Effective Application of ICT in Food and Agricultural Sector — Optical Sensing is Mainly Described —

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SUMMARY   This paper gives an outline of key technologies necessary for science-based agriculture. In order to design future agriculture, present agriculture should be redesigned based on the context of smart agriculture that indicates the overall form of agriculture including a social system while the present precision agriculture shows a technical form of agriculture only. Wireless Sensor Network (WSN) and the various type of optical sensors are assumed to be a basic technology of smart agriculture which intends the harmony with the economic development and sustainable agro-ecosystem. In this paper, the current state and development for the optical sensing for environment and plant are introduced.

key words: ICT, optical sensing, infrared spectroscopy, fluorescent X-ray spectroscopy, visible spectroscopy, agricultural products

1. Introduction

To achieve a stable supply of high quality crops, measurement of the nutritional state of crops during cultivation and the optimum response to that state are very important. Particularly, in the case of a plant factory, which attracts attention from the viewpoints of food issues, safety and security of food, etc., measurement and control of the nutritional state of crops is essential, in contrast to the case of outdoor-grown farming. Plants absorb essential elements in the form of inorganic nutrients from their roots with water, and the balance of these essential elements in them plays a large role in their nutritional state. Therefore, future Agricultural WSN has to equip various plant sensors to obtain the plant vigor information while the WSN in the present stage mainly covers the weather and soil conditions [1].

Understanding the change in the balance of elements at the level of field cultivation is very important in crop cultivation, and acquiring the correct information on the balance of elements enables control of the amount of fertilizer and the plant's environment. Focusing on the relation between recent unstable climate and crops, it is also very important at the level of field cultivation because external environmental factors such as abnormal climate and air pollution produce a large change in the balance of nutritional state in a plant, leading to a decrease in the yield of crops. We, therefore, decided to survey example applications and possibilities of optical sensing techniques, from X-ray to terahertz (THz) radiation that enable nondestructive, chemical-free, simple, and quick measurement of crops.

2. Spectroscopic Sensing

2.1   Features of Spectroscopic Sensing [2], [3]

Spectroscopic analysis is characterized by comparison with separation analysis. In separation analysis represented by chromatography and electrophoresis, a mixture is basically fractionated to a single chemical species. Conversely, in spectroscopic analysis, the spectrum of a mixture is acquired, a desired chemical species is identified from the spectrum information, and its amount is determined spectrally. Spectroscopic analysis includes absorption, emission, and scattering spectroscopy. Absorption spectroscopy includes many sampling methods (transmission, reflection, diffuse reflection, photoacoustic, etc.). These analysis methods in common have terms of involving the steps of separating and acquiring desired information from mixed information. To conduct spectroscopic analysis, it is essential to understand the chemical discipline, in which multivariate analysis is applied to chemistry, called chemometrics [4], to focus on particular information from mixed information and to analyze its spectrum quantitatively. The strongest features of optical sensing such as spectroscopic measurements are extensive information acquired by large-scale, simultaneous technique measurement using various waveband sources, and the short time required for measurement.

In chromatographic measurement, the information eventually acquired is limited by column selection, whereas in spectroscopic measurement, the primary information contained in the original spectrum has no lack of information. That is, "to save spectrum information" has almost the same meaning as "to store a sample." This feature is a very large advantage in quality measurement and the understanding of the state of plants such as crops. Table 1 shows the main spectroscopic sensing techniques.

2.2   X-ray

To achieve sustainable agriculture with a stable supply of high quality crops and environmental protection in mind, establishment of quick and simple methods for measuring elements in crops is important. Therefore, use of fluorescent X-ray analysis, which enables nondestructive, simultaneous measurement of several elements, attracts attention. Since the wavelength of the fluorescent X-ray corresponds to an

Table 1　The major optical (spectral) sensing.

