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Introduction of Non-Invasive Measurement Method by Infrared Application

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1. Introduction

The infrared light analysis has become an indispensable part of life for humankind. The infrared measurement has been studied in the worldwide, because can be qualitative and quantitative analysis for trace samples. Today, infrared spectrophotometer has been installed in many laboratories and universities, and being used over a very wide field. So, the number of papers on infrared spectroscopy is so many. We also are one of a research group of infrared measurement. Our research policy is "non-destructive measurement using infrared light". In general, blood glucose measurements of the human body to extract blood, and to determine the composition of textile products will break down to samples. If we can measure these value in non-destructive, we can contribute to society. So I described our past "non-destructive measurement using infrared light" research in this document.

2. Measurement system

2.1 FT-IR (Fourier Transform Infrared Spectrophotometer)

In this study, measuring systems are used a FT-IR (IR-Prestige-21 : SHIMADZU, Travel-IR : SensIR Technologies) as in Fig.1. The block diagram of measurement system is shown in Fig.2. The broadband infrared light is interfering by Michelson interferometer, and sent to the sample place. In the sample place, we selected the best method (ATR method, diffuse reflection method, IR fiber probe method) by each sample. We are only using the MCT (mercury cadmium tellurium) detector in IR fiber probe method, using the DLATGS (Deuterated L-Alanine Triglycine Sulphate) detector, appear on the PC as an interferogram signal. This signal transformed by Fourier transformation, we get the IR absorption spectrum. The horizontal axis of spectrum is wavenumber, and the vertical axis is absorbance.

2.2 Attenuated Total Reflectance method (ATR method)

ATR method is performed as follows. We place to the sample on the prism. At this time, if there is a gap, the S/N ratio is lower. Infrared light goes into the prism, and goes forward by repeating the total reflection. When IR light repeats total reflection in the prism, evanescent



Fig. 1. FT-IR (IR-Prestige-21 (A), Travel-IR(B))



Fig. 2. The block diagram of measurement system

lights goes into the sample. Evanescent light attenuates by absorbance in sample surface set on the prism. The absorbed infrared light from the sample is detected.

In the ATR prism, we use the ZnSe prism of plate type and the prism of diamond mounted on ZnSe. Optical path length of the evanescent light to go into the sample is shown in equation 1.

$$dp = \lambda / 2\pi n_1 [\sin^2\theta - (n_2/n_1)^2]^{1/2}$$
(1)

dp: depth of penetration of evanescent light, θ : angle of incidence λ : Wavelength, n_1 : refractive index of ATR prism, n_2 : refractive index of sample

By the equation 1, optical path length of evanescent light in the sample will get longer as the long wavelength side. Therefore, the absorption by the sample is strong in the long wavelength side. Accordingly, coefficient of divide "Absorbance of standard wavenumber" by "Absorbance of each wavenumber" is multiplied by the absorbance at each wavelength. In this calculation, optical path length of the evanescent light is standardize, and to correct the absorbance of spectrum. This calculation method is "ATR correction".

2.3 Diffuse reflection method

If the infrared light irradiated to powder or fibers, we can be measured the diffused reflection light from sample inside and the regular reflection light from sample surface. Infrared light penetrate inside the sample, then repeated the transmission and reflection, and come out of sample. In diffuse reflection method, this light is measured. We used to the UP-IR (Pike Tech) in this method. 30mm diameter hole is in the top of the UP-IR, the sample is placed to cover the hole.

2.4 IR fiber probe method

The infrared light passes through the light source side fiber probe, and irradiated to the sample. The infrared light reflected from the sample goes into the detector side fiber probe, and detected by MCT detector. This method can be irradiated with infrared light directly on the sample for the movement of the measuring place. The fiber probe (REMSPEC IMM-07S) composed of 19 fibers (the light source side 7 and the detector side 12) made by the chalcogenide glass. A fiber diameter is 500 µm, and a fiber probe diameter is 5 mm.

3. The spectrum analysis method

The absorption spectrum has various information of sample by each wavelength. In other words, the absorption spectrum has multidimensional vector information. Therefore, it is to analyze the spectra by multivariate analysis. In multivariate analysis for the use of multiple explanatory variables, it is increasing the amount of information. Thereby to reduce noise to a relative, it is possible to build a greater precision calibration curve. We performed correction to the absorption spectrum, and used to the PLSR in quantitative analysis, and used to the SIMCA method and the KNN method in the pattern analysis.

3.1 Spectral correction

We can extract the maximum information from the spectrum by performed correction to the absorption spectrum. We used to the spectral correction to the normalization and the differential. In the normalization correction, the absorbance of the designated peak is "1", and the coefficient "1/(absorbance of the specified peak)" is multiplied to the absorbance of each wavenumber. For example, there are the measured spectra of sample including material A and B. When you want to get the results of material A, the information of material B in the spectrum is the noise. In here, normalized to all spectra by the absorption peak of material B, and appears only information of material A. In this correction, that can be minimized by measurement error.

On the other hand, the differential correction is a correction of the slope of the spectrum, it is possible to eliminate the effects of baseline. Also, if the wavenumber of several absorption peaks is very close, is able to separate these peaks. The first differential correction is calculated at the slope of each wavenumber in spectrum, the intensity of absorption peaks wavenumber is "0". Derivative spectrum half-width of the higher orders is narrowed, and the noise increases for in lower S/N ratio. For these reasons, we used first differential correction in this study.

