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Application of Infrared Raman Spectroscopy in Analysis of Food Agricultural Products

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As a kind of detection technology based on optical characteristics, spectral detection technology overcomes the defects of traditional detection technology. The common spectrum detection techniques include hyperspectral imaging, Raman spectroscopy and infrared spectroscopy. As a new detection technology, the detection efficiency is high and the time is short. It is easy to realize automation and is suitable for on-line detection of mass production. In the process of yeast culture, the content of glycerol and methanol were monitored in real time. The results show that the application of infrared spectrum detection technology and ATR probe can realize off-line and on-line monitoring of glycerol and methanol. The correlation coefficients of infrared prediction model were 98.65% and 98.09%, respectively. The results showed that it costed 40 hours from the culture stage to the beginning of the addition of glycerol. The time required for methanol consumption was 6 hours. The experimental results proved the possibility of the application of infrared detection technology in the industrial on-line monitoring.

1. Introduction

Poor food intake seriously affects human health. High quality food intake can strengthen people's physique to a certain extent. It plays a good role in promoting the development of human beings, and is beneficial to future generations (Depciuch et al., 2016). In recent years, consumers are increasingly concerned about the food safety issues with the improvement of living standards. Poor food problem at home and abroad caused health problems, such as New Zealand's toxic milk powder, melamine milk powder case in Gansu, Nestle milk powder iodine exceeded, trench oil incident, East Asia's lean meat (Kadik et al., 2015). This harmful food is a serious threat to human health. In order to gain benefits, some unscrupulous traders use additives through illegal means. This will not only undermine the fairness of the market, more importantly, it will lead to disease and endanger human health. Globally, most countries are plagued by food safety issues, and nearly 1/3 of the world's people suffer from a variety of diseases due to food safety issues (Yu et al., 2015). In recent years, food safety has gradually been mentioned on the agenda with the illegal production of food into the consumer market (Zając et al., 2017; Mariani et al., 2017; Bong et al., 2017; Hoo et al., 2017; Salim and Padfield, 2017). It is not only a reflection of the quality of life, but also an important indicator of the state system and the legal system.

As a developing country with a population of 1/4 worldwide, China's food safety issues should not be underestimated. At the same time, as a large agricultural country, China also has a large number of export products. Good food quality can not only improve the integrity of our country in the international arena and establish a good international image, but also can built a responsible performance of human health. Especially in recent years, "tainted milk powder" incident has seriously affected the credibility of the quality of food exports abroad. Therefore, it has become the basis of China's food industry to stop the problem of food into the market (Chowdhry et al., 2015).

In view of the above problems of food safety, it becomes particularly important to ensure the quality of food from the source, production, transportation, storage and consumption of food raw materials. In each of the above links, good detection technology provides an important basis for food quality assurance. The development of all kinds of analysis, detection technology and instrument provides a strong guarantee for the healthy development of the food industry. Compared with the traditional analysis method, the spectral

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detection technology has been favoured by researchers as a non-contact detection method (Bunaciu et al., 2015). Spectral analysis can provide information on the chemical structure of the sample, the concentration of the material and the interaction between the molecules. Therefore, it has been widely used in the fields of food safety monitoring, pharmaceutical industry, chemical industry, material and environment.

2. The spectrum detection technology

2.1 Raman spectroscopy

Raman scattering spectra and infrared spectra have similar spectral regions, but the mechanism is different. The generation of infrared spectrum is caused by the change of the dipole moment of the molecule and the absorption of the material. However, Raman scattering is concerned with the change of molecular vibrational polarizability (Fischer et al., 2016). The two spectra belong to the molecular vibrational spectrum, and it can obtain the sample information from the interaction between the incident light and the sample molecules. India physicist Raman first discovered the Raman scattering effect in 1928. When the energy of the incident light is absorbed by the molecule, the frequency of light is different from the frequency of the scattered light, which is called as Raman scattering effect. For the same material, the molecular vibrational - rotational energy level is certain, and then the Raman frequency shift does not change. Raman scattering effect is the basis and theoretical support of Raman spectroscopy.

If the frequency of incident light is υ, then the scattering light is $\acute{\upsilon}$. We can obtain the Eq $h\upsilon-h\acute{\upsilon}=h\Delta\upsilon$. The change of the $\Delta\upsilon$ frequency is equal to the difference between the rotational and vibrational energy of the sample, which is called Raman scattering. If the sample molecules are in the ground state, when the energy of the radiation is absorbed, the molecule is excited from the ground state to an excited state. In this state, the frequency of the scattered light is less than the frequency of the incident light, and the Raman scattering light is called the Stokes line. As shown in figure 1, if the sample molecules are in an excited state, when the molecules collide with the incident photons, the molecules will transit from the excited state to the ground state.