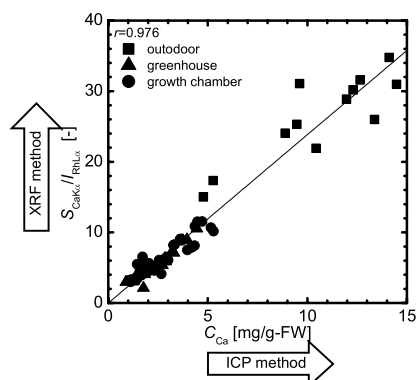| Electromagnetic wave	Measuring method	Measure-ment Object	Measured substance
X-ray	Fluorescent X-ray spectroscopy	Leaf and soil	K▪Ca▪P▪N▪Mg▪Fe▪Zn▪Cu▪S
Ultra Violet (UV)	Fluorescence spectroscopy	Leaf	Saccharides, Pigments, Organic acids, Disease symptom
Visible (VIS)	Color and Shape Analytical Method	Leaf and fruits	Pigments, Vigor State of plants
Visible (VIS)	Spectroscopy	Solar light	Spectrum of outside light
Near Infrared (NIR)	Glove type NIR analyzer	Fruits	Sugar content and spectrum change
Mid Infrared (MIR)	FT-IR/ATR	Leaf and fruits	Moisture content, Mono, Di and Oligosaccharides, Nitrogen, Agricultural chemical, Acids
THz	Spectroscopy	On going	Basic Research for Saccharides Sensing
Radio wave	Dielectric spectroscopy	On going	Hydrogen bonding network
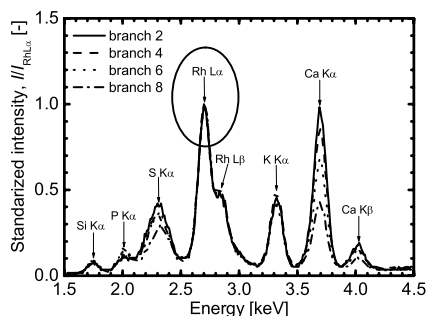
Fig. 1　Normalized X-ray fluorescence spectrum.

Fig. 2　Comparison between the dimensionless area intensity with the Ca component value measured by ICP.

energy difference specific to each element between its inner and outer shells, the constituent elements of a sample can be analyzed by obtaining the fluorescent X-ray energy experimentally [5]. Fluorescent X-ray analysis has been used for the determination of production area and microelement analysis of aroids [6]. Application of fluorescent X-ray analysis to acquire information on elements in leaves of crops are introduced here [7].

Figure 1 shows the fluorescent X-ray spectrum of a leaf of a tomato. This figure shows a spectrum for which the fluorescent X-rays were normalized using the peak intensity of RhLα (approximately 2.71 keV) generated by irradiation. Figure 2 shows the result of comparing the integrated intensity of the Ca peak with the analytical value of content in a leaf by plasma emission spectrometry, a standard method of quantitative analysis of elements [7]. The correlation coefficient of Ca between the normalized fluorescent X-ray intensity and the content in a tomato leaf was 0.976, which showed good linearity, demonstrating that Ca was measured quantitatively. A good correlation was also found with potassium. When fluorescent X-ray spectroscopic measurement was conducted on raw tomato plant leaves of both blossom-end rot and normal tomato plants, a difference in the balance of Ca in the plant was found between both types of plants; the value for the abnormal plant was smaller than that for the normal plant [7]. In this way,

an advantage of fluorescent X-ray spectroscopy is real time, large-scale, simultaneous measurement of elements such as K, P, and Fe, the advantage of acquiring information on nutrient elements in plants by fluorescent X-ray spectroscopy in a farm field being demonstrated.