3.2 Partial Least Squares Regression (PLSR)

We are using PLSR for a quantitative analysis. PLSR has not the Multilinear regression (MLR) exists multicollinearity, Measurement accuracy of PLSR is better than Principal Components Regression (PCR) in a small number of factors. In the PLSR, the explanatory variables are the infrared spectra, the objective variables are the reference values. The explanatory variables and the objective variables are assumed to each have an error margin, extracted to PLS factors, calculate a regression, and new objective variables are calculated. Next, a similar calculation using the new objective variables and explanatory variables, add a PLS factor, re-calculate the objective variables. A number of PLS factors increase, and the Standard Error of Calibration (SEC) is smaller.

But, increasing the number of factors too, applies Standard Error of Prediction (SEP) increases (Over Fitting). Therefore, we validate the optimal number of PLS factors by Leave-one-out method. The Prediction Residual Error Sum of Squares₁ (PRESS₁) values calculated from the objective variables by the following equation 2

$$PRESS_n = \sum (y_{obs} - y_{ref})^2$$
(2)

y_{obs}: new objective variables, y_{ref}: reference values

After, the new objective variables are calculated by calibration curve adding a new PLS factor. $PRESS_2$ value is calculated from the objective variables obtained again. If the residual is significant before and after (The difference between the $PRESS_1$ and $PRESS_2$), adding the PLS factor. If the residual is not significant before and after, select the model that was built before. After, we measured to the spectrum of sample of unknown amount, and calculated by using calibration curve and this spectrum. By the above process, it is possible to be measured quantitatively of unknown sample.

3.3 Soft Independent Modeling of Class Analogy (SIMCA)

We used SIMCA for the qualitative analysis. A class is made by infrared spectra of known sample and builds a classification model. Each class is analysed by analysis of principal component and the distinction space is set. This space is called SIMCA box. It is classified into the class suited most by applying infrared spectra of unknown sample to SIMCA box. Moreover, the rest error is calculated by applying each spectrum that composes the class to other classes. And, Discrimination Power that can specify the factor in which it distinguishes between classes is obtained. We confirmed the validity of the classification model constructed by using Discrimination Power.

3.4 K-Nearest Neighbor method (KNN)

KNN method is one of pattern analysis to determine the class by comparing the similarity between the patterns not based on specific statistical distributions. To determine the class of an unknown sample is made on "voting". First, calculate the Euclidean distance between samples for the known and unknown class samples. Next, select a known class samples for the number of "K" close to the distance from an unknown class sample. "K" is odd number. The class of an unknown sample is determined to a most numerous class in the "K".

For example, if the "K=5", analyse the closest class of 5 samples from an unknown sample class. Five classes (1,2,3,3,3), (1,3,3,2,1) are classified at Class "3", (1,1,2,1,2), (2,1,3,1,1) are classified at Class "1". For such analysis, impact on the accuracy of the analysis is a combination of variables used to calculate the distance and the number of "K".

4. Development of non-invasive measurement of blood glucose of diabetic

4.1 Background

Recently, increasing of diabetic has been brought to public attention. According to WHO, the number of diabetics is 170 million. To treat diabetes, diabetics should always check blood glucose monitoring. Therefore, they need to self-monitor blood glucose (SMBG).

SMBG is measured by blood sampling method, but this method the patient suffering and stress, including issues such as the risk of infection. And, the economic burden on patients is very large, because medical needles and measurement kit are disposable. Medical expenses of diabetes and its complications are estimated at about 3,000 billion dollars worldwide, and are expected to continue to increase in the future. Those various studies have been conducted around the world, because the medical expenses have become large economic markets. But, the effective blood glucose measurement method to overcome these problems, have not yet been developed. Therefore, it is desired to develop a method to measure non-invasive blood glucose measurement. Over the past few years, several studies have been made on non-invasive blood glucose measurement based on ATR infrared spectroscopy. The purpose of this study is to examine the accuracy of blood glucose in clinical trial.

4.2 Measurement system for non-invasive measurement of blood glucose

This study used FT-IR (Travel-IR) and ATR method. The block diagram of measurement system is shown in Fig.3. In the ATR prism, used to the prism of diamond mounted on ZnSe (3 times reflection).

The measurement part is the tip of the left hand middle finger of subject. The middle finger was washed with ethanol. The 5µl squalene oil was applied on the prism by micropipette in each measurement. Squalene oil is used as an internal standard method described below. The measurement part of subject put on the prism, pressed from above with a constant pressure. We measured in this state, and got the absorption spectrum including the blood glucose value information.



Fig. 3. Non-invasive measurement system for blood glucose

The absorption spectrum was applied to the ATR correction. We used 1800 cm⁻¹ wavenumber in standard wavenumber of ATR correction, because absorption peak and noise are not in this wavenumber. After, all measured spectra were applied data correction between 2700 cm⁻¹ and 1750 cm⁻¹ to remove the absorption noise of diamond prism, and, were applied normalization correction in the absorption peak of squalene oil. We used these corrected absorption spectra in analysis. In the measurement condition, measurement wavenumber range is 4000~700 cm⁻¹, resolution is 4 cm⁻¹, and accumulation is 30 times.

4.2.1 Internal standard method by squalene oil

In measuring the subject's blood glucose value, the good accuracy calibration curve is essential. To improve the accuracy of the calibration curve must be accurately extract glucose information on the infrared absorption spectrum.

In the ATR method, it is important to stick a sample to the prism. Many people of diabetes are elderly, person with dry skin on the fingertips are also often elderly. Squalene oil is used as internal standard method for the different dry skin of the subject's finger surface. To eliminate the effects of dry skin by applying the squalene oil, we can measure the subjects under the same conditions. And, there is no effect of squalene oil to apply normalization correction in the absorption peak of squalene oil. Furthermore, the S/N ratio of the spectrum is better, because to block the air from between the finger and prism by the oil.

