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Analysis Technology of Residual Solvent of Printed Inkjet Ink with Near-Infrared Spectroscopy

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Abstract

Near-infrared (NIR) spectroscopy for analysis of residual solvent of printed inkjet ink on-site is newly developed. In the industry of water-based inkjet ink, heat drying process is performed after printing. However, residual solvents remain on the printed matter after the drying process, and these residual solvents affect ink-fixing properties. Gas-chromatography (GC) or gas-chromatography mass-spectrometry (GC/MS) is conventionally used for analyzing residual solvent of the printed matter. However, this method takes several days to obtain results. To analyze residual solvent on-site, NIR spectroscopy is developed, and the value can be quantitatively predicted on-site, and easily. Also, spatial resolution is improved with NIR compared with GC/MS measurement. Therefore, spatial distribution information can be obtained. Here, NIR spectroscopy for analyzing residual solvents in a short period of time, evaluating easily, and on-site is reported. Also, the relationship between residual solvent and fixing properties of the printed matter is studied in detail. The principle of measurement, and some application examples and relationships with fixing properties of the printed matter are reported in this paper.

Motivation

In the business of water-based inkjet ink for high-speed printing, printing speed and high image quality printing is required for offset coated paper. Inkjet printing for offset coated paper with water-based ink is technically difficult, however high image quality is required as well as that of conventional offset printing system [1]. Drying speed of water-based inkjet ink is known to be relatively slow because of organic solvent in the inkjet ink. It is well known that water-soluble organic solvent has relatively high boiling point.

Figure 1 shows functionality of inkjet processes. Recently, in the business for high-speed printing, drying process with heating, for example, heated drum and hot air dryer and so on (sometimes light exposure drying) is applied in the printing machine after printing. Recently, drying process of inkjet ink is hot research topic for recent inkjet science. Even after drying, residual solvents remain on printed matter and these residual solvents affect fixing properties. For example, when heated drum contacts with printed matter with residual solvent, breakdown phenomena of printed ink are observed. Therefore, quantitative measurement of residual solvents after drying process is technically very important for developing inkjet system and inkjet ink.

Usually, gas chromatography (GC) or gas chromatography-mass spectrometry (GC/MS) has been used for evaluating residual solvents of printed inkjet ink [2]. Figure 2 shows comparison of GC/MS method and newly developed NIR method.

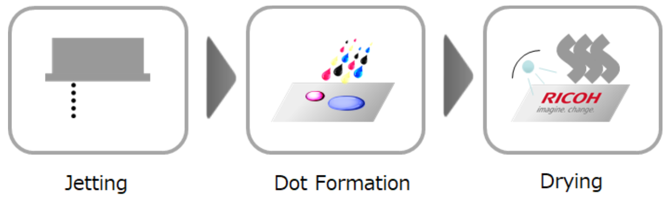


Figure 1. Printing and drying process flow of inkjet ink. Inkjet ink has function of jetting process, dot formation process, and drying process.

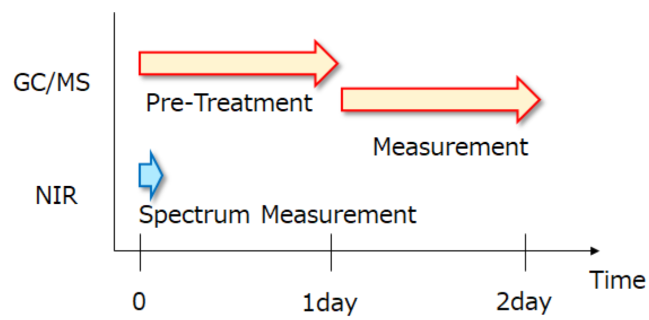


Figure 2. Comparison of measurement time of NIR and GC/MS. GC/MS method needs very long time to obtain results.

Conventional GC/MS methods need very long time (a few days) to obtain results. At least 1 day is needed for pre-treatment of sample, and measurement is for almost 1 days. Therefore, more convenient method is needed for development.