2.3　Ultra Violet (UV)

With a portable fluorescent measuring system that enables field observation of the plant fluorescence spectrum and a fluorescent lidar system that enables lateral observation, information on the formation and loss of chlorophyll, the main molecule of photosynthesis, can be obtained by laser-induced plant fluorescence, and the increase and decrease in the fluorescence spectra of secondary metabolic products, the result of physiological activities, can be measured [8]. To diagnose photosynthesis of tomato vegetation cultivated in a plant factory, Takayama et al. [9] used a chlorophyll fluorescent image measuring system consisting of a chlorophyll fluorescent image measuring section containing a charge-coupled device camera with a large light-emitting diode panel light source of 60 cm × 60 cm ($\lambda < 650$ nm) for irradiation of excitation light and a long-path filter ($\lambda > 700$ nm) loaded; a drive section to raise and lower the image measuring section in accord with the height of the tomato vegetation; an analysis/diagnosis section to analyze the measured fluorescent images and diagnose the plant; and a travel section to load these sections and travel on the paths in the plant factory, and measure the tomato plants in the plant factory.

With the usual fluorescence technique, measurement is generally conducted at a single excitation wavelength and fluorescent wavelength to identify the presence of specific substances; several types of substances can be identified with a combination of several excitation wavelengths and fluorescent wavelengths. While aforementioned fluorescence measurements are simple, it can acquire only less information on the optical properties of active molecules than spectral spectrum measurements. Measurement using an excitation /fluorescence matrix that is obtained by scanning continuously both the excitation wavelength and fluores-

cent wavelength and by measuring the fluorescence intensity has been attempted [10]. Sugiyama, who gave a name "fluorescent fingerprint" to this excitation emission matrix, conducted determination of the production area of mango, simultaneous quantitative determination of mycotoxin, and estimation of the mixing ratio of buckwheat and flour by fluorescent fingerprints created using excitation wavelengths of 200–340 nm and an analysis method using partial least squares regression analysis, demonstrating that fluorescent fingerprints can be applied to food/crops containing various ingredients [11].

2.4   Visible (VIS)

Light in the visible region has been used for evaluation of the state of growth of plants on a daily basis from ancient times. Since red and blue lights are mainly used in photosynthesis by leaves of plants, leaves appear green. Diagnosis of plants using the color of the leaf has been conducted from the past; in the field of agriculture, single-photon avalanche diode (SPAD) devices [12] are generally used to measure the amount of chlorophyll contained in plant leaves as a SPAD value (a value indicating the content of chlorophyll), which is necessary to know to determine the condition of plants. Recently, CropSpec [13], a device to measure the state of growth in a noncontact manner using a laser based on a similar principle, has become available, which is designed as a system which is loaded on a tractor to enable measurement in a large cultivation area and adjustment of the application amount of fertilizer.

With recent high image quality and price reduction in digital cameras, visible images are generally obtained using a general-purpose digital camera. Here, a simple method of acquiring color information of crops in their natural environment is introduced [14], [15]. Since the color of crops originates from endogenous pigment, a secondary metabolic product resulted from metabolism; they reflect information on components such as nutrient and pigment levels and information on cultivation conditions under which the color appears. Color image analysis technology is not only effective for color evaluation, but also for acquisition of information on shape or size, which is difficult to understand quantitatively. The red-green-blue (RGB) value of a color image taken with a digital camera can be expressed by means of a power function using the amount of light the elements of the camera receive (received light sensitivity Hm) as the base.

$$RGB = a \cdot Hm^b \tag{1}$$

where the coefficient a is a parameter characterizing the color of the irradiating light, and the coefficient b is a constant. A relation between normalized Hm and normalized RGB value of an obtained image is expressed as a curve irrespective of color in the standard color chart image that contains red, green, and blue criteria for quantitative evaluation of color information.

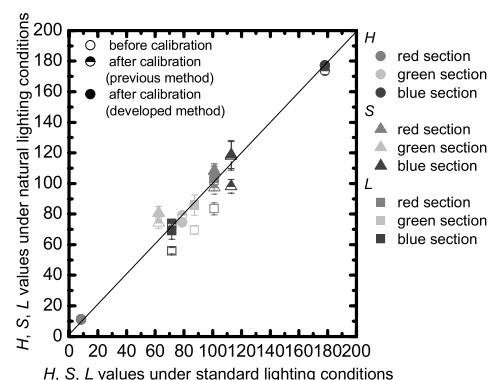Since coefficient *a* is a color parameter that can be calculated from the irradiating light information, the RGB

Fig. 3   Color correction result of the color chart image.

value of a color chart can be calculated from Eq. (1) by choosing three wavelengths that characterize natural light. Therefore, an image taken under natural light can be corrected by comparing the RGB value of a calculated virtual color chart image with that of an actual color chart obtained in a reference light source. As shown in Fig. 3, the hue, saturation, and lightness values are almost the same between a corrected and reference image, showing that color correction of an image taken under natural light is possible. There is a possibility that evaluation of the state of growth of plants made visually can be analyzed objectively by applying color correction to an image taken under natural light.