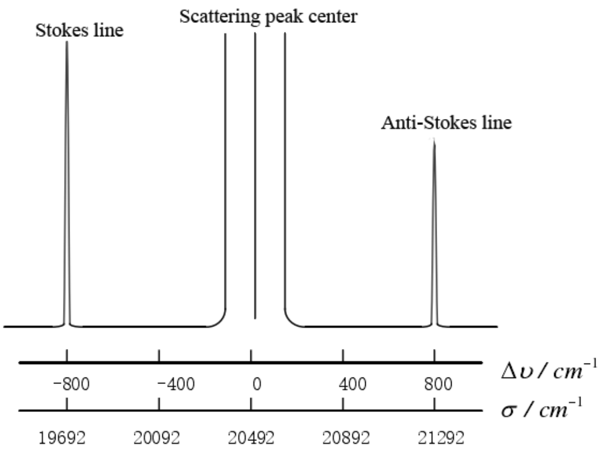

Figure 1: The frequency relationship of Raman scattered light and incident light

2.2 Infrared spectrum detection technology

In organic molecules, the chemical bonds or functional groups of the constituent materials have special vibrational frequencies. If the frequency of the incident light is the same as the frequency of the vibration of a certain functional group, the light at the wavelength will be absorbed by the material molecules, thus causing the decrease of the incident light energy (Genchev and Erbe, 2016). The infrared radiation is selectively absorbed by the molecule, which leads to the change of the molecular dipole moment and the change of the molecular vibrational rotational energy level. The material molecules will change from the ground state to the excited state, thus forming the absorption spectrum of the material molecule called infrared absorption spectrum. In this way, when the infrared light source passes through the measured material, the infrared absorption spectrum of the sample is obtained by detecting the infrared radiation passing rate $T(\lambda)$ or the absorbance $A(\lambda)$. The infrared transmittance $T(\lambda)$ of a certain advantage is the ratio of the intensity of $I(\lambda)$ and the intensity of the light source $I_o(\lambda)$.

$$\mathrm{T}(\lambda)=\frac{I(\lambda)}{I_o(\lambda)}\times 100\% \tag{1}$$

The absorbance A(λ) is the logarithm of the reciprocal of the transmittance at a certain wavelength.

$$\mathrm{A}(\lambda)=\lg\frac{I}{T(\lambda)} \tag{2}$$

It can be seen that the transmittance spectrum and absorption spectrum can be converted. The transmittance spectrum can directly see the infrared absorption degree of each wave of the tested material, but there is no relationship between the absorption and the absorption of the material. However, the absorption spectrum is different, and it has a very direct relationship with the infrared absorption of the material. Based on this, infrared absorption spectroscopy can be applied to the quantitative detection, and the current infrared spectrum is mostly expressed by infrared absorption spectrum. As shown in figure 2, the most common infrared spectrograms usually take the wavenumber υ as the abscissa and the absorbance A(υ) as the ordinate.

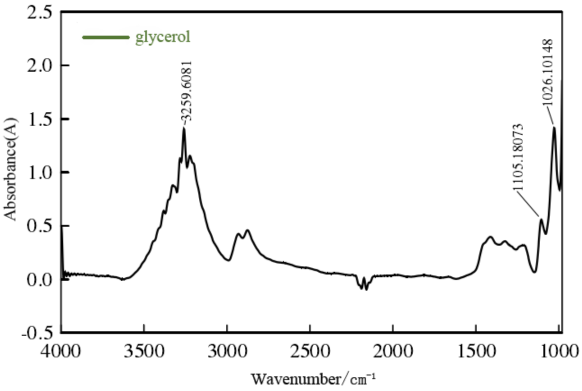

Figure 2: Infrared spectrum of glycerol

It can be seen from the figure that the glycerol has different infrared absorption intensity at different wave numbers, and the infrared absorption peak appears diversification. The infrared spectrum of the electromagnetic wave region is between 4000-400cm^{-1}. It can be divided into 3 regions according to different forms of vibration, which includes X-H stretching vibration region (4000-2500cm^{-1}), three frequency area (2500-2000cm^{-1}) and double frequency area (1500-400cm^{-1}). For each molecule, the atoms are bonded together by a chemical bond to form a separate substance.