Here, NIR spectroscopy is introduced for analyzing residual solvents in a short period of time (a few minutes), evaluating easily, on-site and almost real-time. At first, the correlation between NIR and GC/MS is obtained and we call it "prediction model". Once the prediction model has been made, the residual solvent quantity is obtained from only NIR reflectance spectrum. The results can be estimated very quickly, and this method is very easy-to-use. And spatial resolution will be improved (5 mmϕ) compared with GC or GC/MS (10 mm x 40 mm). Therefore, spatial distribution evaluation will be possible with NIR.

The principle of measurement and application results are described in this paper. Also, the relationship between residual solvent and fixing properties of printed matter is studied in detail.

Method

Overview

The process of analyzing residual solvents with NIR is shown. At first, "prediction model" is necessary for NIR measurement. To make a prediction model, the correlation between NIR spectrum and GC/MS value must be obtained. First, NIR reflectance spectrum of printed matter is measured. NIR reflectance spectrum has baseline shift due to surface scattering of light, and peak-overlap among various materials. For these reasons, NIR analysis is difficult to analyze with simple methods such as FT-IR spectroscopy and UV-Vis spectroscopy.

In the field of agricultural science, NIR spectrum combined with multiple classification analysis method has been successful for measurement of material concentration such as water amount in the fruit [3,5]. We apply this method for measurement of residual solvents in the printed inkjet ink. Now, partial least square method, which is one of the methods of multiple classification analysis is explained.

Partial Least Square (PLS) Method

When we acquire the correlation between NIR and GC/MS, PLS method is used. PLS method is described by the following equation (1). xn is spectrum peak intensity of each wavelength, and bn is regression coefficient of each wavelength.

$$\text{Solvent} = \sum_{n} b_n x_n + \text{const.} \tag{1}$$

Each spectrum intensity and regression coefficient multiplication at each wavelength are summarized, so residual solvent is obtained from spectrum data mathematically. PLS method is one of the multiple classification analysis methods to obtain bn and constant term. To perform this method, reference residual solvent value must be obtained by using GC or GC/MS method and NIR spectrum in the same condition. To decrease the prediction error, validation method and principle component analysis method are used, and the appropriate principle component number is calculated. Once bn and constant value are obtained, residual solvents are predicted without GC or GC/MS measurement as described in Fig.3.

Second derivative of NIR spectrum

Raw NIR spectrum has baseline shift due to measurement noise. NIR spectrum has two types of noises; one is additional noise(a), and the other is multiplication noise(bλ). Additional noise is up-down shift of spectrum due to surface scattering of light, which is independent of wavelength.

$$g(\lambda) = f(\lambda) + b\lambda + a$$
$$g'(\lambda) = f'(\lambda) + b$$
$$g''(\lambda) = f''(\lambda) \tag{2}$$

Multiplication noise is dependent of wavelength and ever-increasing noise. To cancel the effect of noise, second-derivative operation of NIR spectrum is performed. In the equation (2), f(λ) is scattering-free spectrum, and g(λ) is actually measured spectrum. g(λ) has both additional noise and multiplication noise.

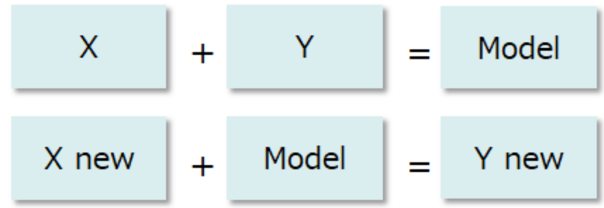


Figure 3. The diagram of prediction model. X is NIR spectrum data set, and Y is reference GC/MS residual solvent value. X new is unknown (new) NIR spectrum data set, and Y new is predicted residual solvent of unknown sample.