2.5   Infrared (IR)

Infrared radiation is used in many fields, and a combination of different names is used in each field [16]. Since this article describes optical sensing of the state of growth of plants, a name in the field of spectroscopy is used. Since most molecules are in the ground state, a transition from the ground state (vibrational quantum number v = 0) to the first excited vibrational state (v = 1) occurs by absorption of infrared radiation. Absorption corresponding to this transition is called a fundamental mode. Absorption corresponding to an overtone is generated by a transition to a higher vibrationally excited state; however, these transition probabilities are generally low. The absorption intensities of overtones observed in the near infrared region, therefore, are generally very weak.

In a farm field that requires nondestructive, on-the-spot analysis of solid and liquid samples such as soil, water, plants, and fruit, mid-infrared radiation is seldom used, and near-infrared radiation (NIR) is mostly used [17], [18]. The reasons for this are that absorption of samples is strong in the mid-infrared region, and that agricultural samples contain plenty of water, which significantly interferes with the measurement. Another reason is that crops are in the complex system consisting of many components, therefore, a great many bands are observed in the mid-infrared absorption spectrum, leading to difficulty in spectrum analysis.

With the attenuated total reflection (ATR) method, which has rapidly become popular in recent years; how-

ever, the mid-infrared absorption spectra of solid and liquid substances can be measured comparatively readily. Since the spectrum in the mid-infrared region contains much more information than the spectrum in the near-infrared region, the chance of using mid-infrared spectroscopy in farm fields seems to increase with popularization of the ATR method. Conversely, features of near-infrared spectroscopy, in which a vibrational transition corresponding to an overtone and a combination tone is observed, permit high permeability into materials and the use of fiber optics. These properties have many advantages in a farm field, such as nondestructive measurement of fruit components using transmitted light. Since a very complex spectrum with broad band width is obtained in the near infrared region, it is essential for analysis of near infrared absorption spectra to extract information using techniques such as chemometrics and two-dimensional correlation spectroscopy [19].

Microelectromechanical systems (MEMS) Fourier transform infrared spectroscopy (FTIR) [20] is introduced as a new device that may become essential for sensing in a farm field, though they are not yet applied technologies in the field. MEMS technology to fabricate mechanically operable structure as well as transistor circuits on a silicon chip by semiconductor microfabrication technology is also used widely for sensor development. Since FTIR can detect spectra specific to materials such as water, saccharides [21] and CO_2, Hamamatsu Photonics K.K. uses MEMS to develop micro-FTIR having a wide band from near infrared radiation to mid-infrared radiation [22]. The band is just from 1000 to 2000 nm at present because of the constraint of a light source. Future development of a new light source is predicted, so that wide application to field measurements of plants can be expected.

2.6 THz

Terahertz waves are electromagnetic waves in the frequency range 0.3–10 THz and a wavelength region of 1000–30 μm, i.e., in the frequency region between light and electric waves. The name terahertz is derived from a fact that this frequency is measured in units of THz; it is a longer wavelength than visible light, and shorter wavelength or higher frequency than electric waves. Electromagnetic waves between visible light and electric waves are also called far infrared radiation or submillimeter waves as well as terahertz waves, though there is a little difference in the range of definition. Development of electromagnetic wave technology in this frequency region has been delayed so far; it has been seldom used not only in basic research but also in industry; it is why the terahertz region is called an undeveloped electromagnetic territory.