4.2.2 How to calculate the blood glucose value from the spectrum

We calculated the blood glucose value by using absorption spectra and PLSR. The invasion type blood glucose sensor (Antsense-2, DAIKIN) by enzyme electrode method is used for the measuring the reference blood glucose value.

First, we developed the calibration curve by PLSR, the measuring absorption spectra were used as the explanatory variable, measuring the blood glucose values by Antsense-2 were used as the objective variable. In calibration curve, the horizontal axis is the Antsense blood glucose value, and the vertical axis is the estimated blood glucose value by PLSR. Next, we measured to the new absorption spectra to measure the blood glucose value. Then, the blood glucose was calculated by using the measured absorption spectrum and calibration curve. And, we calculated the SEC and the SEP. Their values were used as the evaluated the accuracy of the calibration curve.

4.2.3 Error Grid Analysis (EGA)

EGA was developed by William L. Clarke in the University of Virginia. EGA is an indicator of clinical efficacy of blood glucose sensor. In fact, an error grid has been assembled to stay in the ideal range of $70 \sim 180 \text{ mg/dl}$ blood glucose value.

The Clarke grid of EGA is shown in Fig.4. The horizontal axis is the actual blood glucose, and the vertical axis is the blood glucose value obtained from the developed blood glucose sensors. In this study, when measuring the blood glucose must be clinically effective. We judged the efficacy as a blood glucose sensor using the EGA.

4.3 Absorption spectra of glucose, squalene oil, and finger

In measuring the blood glucose value, must know the absorption peak of glucose spectrum.

In addition, we need to know the absorption wavelengths of squalene oil to be used as an internal standard method. Each sample was measured by ATR method (plate type prism). The absorption spectra of glucose powder and squalene oil are shown in Fig.5. The absorption spectrum of glucose has some absorption peaks in 1030 cm⁻¹ (Fig.5-A, C-OH stretching vibration), 1130cm⁻¹ (Fig.5-B, C-O-C antisymmetric stretching vibration), and 1450 cm⁻¹ (Fig.5-C, CH₂ scissoring vibration). The absorption spectrum of squalene oil has some



Fig. 4. Clarke grid



Fig. 5. The absorption spectra of glucose powder and squalene oil

absorption peaks in 1377 cm⁻¹ (Fig.5-D), 1462cm⁻¹ (Fig.5-E), and 2922 cm⁻¹ (Fig.5-F). The absorption peak of glucose and oil were not overlap.

The absorption spectra of the finger in before and after coating to squalene oil are shown in Fig.6. In absorption spectrum of finger, absorption peaks in 1377 cm⁻¹ and 1462 cm⁻¹ did not appear. But, absorption spectrum of finger coated with squalene oil has absorption peaks in 1377 cm⁻¹ (Fig.6-D) and 1462 cm⁻¹ (Fig.6-E). Therefore, it is possible to reduce individual differences in skin surface conditions due to the absorption spectra normalized at the absorption peak of squalene oil. We confirmed that the squalene oil is suitable as an internal standard method, and can measure the blood glucose value by absorption peaks of glucose.

4.4 Non-invasive blood glucose measurement in subjects

4.4.1 Development of calibration curve

The subjects were healthy eight men in their 20s. When developing a calibration curve, glucose tolerance test were performed on each subjects. In glucose tolerance test, first, the



Fig. 6. The absorption spectra of the finger in before and after coating to squalene oil

subjects fasted for 12 hours. Then, subjects are ingested 75 g glucose, temporary increases in blood glucose value of subject. After the glucose tolerance test, we measured to the infrared absorption spectra and the invasive blood glucose measurement in every three minutes 20 times. Furthermore, after breakfast, before and after lunch, before and after dinner, we measured for four days (five times measurement in a day). We measured the total 40 times in one subject. The calibration curve is developed using these infrared absorption spectra.

Fig.7 shows the calibration curve developed in 320 infrared absorption spectra by all 8 subjects. In these results, the average blood glucose of the subjects was 120 mg/dl, correlation coefficient (CC) was 0.79, and measurement accuracy (SEC) was \pm 21 mg / dl. This result in this sample scale has been obtained a significant correlation, but, this result was not satisfactory as a blood glucose measurement system. As the cause of this, it is considered to the individual differences by moisture content of each subject. Therefore, we developed each individual calibration curve using the infrared absorption spectrum of each subjects. The results of individual calibration curves are shown in Table 1. Comparing the individual calibration curves and all subjects calibration curve has improved the



Fig. 7. The calibration curve developed by all subjects

	CC	SEC	A zone	B zone	C zone	D zone	E zone
All	0.79	21	77%	22%	0%	1%	0%
#1	0.90	13	90%	7%	0%	3%	0%
#2	0.95	16	90%	10%	0%	0%	0%
#3	0.71	22	68%	32%	0%	0%	0%
#4	0.71	14	83%	17%	0%	0%	0%
#5	0.90	7	100%	0%	0%	0%	0%
#6	0.84	16	90%	10%	0%	0%	0%
#7	0.67	28	60%	35%	0%	5%	0%
#8	0.96	95	95%	5%	0%	0%	0%

(CC : Correlation coeficience, SEC : mg/dl)

Table 1. The results of all subjects and individual calibration curves by PLSR

measurement accuracy of 6 among 8 subjects. In addition, the EGA results have improved in the same 6 subjects. The individual differences are eliminated by the individual calibration curve, and may be considered to be developed the most suitable calibration curve of each subject. Therefore, we measure blood glucose value of subjects by using the all subject calibration curve and individual calibration curve.

4.4.2 Non-invasive blood glucose measurement by calibration curve

Each subject was measured again 20 times the infrared absorption spectra. We measured the blood glucose value by these absorption spectra and developing calibration curve in section 4.4.1. The result by calibration curve in all subjects and individual calibration curve are shown in Fig.8. The average blood glucose value was 100 mg/dl.