3. Analysis of Raman spectroscopy and Infrared detection

3.1 Effects of different laser sources on pork Raman signal

Due to the different laser wavelength in the detection process, it will cause a certain degree of fluorescence effect, so that some Raman information is covered. Therefore, in the early stage of the experiment, the Raman spectra of 532nm (30mW) and 785nm (100mW) found by two laser sources is compared. It is found that the Raman signal is seriously covered by the fluorescence packet and the analysis results are influenced when the 532nm laser is used. Although the Raman intensity of the 785nm light source is low compared with the 532nm laser source, the Raman information is relatively complete.

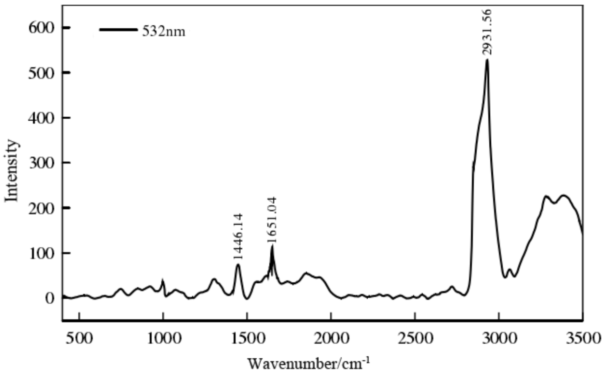

Figure 3: Raman spectra of pork measured by 532nm laser light source

3.2 Change of Raman signal of pork stored for two months at -250℃

With the increase of the storage time of pork in the frozen environment, the two class structures of pork protein changed significantly. 1450cm^{-1} is the bending vibrational Raman peak of methyl and methylene groups. The Raman peak is used to reflect the influence of environmental factors on the measurement of the target material. Because it does not change in the process of meat processing, it can be regarded as a constant. It can be seen from Figure 4 that the wave number 937cm^{-1} is the Raman peak corresponding to the stretching vibration of the C-C bond in the a- helix structure. With the increase of freezing time, compared with the initial fresh pork, the decrease of α-helical structure was observed after two months of frozen pork. The experimental results are consistent with the changes of Raman spectra obtained by the researchers.

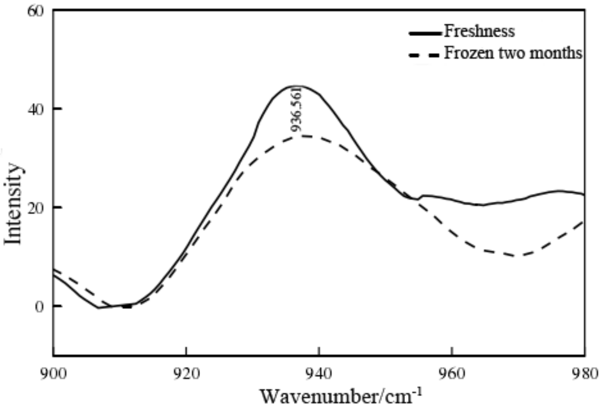

Figure 4: Raman spectra of frozen pork and fresh pork in the range of 800-1500cm^{-1}

3.3 Infrared absorption characteristics of glycerol and methanol

In the process of industrial production, the biological reaction process is a complex process, and the interaction between the material molecules may cause the change of the infrared spectrum. At the same time, the intermediate products are appeared in the process of biomolecular reaction, which can affect the detection environment. The experimental process is a dynamic process, and the reaction of each stage cannot be controlled. However, in order to simulate the real situation as much as possible in the actual production process and reduce the experimental error, before the online experiment, we should do a good job of off-line detection and establish a good prediction model, so as to eliminate unnecessary errors to the maximum extent. As shown in Figure 5, the C-O bond symmetry and the antisymmetric stretching vibration absorption peak of glycerol in the range of 1115-1000cm^{-1} were found in the infrared spectrum of pure glycerol. There are three distinct peaks at 1037cm^{-1}, 1026cm^{-1} and 1020cm^{-1}, respectively. Methanol solution has obvious C-O infrared absorption peaks in 1020cm^{-1}. The infrared absorption peak can be used as the characteristic peak of glycerol and methanol.

In order to study the effect of the culture medium on the infrared absorption peak of glycerol and methanol, we collected the infrared spectra of glycerol (methanol) at different concentrations. When the medium was added, the infrared absorption peak of glycerol was shifted. At the same time, with the increase of glycerol concentration, the absorbance of 1060-1025cm^{-1} increased gradually, and there was a certain proportion.