Since information on the terahertz frequency region relates to important dynamic behaviors, such as dielectric dispersion of materials, lattice vibrations, skeletal vibration of molecules, twisting vibrations, and rotations, there is a possibility that it will become a promising technology in application to agriculture. Since terahertz waves are in the
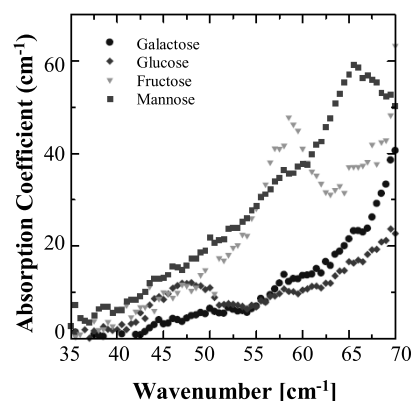

Fig. 4 THz spectra of monosaccharides.

shortest wavelength region showing permeability into materials and they are the longest wavelengths having linearity of the waves, imaging using terahertz waves is one of the most important applied technologies [23]. Figure 4 shows terahertz spectral spectra of sugars that serves as base points of life activities and have functions as information transmitters [24]. It shows that there are "fingerprint regions" of sugars in the terahertz frequency region as well as in the mid-infrared region. Terahertz waves also showing permeability of the wave is expected to be used for nondestructive testing inside a container or a bag.

3. **Application of IR Radiation**

3.1 NIR Application

As typical popularized technology using near infrared radiation (NIR), there is a nondestructive method for measuring sugars of fruit such as orange and apple; two significant developed products using this technology are introduced here. One is a glove-type near infrared spectral sensor developed by Dunamist in the Development Center of Hamamatsu Photonics K.K.; when fruit is just held, high precision field measurement of the spectral spectrum is possible [25]. The other is a measuring instrument based on a new measuring principle called the three-fiber-based diffuse reflectance spectroscopy (TFDRS) method designed by Industrial Technology Center of Nagasaki [26]. This method does not require a continuous spectrum of reflected light, a spectroscope, or a halogen lamp to provide white light. Since a spectroscope is not used, component costs decrease significantly, and with no need for a halogen lamp, not only is idling time to stabilize the emission spectrum not required, but also power consumption decreases significantly. As a result, small power source batteries can be used satisfactorily, and further downsizing and weight saving become possible.

3.2 Measuring Method of Nitrate-State Nitrogen

The amount of nitrate-state nitrogen in plants is one of the important nutritional state indexes, and the high promise of
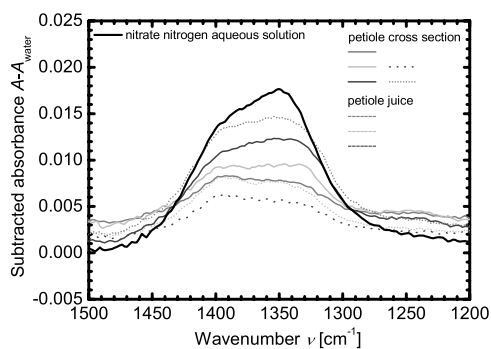
Fig. 5 The spectrum of absorbance difference between the juice and water and that between the petiole cross section and water.

Fig. 6 Spectral processing by the tasting robot.

Fig. 7 pH-dependency of absorbance spectra of G6P.

quantitative determination of nitrate-state nitrogen using the spectrum of leaf stem juice has been confirmed [27]. Measurement using juice; however, is troublesome in an actual cultivation field. A method of simply measuring the spectrum of a cut surface of a leaf stem [28] to acquire spectrum information equivalent to that of juice in a cultivation field is described here.

Figure 5 shows the absorbance spectrum of the cut surface of a leaf stem, a supply route of aqueous nitric acid and nutrients. The spectrum of the cut surface of a leaf stem is quite similar to that of aqueous nitric acid at 1350–1400 cm^{-1}. These measurement results show experimentally that infrared radiation spectral measurement of a leaf stem is a simple and quick quantitative method for nitric acid. The aforementioned measuring method is considered effective for cultivation management from the viewpoint of plant physiology.