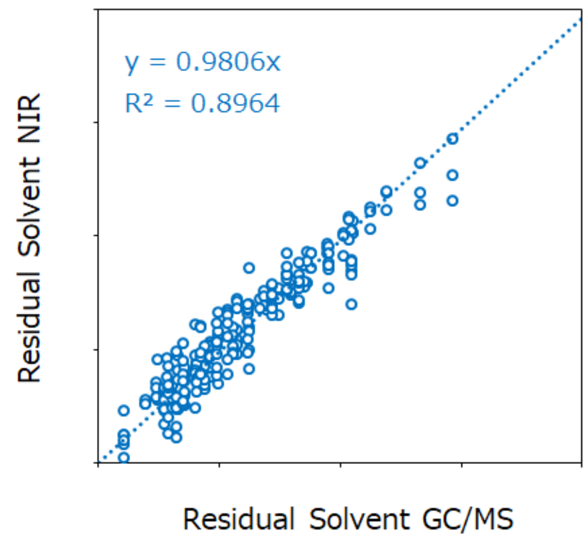


Figure 4. Prediction model of residual solvents with NIR and PLS method. Almost GC/MS equivalent accuracy is obtained.

However, if second-derivative operation is performed, noise is theoretically cancelled, and scattering-free spectrum is obtained.

Additionally, in second-derivative operation, smoothing operation is performed at the same time. Savitzky-Golay filter [4,6] is usually used for smoothing the spectrum. It is known that smoothing effect is high with this method. In this research, we used this method.

Example of Prediction Model

Figure 4 shows an example of prediction model of residual solvents. This model is obtained by PLS method and validation method. Almost GC/MS equivalent accuracy is obtained.

Prediction

When we perform PLS analysis, NIR spectrum data "X" and GC/MS value "Y" are prepared. We analyze "X" and "Y" with PLS method, then prediction model is obtained. When new unknown NIR data "X-new" are obtained, this prediction model is applied, and residual solvents "Y-new" is obtained numerically.

Essential Point of Making Prediction Model

When the prediction model is made, the model needs to contain various-situation data. Various situations mean not only controlling drying temperature and drying time, but also paper species, ink thickness, jetting processes, drying processes (air drying or light exposure) and so on. When the model contains various-situation data, the model can get general versatility and application area will be expanded.

Results

Product Ink testing on site

Our NIR equipment is very simple and portable. Therefore, we can evaluate residual solvent in anywhere. Inkjet ink under development can also be tested in the production testing on site and data can be obtained in almost real-time. Figure 5 shows one of the testing results of production machine testing.

Two prediction models are used; first, solvent A prediction model, second, solvent B prediction model. The amount of each residual solvent in the same ink sample can be obtained from one NIR spectrum data at the same time. We also evaluate the spatial distribution of printed matter with NIR. As printing speed increases, drying time decreases, and each amount of residual solvent increases. These results are reasonable. Good agreement with GC/MS measurement is also confirmed.

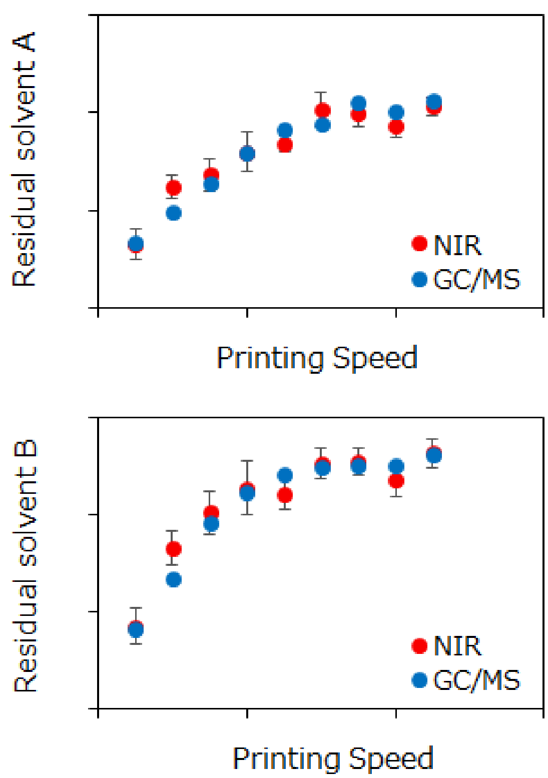


Figure 5. Application example of NIR, which is performed on-site near the production machine. Each amount of residual solvent is estimated from its prediction model which is made with PLS method.

