

For quick NIR determination, machine learning algorithms construct mathematical models based on fidelity to the measured data. Common machine learning techniques for NIR analysis include neural networks, logistic regression, and support vector machines (SVM). Making predictions and learning about undiscovered spectral features are the main goals of machine learning paired with spectral data mining. An effective technique for fine-tuning kernel mapping functions is least squares SVM (LSSVM). A type of kernel function is used to translate the original data onto a high-dimensional space in the basic principle of LSSVM. This process is followed by linear regression between the dependent variable and high-dimensional data[14].

The LSSVM has a global optimum and is accurate when dealing with nonstationary and nonlinear data. The choice of the kernel and the application of its parameters determine the distribution of feature samples in high-dimensional space. Resistance to collinear effects, which are intrinsically present between spectral data at various wavelengths, can be determined using the right kernel function [15].

The purpose of this work was to evaluate the use of various kernel functions integrated in LSSVM models as the best machine learning type calibrations when employing NIR technology for the quantitative estimation of the COD in polluted water samples. The Beer- Lambert law, which describes the NIR spectrum as a linear response to a pure chemical component, was used to build the calibration models in the NIR analytical sector. The regression module is written as follows:

$$\mathbf{y = W^t x + b + \varepsilon;}$$

where $y = yi \mid I = 1, 2,... n$ represents the target component concentration for n samples and $x = xi \mid I = 1, 2,... n$ represents the NIR spectral data. The i-th sample's p-dimension vector is called xi. Wt and b are the vectors of the regression coefficients, and is the vector of the regression error[14,15].

Recent IR applications in catalytic research and in situ IR cell reactors

Because IR spectroscopy is a method frequently used to characterise catalysts, there are many compilations and reviews of the many experimental methods. Among the most popular methods are transmission-absorption, diffuse reflectance, ATR, specular reflectance, and photoacoustic spectroscopy. The principal information obtained with all these techniques is equivalent, and local availability and experimental necessities, such as the sample particle size and the molecular extinction coefficient of the sample, may dominate personal choices. The vast majority of experiments are currently performed in the transmission–absorption and the diffuse reflectance mode. IR plays an important role in characterization of heterogeneous catalysts, and that is the reason that a large number of publications (including this one) deal with that subject [16].

This comprises surface modifications brought on by temperature treatment, catalyst precursors, spectrum properties of reaction components, and many more. The selection of the proper probe molecule is crucial since it will affect the features of the probed solid that are determined and, consequently, the structure-activity connection that is established. Applications of various probe molecules, including both the most popular and less commonly employed compounds, have been reported in the scientific literature over the past five years [17].

The following materials are mentioned in the literature quotations as examples of applications in catalytic research: ammonia, carbon monoxide, carbon dioxide, nitrogen oxide, methanol, ethanol, cyclohexanol, dibenzenes, chloroform, heavy water (D2O), dimethylether, benzaldehyde, ethene, propene, butenes, nitrogen, and 2,4,6-tri-tert-butylpyridine [18,19,20,21,22,23,24].

Ammonia adsorption has been researched to characterise the selective poisoning of acid sites on sulphated zirconia. According to IR spectroscopic investigations, the Brnsted and potentially Lewis's acid centers make up the strong acid sites, whilst the Brnsted acid sites make up the majority of the intermediate-strength acid sites. Despite not completely ruling out the possibility of the stronger acid sites playing a role, the results of selectively poisoning the sulphated zirconia with ammonia show that Brnsted acid sites of intermediate strength are active for n-butane isomerization at 423 K [25,26].

have looked into the surface characteristics of high surface area ceria samples, both reduced and unreduced. They used the adsorption of pyridine, pyrrole, acetonitrile, CO2, CO, and dimethyl ether as the probe molecules for this purpose. IR investigations on the adsorption of carbon monoxide on Cu/SiO2 and Cu/SiO2-TiO2, Ni/SiO2, the nickel-magnesia catalyst used to convert methane into CO2, Au/TiO2, and Pt-Au particle catalysts have examined the acidity of sulphated zirconia by CO and ammonia adsorption. The acidity of zeolite was measured using nitrogen and carbon monoxide [27,28].

CONCLUSION

In the ever-evolving field of chemical engineering, the application of advanced analytical techniques is paramount to ensuring precision and efficiency. Among these techniques, Infrared Spectrometry (IR) stands out as a valuable tool with the capacity to decode molecular complexity, monitor chemical reactions in real-time, and enhance industrial operations. Particularly, the utilization of Near-Infrared (NIR) spectroscopy has gained significant attention in bioprocess monitoring, offering real-time measurement capabilities for various analytes. These measurements find applications in automatic control, process optimization, and online quality assessment. Despite its potential, implementing NIR spectroscopy in bioprocess monitoring remains challenging due to the unique complexities of bioprocesses. While numerous studies have explored this domain, this article takes an application-oriented approach, emphasizing practical aspects, especially the online configuration. NIR spectroscopy operates in the near-infrared region of the electromagnetic spectrum, leveraging vibrational energy changes in molecules. These changes occur due to variations in dipole moments, resulting in overtones and combination bands within the NIR range. However, overtones are weaker than fundamental absorptions, and their occurrence depends on molecule-specific factors. Recent advances in IR spectrometry, particularly Fourier Transform Infrared (FTIR) spectrometry, offer several advantages, including multiplex advantages, high signal-to-noise ratios, precise wavenumber measurements, and ease of data manipulation. FTIR spectrometry's applicability extends to characterizing coals, catalysts, and catalytic reactions.

This work specifically focuses on the application of various kernel functions within LSSVM models for quantitative estimation of Chemical Oxygen Demand (COD) in polluted water samples using NIR technology. The Beer-Lambert law guides the calibration models, demonstrating the versatility of NIR spectroscopy.

In addition to bioprocess monitoring, IR spectroscopy finds extensive use in catalytic research, offering insights into catalyst characterization and surface modifications. Various experimental methods such as transmission-absorption, diffuse reflectance, ATR, and more provide essential information for heterogeneous catalyst studies. The choice of probe molecules significantly influences the outcomes of these studies.

In conclusion, the integration of cutting-edge analytical techniques like NIR and FTIR spectroscopy, combined with machine learning, has revolutionized chemical engineering and catalytic research. These methods enable precise monitoring, characterization, and optimization, contributing to advancements in various industrial applications and environmental analysis.

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