3.3 Outline of Tasting Robot

When the recent fitness boom and the problem of home care of elderly people are considered, the social needs for realization of a partner robot having five senses is expected to increase in future. Mie University and NEC System Technologies, Ltd. developed jointly the world's first partner robot "health/food advisor robot (tasting robot)" having a "sense of taste" in July 2006 with support of the new energy and industrial technology development organization [29]. The tasting robot having an infrared sensor analyzes offered food for a few seconds, and gives advice on health and food. Since there was also an idea and feasibility of letting a robot have a sense of taste, the tasting robot was designed and developed for entertainment value to imitate a sommelier. The tasting robot is NEC's partner robot PaPeRo [30] with an infrared sensor loaded; arms tailored to the size of PaPeRo were made, and an infrared sensor that plays the role of a human tongue was integrated. It analyzes the infrared absorption spectrum information of food to estimate the type of food based on the presence and content of a characteristic component. In addition, the robot gives advice on food and health by matching with the personal body information registered beforehand. The obtained spectrum is processed
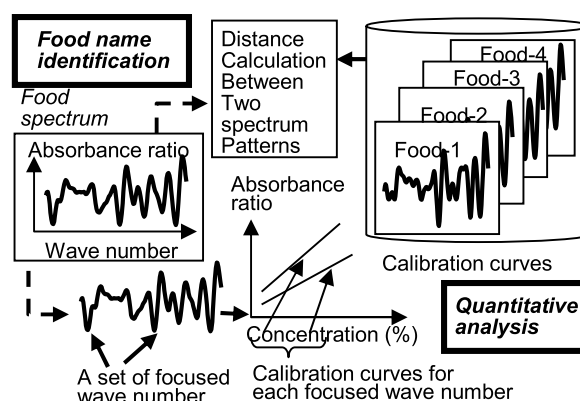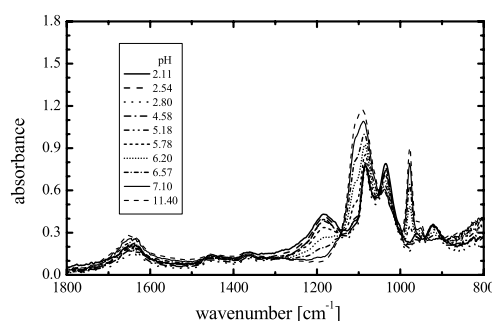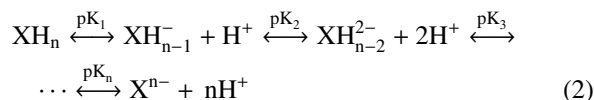
independently by quantitative analysis based on an analytical curve and by estimation of the type of food based on pattern recognition. Figure 6 shows the schematic view of the process.

Quantitative analysis is made by studying beforehand the concentration dependence of spectral characteristics of the main components of food. In estimation of the type of food, the obtained spectrum is treated as a pattern, and a pattern recognition technique is used to identify and classify food. To do so, it is necessary to accumulate spectra of various foods beforehand and store them with the names of the foods in a dictionary. Then, expansion of the robot to a sommelier robot was attempted, and this new robot was registered in the Guinness Book of World Records 2008 [31] as a world's first sommelier robot.

3.4 Ionic Dissociative Metabolites

The pH-dependency of the MIR spectra in aqueous solution of the organic dissociative materials in metabolic pathway, such as saccharide phosphates (G6P, F6P), adenosine and its phosphates (ATP, ADP AMP), was studied [32]. The series of molar absorbance spectra for these reagents were obtained in pH range of about 2 to 11 with the FT-IR/ATR method. The ATR spectrum of the ionic dissociative material in the aqueous solutions considerably changes with pH. In Fig. 7 [32], the molar absorbance spectra of G6P aqueous solution with different pH are presented. The pH-

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dependency of the ATR absorbance spectrum for an ionic dissociative material XH_n in the aqueous solution could be explained by the equilibrium shift among the ionic dissociation components (ionic species).