In the result of blood glucose value calculated by all subjects calibration curve in Fig.8-(A), the SEP was ±32 mg/dl. This result was not good. On the other hand, in the result of blood glucose value calculated by individual calibration curve in Fig.8-(B) the SEP was ±13 mg/dl,



Fig. 8. The result by developed calibration curve in all subjects and individual

this result was dramatically improved. And, by the EGA result, A-zone is 90%, and B-zone is 10%, this result was shown to be clinically effective. It is also considered to the impact of individual differences as this reason. Evanescent light is measured to invasion into the finger of about $0.3~2 \mu m$ in the ATR method, and, it is considered the infrared light not get to the blood vessel inside finger. Therefore, we are considered measured the interstitial tissue fluid. When the glucose comes out in tissue fluid from blood vessel, there is the time difference in between individual. So, if the subject measure the blood glucose by the calibration curve including other subjects information, the result have come to greatly affect these individual differences. For the above reasons, we measure the blood glucose value by using individual calibration curve of each subject.

4.4.3 Verification of the calibration curve by loading vector

In order to verify the validity of the calibration curve, we focused on the weighting of the loading vector obtained from the developed calibration curve. The loading vector is the calibration curve of data (infrared absorption spectra). In other words, the loading vector shows the wavenumber band to the impact to the calibration curve. The weighting of the loading vector by individual calibration curve in section 4.4.1 is shown in Fig.9-(A). The horizontal axis is the wavenumber, and the vertical axis is the weight of the loading vector.

There are absorption spectra three weighting curves because the number of PLS factors (principal components) obtained are three factors. In Fig.9-(A), in this loading vector, the wavenumber in 1220 cm⁻¹ (Fig.9-(A)-A), 1150 cm⁻¹ (Fig.9-(A)-B), 1020 cm⁻¹ (Fig.9-(A)-C) were found to significant impact on the calibration curve.



Fig. 9. The weighting of the loading vector and each blood glucose value

Fig.9-(B) shows the infrared absorption spectra in large discrepancy between the subjects blood glucose value. In Fig.9-(B), characteristic absorption peaks can be found in 1220 cm⁻¹ (Fig.9-(B)-A'), 1150 cm⁻¹ (Fig.9-(B)-B'), 1020 cm⁻¹ (Fig.9-(B)-C'). It is proportional to the blood glucose value and the absorbance in 1220 cm⁻¹ and 1020 cm⁻¹, and found a negative proportional relationship in 1150 cm⁻¹. The weighting of the loading vector is almost

matched by changes in infrared absorption spectra of blood glucose variability. From the above, it has been shown to accurately measure the blood glucose value from the glucose information in this method. Therefore, we can be proposed as a non-invasive blood glucose measurement by the infrared spectral measurements.

4.5 Clinical application of measurement system

We have measured the diabetics that have been actually measured blood glucose. Subject is four diabetics. We were measured before and after meals for 4 to 5 days in each subject. First, we developed the individual calibration curve of each subjects by using the PLSR analysis and infrared absorption spectra obtained in the three-day measurement. Then, the measured infrared absorption spectra in the 1-2 day were substituted in the developed calibration curve, and the blood glucose value was estimated.

Table 2 shows the blood glucose data for each subject obtained by the conventional method for three days from the first day, and the results of the developed calibration curve for each subject by using the measured infrared absorption spectra. And Fig.10 shows the calibration curve of subject #1. From these results, this measurement system can be constructed to calibration curve for measuring blood glucose of diabetics, because, significant correlation has been obtained in this sample scale. The result of subject #4 show very good results than the other subjects. As this cause, the number of samples is very few for construct calibration

Subject #	Number	Ave.	Max.	Min.	S.D.	C.C	SEC
1	15	226	339	156	56	0.758	± 35
2	16	216	330	150	44	0.519	± 37
3	10	157	221	108	41	0.645	± 29
4	9	113	203	58	44	0.997	± 3





Fig. 10. The calibration curve of subject #1

curves, and the average blood glucose value is small. In addition, it is considered to overfitting, because the PLS factor number is 5.

The spectra of diabetics as measured by the fourth day and fifth day were substituted in the individual calibration curve of each subject. Table 3 shows the accuracy of predicted blood glucose value and the EGA result. In addition, the scatter diagram of the Clark grid result of each subject is shown in Fig.11. From the EGA result, all data with one exception of subject #4 data are plotted in A and B zone of clinically safety ranges. Improvement of measurement accuracy is better, but, the important in clinical practice is give first aid when the blood glucose value showed abnormal. Therefore, from a good EGA results, this system can be treated as a reasonable measurement method of blood glucose value in diabetics in clinical practice.

Subject #	SEP	EGA-Zone					
Subject #		А	В	С	D	E	
1	± 70	50%	50%	0%	0%	0%	
2	± 60	67%	33%	0%	0%	0%	
3	± 49	20%	80%	0%	0%	0%	
4	± 59	45%	45%	0%	10%	0%	



Table 3. The accuracy of predicted blood glucose value and the EGA result

Fig. 11. The Clark grid result of each subject

To measure simply place a finger on the prism, this system has the advantage of measuring blood glucose value very easily for diabetics in many elderly. In addition, the burden on nurses is reduced, because the patient can measure in their own. Since the measurement time is about 1 minute, it is possible to measure the many patients in a short time. This is a worthwhile part in the clinical practice. When this system is used as a self-monitor blood glucose sensor of diabetic patients, the measurement error is a large. In particular, SEC of the subject #4 was \pm 3 mg/dl, but SEP has become extremely large forecast error in \pm 59 mg/dl. This cause is considered to the over-fitting, when building a calibration curve as previously described. In PLSR, if the increasing the number of the PLS factor, SEC is a smaller, SEP becomes large. Therefore, it is necessary to construct a standard curve with the optimal

number of the PLS factors. From the comparison of the SEP and SEC, the optimal number of PLS factors for this measurement system is considered to be 2 or 3. Thus, with less data in after the start of measurement, we shall construct the calibration curve careful in the number of PLS factors. To improve measurement accuracy, we need to consider improving the system. If increased in the amount of information obtained from absorption spectra, we can be measured blood glucose value more accurately. That is, if increased the amount of infrared light obtained from the subjects' finger, the measurement accuracy is improved.