This evaluation time is few minutes, and the evaluation efficiency is highly improved compared with conventional methods.

Study of Fixing Property

The relationships between residual solvent, mechanical property (adhesion force) and fixing properties (breakdown phenomena) of the printed matter are studied in detail.

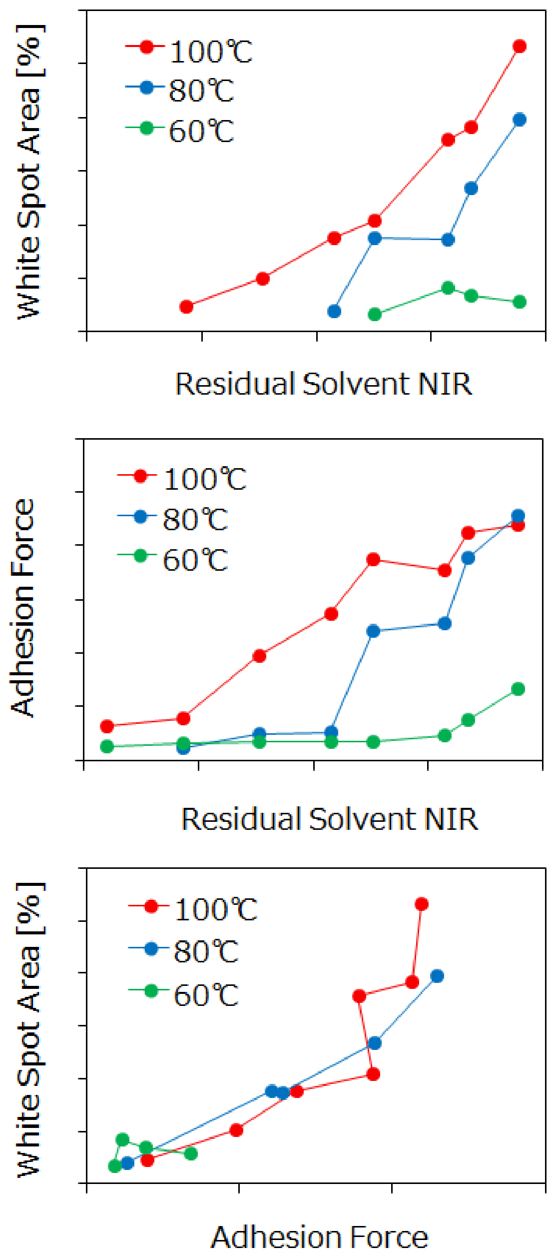


Figure 6. The relationship between residual solvent and fixing property of printed matter. Residual solvent was measured with NIR. The value of temperature means contact temperature with heated Al probe of few millimeter diameter.

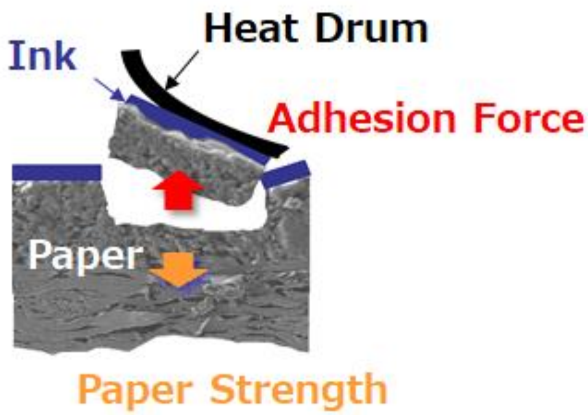
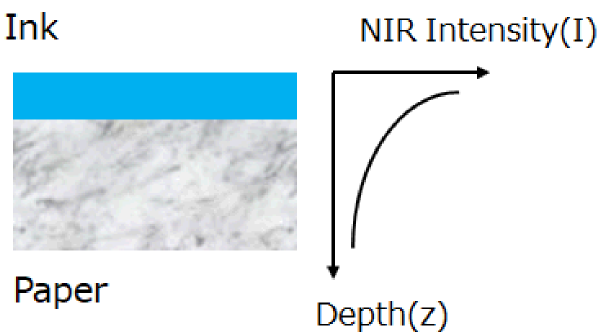