$$XH_n \xleftrightarrow{pK_1} XH_{n-1}^- + H^+ \xleftrightarrow{pK_2} XH_{n-2}^{2-} + 2H^+ \xleftrightarrow{pK_3}$$
$$\cdots \xleftrightarrow{pK_n} X^{n-} + nH^+ \tag{2}$$

Henceforth, the spectrum of each ionic species was assumed to be not affected by the hydrogen ion concentration and to satisfy the spectral additivity for the ionic species. Then, the spectrum from which the pure water spectrum was subtracted can be decomposed by the assumed spectra of the ionic species, as follows:

$$Abs(\nu, pH) = \sum_{i=0}^{n} c_i(pH) Abs_i(\nu) \tag{3}$$

Here, ν denotes the wavenumber, $Abs(\nu, pH)$ is the subtracted spectrum per unit molar of the reagent. c_i (pH) are the fraction of the reagent's total concentration for the i-th ionic species with the charge $-i$, and $Abs_i(\nu)$ are the molar absorbance spectra of the i-th components. According to the theory of dissociation equilibrium, the fraction for the i-th component c_i (pH) can be expressed as a function of pH with the parameters of the dissociation constants pK_i.

$$c_0(pH) = \frac{[XH_n]}{C} = \frac{1}{1 + 10^{pH-pK_1} + 10^{pH-pK_1} 10^{pH-pK_2} + \cdots + 10^{pH-pK_1} \cdots 10^{pH-pK_n}}$$

$$c_1(pH) = \frac{[XH_{n-1}^-]}{C} = \frac{10^{pH-pK_1}}{1 + 10^{pH-pK_1} + 10^{pH-pK_1} 10^{pH-pK_2} + \cdots + 10^{pH-pK_1} \cdots 10^{pH-pK_n}}$$

$$c_2(pH) = \frac{[XH_{n-2}^{2-}]}{C} = \frac{10^{pH-pK_1} 10^{pH-pK_2}}{1 + 10^{pH-pK_1} + 10^{pH-pK_1} 10^{pH-pK_2} + \cdots + 10^{pH-pK_1} \cdots 10^{pH-pK_n}}$$

$$\vdots \tag{4}$$

Here, C denotes the total concentration of the reagent in the aqueous solution. The dissociation constants pK_i of the reagents were found in the literatures [33], [34]. Performing the multiple linear regression analysis by using the model formula in Eqs. (3) and (4), the molar absorbance spectra of ionic species for G6P, as well as corresponding monosaccharide; glucose, were obtained. Two ionic species for G6P were obtained in the pH range measured: G6P$^-$ and G6P^{2-}. Using the molar absorbance spectra of the ionic species of the dissociative materials obtained in this procedure, the molar absorbance spectra of the dissociative materials in aqueous solution for any pH could be reconstructed.

In Fig. 8 [32], the synthesized spectra for G6P at pH 5.78 and pH 7.10 are compared with the observed spectra prepared in these pH values. The agreement of these spectra was fairly well. This suggests that it will be possible to construct a quantification system of the concentrations of the organic dissociative materials in varying pH.

3.5 New Developments on Tasting Based on IR Spectroscopic Analysis

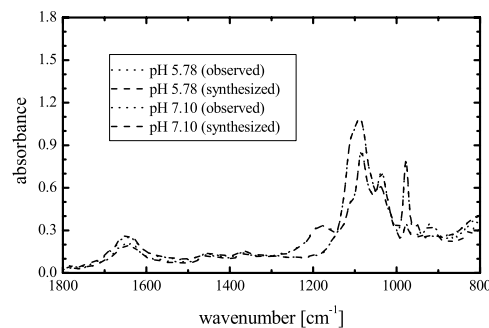Examples in which wine, a typical favorite beverage, is used