4.6 Conclusion of non-invasive measurement for blood glucose by IR spectroscopy

We can confirm non-invasive blood glucose measurement system developed in this study is effective tools in clinical practice. In this measurement system, there is no pain which was felt by many diabetics so far. Because measurement time is 1 minute, it can be measured very easily and quickly. There is no stress to the patient, can measure to blood glucose value several times a day because the measurement time is very short.

Future challenges of this study are shown below. The number of subjects and the number of measurement times must be increasing. We must show in this measurement reproducibility. And, we must show that this system can be applied to any subject. If the blood glucose measurement sensor has been developed in this measurement method, future, this research will contribute significantly in community of increasing diabetics.

5. Non-destructive analysis of the composition and mixture ratio for textile products based on infrared spectroscopy

5.1 Background

This section describes a Non-destructive analysis of the composition and mixture ratio for textile products. In Japan, the composition display of textile goods is obligated by the "Household Goods Labeling law". Therefore, analysis of the composition and mixture ratio for textile products in accordance with JIS method (L 1030-1,-2) are executed. But, existing methods is the destructive inspection, and a lot of time (six hours or more) and proficiency is necessary for the analysis. Also has concern about the safety and the environmental impact of such tests to use chemicals such as organic solvents. In addition, if the amount of remaining dirt on the sample is very small, if the remaining dirt color is same color of sample, the dirt cannot be verified visually.

In here, it proposes the application of the infrared spectroscopy for improve those problems. The method that we propose is non-destructive measurement, quickly and easy. We measured an infrared absorption spectrum of a textile by using a FT-IR. And we examined the possibility of a composition classification and a mixture ratio calculation by chemometrics. These experiments showed that the measurement system was effective.

5.2 Analysis of the composition and mixture ratio for yarn products by ATR

5.2.1 Measurement system for yarn products

Measuring system in this study, FT-IR (IRPrestige-21) and ATR method (DuraSampler-IR) was used. Measuring system is shown in Fig.12. The measuring yarn is folded, and set to cover on the prism. After, the measurement part of the prism and yarns were contacted by



Fig. 12. Measurement system for yarn products

pressing parts from above. IR spectrum is measured with this device. It is quickly because the measurement time is about two minute. The resolution, the accumulation, the measuring wavenumber range set at 4 cm⁻¹, 50 times, 4000~500cm⁻¹ (wavelength 2.5~20 μ m) measurement condition.

5.2.2 Analysis of the composition of yarn products

We used 7 samples, Cotton, Silk, Hemp, Wool, Polyester, Rayon, and PET. We used the KNN method to determine the composition of textile products. Building a KNN space was divided into seven classes by type for each spectrum. KNN space was built by a total 140 spectra by 20 spectra for each sample. 10 spectra of each sample as an unknown sample are put into space. We tried each spectrum to be divided into classes. KNN space was constructed in wavenumber range in 1800-650 cm⁻¹. Because, there were characteristic peaks of each samples in this wavenumber range.

The result of qualitative analysis for each sample is shown in Table 4. Results showed that all samples are classified correctly from Table 4. Therefore, it is possible to the qualitative evaluation in a single composition yarn by this measurement method. We were able to determine the cellulose yarns of cotton and hemp, is very good results.

Infrared absorption spectra of cotton and hemp are shown in Fig.13. These spectra in Fig.13 are very similar, because the main component of cotton and hemp is cellulose. Very different point is the absorbance intensity of 1180 cm⁻¹ (Arrow in Fig.13). This absorbance

	Cotton	Silk	Wool	Hemp	Polyester	Rayon	PET
Cotton	10/10	0/10	0/10	0/10	0/10	0/10	0/10
Silk	0/10	10/10	0/10	0/10	0/10	0/10	0/10
Wool	0/10	0/10	10/10	0/10	0/10	0/10	0/10
Hemp	0/10	0/10	0/10	10/10	0/10	0/10	0/10
Polyester	0/10	0/10	0/10	0/10	10/10	0/10	0/10
Rayon	0/10	0/10	0/10	0/10	0/10	10/10	0/10
PET	0/10	0/10	0/10	0/10	0/10	0/10	10/10

Table 4. The result of qualitative analysis for each sample by KNN



Fig. 13. Infrared absorption spectra of cotton and hemp

intensity difference is the difference between the percentage of cellulose in cotton and hemp. And, the cotton and hemp has slightly different components (such as pectin) present, but those absorption peaks are very small. In this method to accurately measure this subtle difference, qualitative analysis for each yarn was possible.

5.2.3 Measurement of mixture ratio of mixed yarn

In textile products, the mixed yarn including multiple compositions is present. In the mixed yarn should seek the composition and percentage of each composition. Measurement of composition percentage of mixed yarn, we used cotton and polyester mixed yarn samples 45 kinds. These yarns were measured 5 times each spectrum, the average of the measured spectra. Developing a calibration curve by PLSR, focusing on the absorbance wavenumber specific absorption peaks in the components of the cotton and polyester in average spectra. Substituting the spectrum of the unknown sample to the calibration curve, calculated the composition percentage of cotton.