Figure 7. The model of breakdown phenomena of printed matter. When adhesion force of surface ink is higher than paper strength, breakdown phenomena will probably occur.



$$I = I_0 \exp(-Az)$$

Figure 8. Depth dependence of NIR light behavior. In this case. NIR diffuse reflectance measurement obey Kubelka-Munk theory. NIR light intensity decay exponentially with depth.

Residual solvent is measured with NIR, and also adhesion force between contact Al probe and printed matter of spot size of few millimeters is measured at the same time. The area of white spots in percent unit is also measured by using optical microscope and image analysis. This experiment is supposed to hot-offset phenomenon. The amount of residual solvent increases, the area of white spots increases. And white spot area increases with contact temperature. As residual solvent increases, adhesion force of printed matter also increases. Contact temperature dependence of adhesion force is also confirmed in this experiment. As contact temperature increases, adhesion force also increases. The area of white spots of printed matter is strongly correlated with the adhesion force of printed matter.

To understand this phenomenon, an ink fixing model is proposed as shown in Fig.7. Residual solvent affects adhesion force of surface ink and paper strength. If the residual solvent is rich, adhesion force becomes higher and paper strength becomes weaker.

When adhesion force is higher than paper strength, breakdown phenomena will probably occur. When residual solvent increases, the adhesion force will increase, and paper strength will decrease. The area of white spots may depend on both surface adhesion force of ink layer and paper strength. In this case, the ink layer and the small portion of the paper are destroyed, and they detach from the bulk of the paper. As the result, white spot areas are generated, and adhesion force and the area of white spots are strongly correlated.

Adhesion force of surface ink layer and paper strength are wanted to be measured quantitatively at the same time. However, quantifying paper strength is technically difficult. Also, measurement of residual solvent in surface ink layer and paper layer separately is also difficult. Therefore, measurement of depth-profile of residual solvent is our future work.

Figure 8 show depth dependence of NIR analysis principle. In this case, NIR reflectance measurement is described by Kubelka-Munk theory, and NIR light intensity decay exponentially with depth. This theory is considered, and we will develop our NIR measurement technique.

Conclusion

NIR technology can be applied to evaluating residual solvent of printed inkjet ink. Compared with the existing method, this method has the merits of getting results very quickly, evaluating on-site, easy to use, and improved spatial resolution. This equipment is simple and portable, so we can evaluate anywhere.

Residual solvent of ink under development can be evaluated near the production testing area on-site. Results will be obtained quickly, and we can see the results and development efficiency is highly improved compared with the conventional method.

The residual solvent value of each solvent species can be predicted from prediction model of each solvent species with PLS method. Each solvent value can be obtained at the same time from one NIR spectrum measurement.

The model of the breakdown phenomena is proposed with measurement of residual solvent, adhesion force, and the area of white spots at various contact temperature. Adhesion force and residual solvent and the area of white spots have highly correlated each other.

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Author Biography

Eiichi Mori obtained his master's degree in solid state physics at the Tokyo Metropolitan University in Japan in 2011. In the same year, he joined Ricoh Company, Ltd. He has been engaged in the development of organic photoconductor, water-based inkjet ink and analysis methods of inkjet ink. The topics of his research include evaluation technique of inkjet ink, simulation and analysis of inkjet properties.