Fig. 8 Comparison of the synthesized spectra for G6P at pH 5.78 and 7.10 with the observed spectra.
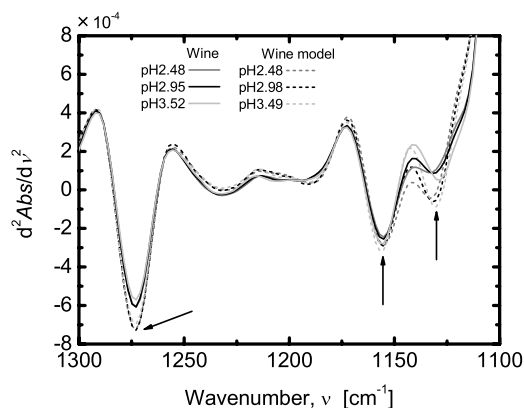

Fig. 9 Spectra of the model wine and the wine with varying pH.

to extract features of food based on infrared spectroscopy information are described [35]. Ionic dissociative components such as organic acids hold the key of taste and quality of wine. A relation between ionic dissociative components and infrared spectroscopy information is described here. Figure 9 shows spectra of wine with pH changed and a wine model prepared by blending the main components (ethanol, glucose, fructose, acetic acid, citric acid, lactic acid, malic acid, succinic acid, and tartaric acid). Increase and decrease of absorption and shifts of a number of peaks are observed near 1130, 1155, and 1272 cm^{-1} in the spectrum of the wine, and their behaviors are the same as those in the spectrum of the wine model. The result of analysis of infrared absorption spectral characteristics of components in the wine model using dissociation equilibrium theory shows that the change in the spectrum of the wine model originates from the organic acids in wine. Then, since the spectrum of wine is similar to that of ethanol, a method of extracting information on components other than ethanol in wine is described.

Figure 10 shows spectra of the wine and wine model with spectra of water and ethanol deducted, and the synthesized spectrum calculated by considering the concentration and pH of components in the wine model.

The main absorption bands almost agree, and it is seen that information on components specific to the type of wine other than ethanol in wine is extracted. Like this, analysis of the infrared absorption spectrum of wine enables extraction
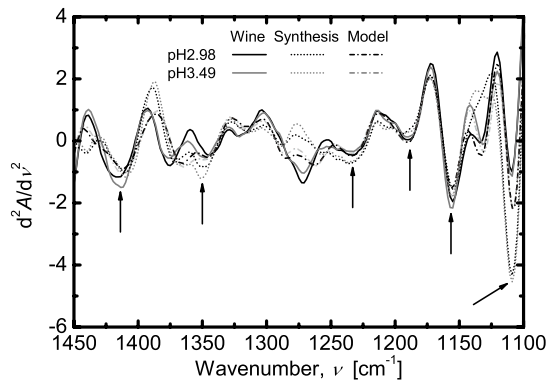
Fig. 10 Wine, wine model and synthetic spectra with varying pH (the difference between water and the ethanol).

of quality information and identification of the type of wine.

4. Conclusion

These days, when genes are decoded at high speed, establishment of a twinned, phenotypic, exhaustive measuring system is an urgent need [36]. Therefore, interesting research on the sensing of functions of plants is introduced. The stem and trunk of plants have conduit and sieve tubes in them; conduit tubes transport water containing minerals from the roots, and sieve tubes transport starch produced by photosynthesis in the form of aqueous sucrose (aqueous sorbitol in the case of rosaceous fruit such as apple, pear, and peach). The stem plays the role of a wave guide tube to guide far-red light (> 700 nm) obtained from sunlight to the roots. Far-red light delivered to roots regulates the expression of aquaporin genes in roots through a signal transduction system via phytochrome A, and roots under the ground also register light as an environmental signal [37]. In relation to plant phenomics, various visualization technologies for the root zone at the laboratory level have been reported; the day when the root zone can be monitored in a farm field seems to be approaching [38]. At present, when three-dimensional modeling of structure and functions of plant is about to reach the stage of practical use and expecting that information and communication technology and sensing technology introduced here will be integrated together in the near future and arranged as a cultivation management system in a farm field.

Acknowledgments

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