The absorption spectra of the yarn are shown in Fig.14. In the Fig.14, "C" shows for the percentage of cotton, and "P" shows for the percentage of polyester (C100P0 : 100% cotton yarn, C90P10 : 90% cotton and 10% polyester mixed yarn,..., C0P100 : 100% polyester yarn). These absorption spectra are changing the percentage of mixed of the cotton and polyester in increments of 10 %. There are several wavenumber ranges of absorbance changing just like the mixture ratio. The absorbance of 3392 cm⁻¹, 1624 cm⁻¹, 1226~1039 cm⁻¹ peaks are proportional to the percentage of cotton. And, the absorbance of 1738 cm⁻¹, 1409 cm⁻¹, 1298 cm⁻¹ peaks are proportional to the percentage of polyester. Therefore, by analysis in the wavenumber range including these characteristic absorption peaks, we can determine the mixture ratio. Using the spectra of cotton and polyester mixed yarn, the results of PLSR in wavenumber range in 3000~700 cm-1 is shown in Fig.15-A. The absorption spectrum was subjected to spectral correction and differential for the measurement S/N ratio in order to standardize. The horizontal axis represents the composition percentage of cotton, and the vertical axis is the estimated value of cotton from the PLSR. The results of the correlation coefficient and the measurement accuracy (SEC) were 0.988 and ±3.4%. This result indicates a highly significant correlation. This calibration curve is considered to be reasonable. Thus, this calibration curve is good result, we used this calibration curve of cotton and polyester mixed yarn.



Fig. 14. The infrared absorption spectra of the mixed yarns

And for the validated on calibration curve, the 10 samples were measured. The validation result of the calibration curve is shown in Fig.15-B. The result of SEP is $\pm 6.2\%$. To view the percentage of mixed yarn in increments of 5 %, measurement error is preferably less than \pm 2.5%. This result cannot accurately display the percentage of mixed yarn. As a cause, it is a small number of spectrum using in the calibration curve. Therefore, the next a problem to be solved, increased the number of spectra without lowering the accuracy of the SEC, and to create a more reliable calibration. If we have overcome the challenges, it is possible to reduce the SEP of the percentage of mixed yarn, and possible to measure accurately the percentage of mixed yarn.



Fig. 15. The calibration curve and validation result for mixed yarn

5.3 Analysis of the composition and mixture ratio for fabric products by diffuse reflection method

5.3.1 Measurement system for fabric products

There are yarn products as well as a lot of fabrics products. We have to measure analysis of the composition and mixture ratio for fabric products. Measuring system for fabric products, FT-IR (IRPrestige-21) and diffuse reflection method (UP-IR) was used. Measuring system is shown in Fig.16. The sample fabric is placed to cover the hole of the top of the UP-IR, and a mirror mounted on the sample fabric.



Fig. 16. Measurement system for fabric products

As test samples, we used 38 fabrics of cotton 100%, 42 fabrics of polyester 100%, 71 mixed fabrics of cotton - polyester (CP sample). In the sample, there are woven fabric and knitted fabric, colour and thickness is different respectively. The ratio of polyester and cotton in P/C sample is also various. In measurement of spectrum, measuring range, resolution, and accumulation were 4000~700 cm⁻¹, 4 cm⁻¹, and 20 times. In addition,we were measured in five points on each sample to measure the entire fabric.

5.3.2 Analysis of the composition of cotton and polyester fabric products

The composition of the fabric products were analysed using these absorption spectra and SIMCA. The fabric samples are classified into 100% cotton class (Class C), cotton and polyester mixed fabric class (Class CP), 100% polyester class (Class P). For the development to classification model, the absorption spectra of the 100% cotton and the 100% polyester were used each 20 samples (100 spectra), the absorption spectra of mixed fabric were used 35 sample (175 spectra). The remaining sample spectra were used to validate the classification model. We constructed four times classification models by SIMCA, and tried the classification of the spectrum. Those models changed random the combination of spectrum for class making and spectrum for verification and were constructed.

The result of constructed classification model is shown in Table 5. A high distinction rate was obtained in each model. From these results, the information on each sample was able to be extracted accurately by SIMCA. Especially, the percentage of correct answers in Class C

	1st	2nd	3rd	4th
Class C	97%	93%	93%	97%
Class CP	95%	94%	96%	97%
Class P	81%	81%	91%	88%

Table 5. The result of constructed classification model

and Class CP is all over 90 %. Meanwhile, the percentage of correct answers in Class P is lower than other classes. As this cause, it is considered the polyester included different components as the polyethylene terephthalate (PET) and poly trimethylene terephthalate (PTT). The first differential spectra of cotton and polyester and discrimination power are shown in Fig.17. Discrimination power indicates the magnitude of the effect of each wavelength, when the samples are classified into each class. By Fig.17, it was confirmed that it had been classified by composition information because main peak of discrimination power was corresponding to peak of spectra. Therefore, the validity of classification model was shown.



Fig. 17. The first differential spectra of cotton and polyester, and discrimination power

5.3.3 Measurement of mixture ratio of fabric products

We must seek a mixture ratio of the sample, when the sample is classified as mixed fabric by SIMCA method. Therefore, mixed ratio determined using the PLSR. The samples and measurement method are same to section 5-3-1. However, the average spectrum of five spectra obtained from one sample was used as a measured absorption spectrum of this sample. We developed the calibration curve by using absorption spectra and known mixture ratio. In this time, the known mixture ratio is used the mixture ratio of the polyester.