Compared with pure methanol solution, the infrared absorption peak of methanol was changed after adding the medium. The infrared absorption peak appears near the wavenumber 1016cm^{-1}, which is somewhat different from that of 1020cm^{-1}. At the same time, with the increase of methanol concentration, the infrared absorption of the infrared absorption peak gradually increased, showing a certain proportion.

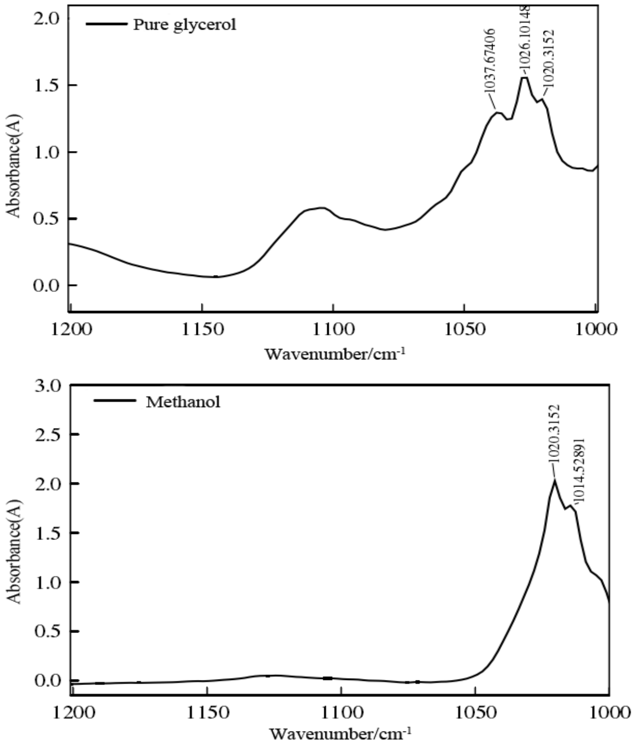

Figure 5: Infrared spectra of glycerol and methanol

3.4 The results

With the development of Raman spectrometer and the improvement of data processing technology, Raman spectroscopy detection technology has gradually attracted the attention of researchers as a new type of food detection technology. The Raman spectrum has a unique fingerprint region in the chemical structure of protein structure, which makes it more important in the analysis of protein structure and is used to detect muscle foods. By analyzing the change of pork Raman spectrum in different freezing thawing process, it can be concluded that 785nm has more advantages when 532nm and 785nm laser light source are used to detect pork Raman spectrum. It preserves the most complete Raman signal in the 800-1200cm^{-1} range. With the increase of freezing times, the intensity of the 1645-1685cm^{-1} Raman peak of the amide I band decreases gradually. Due to the decrease of the C-C stretching vibration near 937cm^{-1}, the a-helix structure is also reduced in the two grade structures of the protein. After two months of freezing, the ratio of Raman peak intensity of amide I band 1650cm^{-1} in the two-level structures of protein in pork to 1450cm^{-1} will decrease. The results showed that the protein structure changed significantly after freezing treatment. This change can be obtained by Raman spectroscopy.

As a fast, accurate and non-destructive detection technology, infrared spectroscopy has been widely used in food and drug testing. The content of glycerol and methanol in Pichia pastoris was monitored in real time. The results show that the application of infrared spectrum detection technology and ATR probe can realize off-line and on-line monitoring of glycerol and methanol. The correlation coefficients were 98.65% and 98.09%, respectively. The results showed that the time required for methanol consumption was 6 hours from the beginning of the incubation period and the glycerol was used to the time of glycerol depletion for about 40 hours. The experiment proved that the application of infrared detection technology and industrial production in the online real-time detection of the detected substances.

4. Conclusions

In recent years, the problem of food safety and environmental pollution caused by food safety issues has been a wake-up call. It has gradually raised concerns about how to ensure food safety and high quality in the market. The traditional detection technology has many defects, such as low efficiency, long time consuming and strong destructiveness. As a kind of detection technology based on optical characteristics, the common spectrum detection technology includes hyperspectral imaging technology, Raman spectroscopy, near infrared spectroscopy, infrared spectroscopy and so on. As a new detection technology, spectral detection has the advantages of high efficiency and short time consuming. It is easy to realize automation and is suitable for on-line detection of mass production. At the same time, it is gradually favoured by researchers as a non-contact non-destructive testing technology.

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