The measurement result is shown in Fig.18-(A). In this Fig.18-(A), this result has a highly significant correlation. And, SEC is 2.9 %. To display in increments of 5 % to the product mixture ratio, SEC needs to be less than 2.5 %. If you check the Fig.18-(A), the sample near the reference mixture ratio $40\sim50$ % is distant from Y = X. The absorption spectra of this sample (Sample-A) and sample of close to the Y = X (Sample-B) are shown in Fig.19. In Fig.19, the mixture ratio of two samples is very similar, but, the shape of the absorption spectra is different. This was the impact of textile design different of each sample. Ratio of the kind of strings that appear on the surface is different by two sides when the composition is different because of warp yarn and weft yarn. It influences the spectrum shape.



(A) Calibration curve by normal spectra(B) Calibration curve by AVE spectraFig. 18. Prediction result of mixture ratio of polyester in normal spectra and average spectra



Fig. 19. The absorption spectra of sample A and B

Consequently, the diffuse reflectance spectrum was acquired on both sides of these samples.

The top surface and bottom surface in each sample was measured five times, averaged of obtained 10 spectra. Result of calibration curve developed by using average spectra and PLSR is shown in Fig.18-(B). The sample near the reference mixture ratio 40~50 % is close

in Y = X, and SEC has also improved. Furthermore, this system can be measured mixture ratio of mixed fabric products, because we could be obtained the good result which SEC is 1.8%.

5.4 Conclusion of non-destructive analysis of the composition and mixture ratio for textile product

In this paper, qualitative analysis of a single composition yarn could determine the exact composition of all. And, the measurement of percentage of mixed yarn can build a good calibration curve, which can be mixed with non-destructive measurement. IR spectrum with each feature of polyester and cotton and CP fabric sample quickly was able to be acquired by using the diffused reflection method of FT-IR. It turned out that our method was able to be applied from this outcome of an experiment to textile goods.

In the future, we need to build calibration curves for mixed yarn of other materials. If measurement method will be developed, could be proposed as a new method having better characteristics for measuring of textile products. The measurement time is about 10 minutes in this system. Since this system has the characteristics of these, bring significant benefits to such the samples of indestructible material determine the historical artefact and cultural heritage. From these results, we propose a new evaluation method of textile products not previously exist.

6. Measurement system of remaining dirt on inner surface of a narrow tubule based on infrared spectroscopy

6.1 Background

There is surely remaining dirt on the used products. In order to use the product for long periods, you need to wash the dirt. Therefore, many studies have been done for the dirty washing techniques and cleaning agents, analysis of remaining dirt. It has been researched in so many fields as the industrial, medical, food, yarn sector. The study of wash technology is so many, but washed cleanliness assessment has been neglected. As one of the reasons, we are under the impression that convinced that the product which satisfactory results were obtained by visual evaluation has not remaining dirt.

Especially, in the medical institutions, must be careful to hospital acquired infections. To prevent hospital acquired infections, cleanness is essential for all medical equipment. In particular, the instruments used in the human body must be aware of the cleanness. If you cannot detect small amounts of remaining dirt by visual evaluation, might be robbed a life. Therefore, the nurse must evaluate the cleanliness of the equipment used after cleaning and sterilizing. So far, the cleanness of medical equipment has been evaluated by visual inspection, test soil method or ATP method. But, these measurement methods have several disadvantages (individual differences, re-cleaning, numerical evaluation is difficult et al). This paper examines the application of qualitative and quantitative evaluation to residual contamination on the medical devices by infrared spectroscopy, and discussed the possibility of a new cleanness evaluation method. It is also difficult to evaluate the cleanness of a narrow tubule which is used by endoscope or drip tube. In this study, we developed a measurement system of the remaining dirt on the inner surface of narrow tubule.

6.2 Measurement system by IR fiber probe method

By the measurement method of remaining dirt on inner surface of narrow tubule, devised a system that combines the cone-shaped mirror and IR fiber probe, as shown in Fig.20. This system is inserted into the narrow tubule. Infrared light passing through the fiber probe is reflected by the cone-shaped mirror, and to irradiate the inner surface of the narrow tubule. If the dirt remains on inner surface of tubule, the infrared light is absorbed by the amount of dirt. Absorbed infrared light is reflected by the cone-shaped mirror, and is detected after passing through the fiber probe. We measured four times for one measured value. The cone-shaped mirror (Bottom diameter and Height: 4mm) placed inside the aluminium pipe. The fiber probe was arranged on 1 mm distance from the top of the aluminium pipe. We measured in this arrangement (1st time), and aluminium pipe was rotated 180 degrees (2nd times), and turn aluminium pipe upside down (3rd times), and aluminium pipe was rotated in the measurements. The resolution, the accumulation, the measuring wavenumber range set at 4 cm⁻¹, 100 times, 4000~900 cm⁻¹ measurement condition.



Fig. 20. Measurement system of remaining dirt on inner surface of narrow tubule

6.3 Qualitative analysis of lard

The remaining dirt of endoscope is excreted from the human body. For example, blood, protein and lipid dirt. We used the lard as a model of triolein contained in the lipid dirt. The absorption spectra of lard and triolein are shown in Fig.21. Many peaks by lard can be seen in spectra (2920 cm⁻¹, 2850 cm⁻¹ : stretching vibrations by CH₂ groups, 1470 cm⁻¹ : scissoring vibration by CH₂ group, 750 cm⁻¹ : bending vibration by CH, 1740 cm⁻¹ : stretching vibrations by C=O, 1160 cm⁻¹ : antisymmetric stretching vibrations by CO). From this absorption spectrum, lard is the ideal remaining dirt model because is very similar to triolein present in the human body.

In the sample preparation, lard and aluminum pipe (ID: 5 mm, OD: 10mm, height: 8 mm) were used as the model substance of the human soil and narrow tubule. Model sample were prepared by the following process. Lard is dissolved in the hexane solution. The aluminum pipe has been kept in the solution for 1 minute. The sample pipe is left in the laboratory for five minutes until the residual hexane is fully evaporated. The dirt on the outer surface of aluminum pipe is wiped off. The weight of aluminum pipe before and after these processes was measured by using the electronic balance. The weight difference of aluminum pipe was used as the remaining amount of the lard (measured value).



Fig. 21. The absorption spectra of lard and triolein

6.4 Cleanness evaluation of inner surface of the narrow tubule by PLSR

This study uses the PLSR analysis to obtain more accurate information contained in the infrared absorption spectrum of contaminants. To measure the amount of remaining dirt on the inner surface of the narrow tubules, first, we measured the infrared absorption spectrum of a known amount of remaining dirt, and the calibration curve was made using the measured infrared spectra by PLSR. Then, measuring the infrared absorption spectrum of an unknown amount of remaining dirt samples, we calculated the amount of deposited from the calibration curve was constructed. The number of sample are 50 kinds, the average amount of remaining lard is 0.65mg. As a cleanness evaluation of inner surface of the tubule, calibration curves were constructed with the PLSR. The analysis wavenumber range is 1800~1000 cm⁻¹.

The correlation scatter diagram of the calibration curve is shown in Fig.22-(A). The absorption spectrum was subjected to spectral correction and differential for the measurement S/N ratio in order to standardize. The horizontal axis represents the amount of lard, the vertical axis is the estimated weight obtained from the PLSR. The results of the correlation coefficient and the SEC were 0.843 and \pm 0.19 mg/cm². This result indicates a highly significant correlation. This calibration curve is considered to be reasonable. The main causes of this, many lard information was considered obtained more than a single absorption peak because we analyzed a wide wavenumber band including a plurality of absorption peaks on the infrared spectra.

And for the validated on calibration curve, the 10 samples were measured. The estimated remaining dirt value is calculated from assign the measured spectra to a calibration curve. And, we weighed the samples, obtained this weight as the reference value. The validation result of the calibration curve is shown in Fig.22-(B). The results of the correlation coefficient is 0.957, and the SEP is ± 0.10 mg. EI (Evaluation index) method was applied for validation of the calibration curve, the EI value was shown to 21.5%. This value is classified into highly practical rank B. Thus, the amount of remaining dirt on the inner surface of narrow tubule could be measured quantitatively. And shown in Fig.22-(B), substituting the infrared absorption spectrum of minimum coating weight was calculated 0.08 mg by the calibration curve, the detection limit of this method is considered to be less than 0.08mg, as well as other measurement method. These results lead us to the conclusion that the cleanness on the inner surface of narrow tubule can be measured by this measurement system.



(A) The calibration curve for cleanness(B) The validation result of calibration curveFig. 22. The calibration curve and the validation result

6.5 Conclusion of cleanness evaluation by IR spectroscopy

The results obtained in this study, this measurement system was only possible to evaluate the cleanness of the inner surface of a narrow tubule.

The measurement time is about 2 minutes, which is shorter than the other measurement methods. In addition, this system is possible to measure in non-contact and non-destructive, because only the infrared light irradiation. And, we can detect the multiple dirt by using FT-IR. Therefore, even if protein and blood are remained together with lipid contamination, respectively dirt can be detected by this measurement method.

The next challenge is to integrate the fiber and the cone-shaped mirror. When we overcome the next challenges, this measurement system also can be used to long narrow tubules. If there is no dirt, the absorption peak is not detected, only if the dirt is remaining, to detect infrared spectra. From the position of the fiber probe when dirt is detected, the remaining dirt position can be identified. The type of remaining dirt can be identified from the shape of infrared absorption spectrum, and the amount of remaining dirt is detected by using a calibration curve.

By the characteristics of more than, this measurement system has so many advantages, we report as a new method of measuring remaining dirt. Thus, this system is possible to evaluate the cleanliness of the inner surface in narrow tubules. And can be reduce the risk of nosocomial infections in clinical practice.

7. Conclusion

As has been mentioned above, a non-destructive measurement can perform in many areas by using FT-IR. And, Infrared spectroscopy can be measured in quickly, non-contact, nondestructive. Therefore, various sensors will be able to develop by devise of measurement method and analysis method. Infrared spectroscopy can measure liquids and gases. In

addition, infrared spectroscopy can also detect very small concentrations and small quantities such as invisible. So, you will be able to be developed a better measurement systems and sensors that measure did not previously exist.

Challenges of Infrared Spectroscopy, is miniaturization or lighter or less expensive. In the now, these challenges are resolved in the near infrared wavelength range. However, in the mid-infrared wavelength range has not yet been resolved. This is a challenge must be overcome if you want to commercialization. However, if you will be successfully to size down, would be used as more advanced sensors. By using infrared spectroscopy, it will be developed a sensor that can measure accurately than current sensors. We want to propose, the Infrared spectroscopy is not just equipment but can be applied to a variety of measurements. We are wishing, in the future, infrared spectroscopy research will be expanded, and, FT-IR become more familiar measuring device. If that era will be arrival, the people would be receiving significant benefits from the infrared spectroscopy.

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This informative and state-of-the art book on Infrared Spectroscopy in Life sciences designed for researchers, academics as well as for those working in industry, agriculture and in pharmaceutical companies features 20 chapters of applications of MIRS and NIRS in brain activity and clinical research. It shows excellent FT-IR spectra of breast tissues, atheromatic plaques, human bones and projects assessment of haemodynamic activation in the cerebral cortex, brain oxygenation studies and many interesting insights from a medical perspective.

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