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# Colloids and Surfaces A: Physicochemical and Engineering Aspects

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## Approach for detecting localization of inkjet ink components using dynamic-SIMS analysis

Masaya Shibatani<sup>a,b,\*</sup>, Tsutomu Asakawa<sup>c</sup>, Toshiharu Enomae<sup>a</sup>, Akira Isogai<sup>a</sup><sup>a</sup> Paper Science Laboratory, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Japan<sup>b</sup> IJ Industrial Applications R&D Department, Production Engineering & Development Div., Seiko Epson Corporation, Japan<sup>c</sup> Material Analysis & Research Center, R&D Department, Seiko Epson Corporation, Japan

### ARTICLE INFO

#### Article history:

Received 3 August 2007

Received in revised form 15 May 2008

Accepted 18 May 2008

Available online 29 May 2008

#### Keywords:

Inkjet

SIMS

Pigmentink

Glycerin

### ABSTRACT

Organic compounds having high boiling points included in inkjet inks remain in the printed media after printing. It has been said that these residual organic compounds influenced the fastness of pigment ink prints, but details of the analytical methods have not been reported, yet. In this paper, a new analytical method was applied for detecting localization of those organic compounds in inkjet prints after printing. Glycerin was chosen as a typical example of those organic compounds. To analyze the position within the printed paper, deuterated glycerin was formulated in the ink as a probe and dynamic secondary ion mass spectroscopy (SIMS) was applied to detect the deuterium peak in the whole printed paper thickness. It was found that glycerin remained in the range from the bottom of the pigment ink layer to the pigment coating layer of the printed media. This peak was sufficiently detectable for at least 7 days after printing. The maximum peak of residual glycerin was located at the surface of the coating layer of paper. In addition, existence of a filter cake of pigment ink discussed in other work was not confirmed in this study.

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### 1. Introduction

Inkjet inks generally contain organic solvents with high boiling points [1]. The solvent is added to the ink to ensure stable delivery of the ink and to prevent nozzle clogging in inkjet systems. The solvent does not evaporate at room temperature and is thus considered to remain in the printed samples. Therefore, it has been indicated that the solvent affects the preservation of printed images by changing the chalking resistance (scuff resistance) [2]. Although the properties of the solvent have been evaluated by various qualitative analytical methods [3,4], the quantitative relationship between the residing characteristics and the chalking resistance has not been studied. In past works, the correlation between the residence behavior and the chalking resistance was examined by applying glycerin, which is a common high-boiling-point solvent. The amount of residual glycerin in paper was analyzed by using pyrolysis–gas chromatography (Py–GC) [5]. However, in this method, the ink layer on the paper is abraded and the obtained powder is analyzed as a bulk sample. Thus, it is impossible to specify the location of the high-boiling-point solvent. Another problem is that

a wet ink film solidifies with time, which makes abrasive sampling difficult. To solve these problems, the analysis of printed material by using secondary ion mass spectroscopy (SIMS) is considered [6]. However, the SIMS method has been applied only for analyzing the thickness range of solid constituents containing labeled metallic elements and has never been applied for analyzing the depth distribution of organic compounds containing labeled elements.

In this study, we report on the local distribution of glycerin throughout the ink layer and the paper coating layer. Inks containing deuterated glycerin – d8 glycerin – in which all the hydrogen atoms are replaced with deuterium atoms were prepared, and samples printed using these inks were analyzed along the depth direction by using SIMS. The local distribution of the glycerin was shown by observing the ion intensity of deuterium in the secondary ions. The advantage of this analytical technique is that the local distribution of glycerin in the ink layer and at the boundary with the paper coating layer can be observed directly.

### 2. Experimental

#### 2.1. Preparation of inks and samples

Ink containing the following constituents was prepared: 6% solid pigment (quinacridone-magenta: C.I. PR122 and copper phthalocyanine-cyan: C.I. PB15:3), 22% d8 glycerin (Euriso-top Co.),

\* Corresponding author at: IJ Industrial Applications R&D Department, Production Engineering & Development Div., Seiko Epson Corporation, Japan.  
Tel.: +81 266 626813.

E-mail address: [Shibatani.Masaya@exc.epson.co.jp](mailto:Shibatani.Masaya@exc.epson.co.jp) (M. Shibatani).

15% glycerin (Kanto chemical Co.), 0.4% nonionic surface-active agent (Air products Inc.), and 56.6% pure water. This ink was loaded into a commercial inkjet printer and the output samples were evaluated. A solid-printed sample with 31 g/m<sup>2</sup> of ink was introduced into a temperature-programmed desorption mass spectrometer (TDS). For the SIMS analysis, a linear continuous pattern of single dots (each from one droplet of 20 pL, EPSON SC900) was printed on a sheet of paper, which was then subjected to evaluation. Paper samples A and B were prepared from commercially available resin coat-based and photo-grade glossy paper for general inkjet printers.

## 2.2. SIMS analysis

Sector-type SIMS, Imf4, at Cameca, France was used with cesium (Cs) as the primary ions. After the sample surface was coated with platinum (Pt), it was analyzed in the high mass-resolution mode using a primary bias ion voltage of −14.5 kV and an ion current of 10 nA. The diameter of the analyzed circular area was 33 μm, located at the center of an abraded area of 100 μm × 100 μm. The etching of the sample was started after evacuation for 30 min.

## 2.3. Temperature-programmed desorption mass spectrometry (TDS)

The mass spectrum of the gases emitted into vacuum at room temperature (22–24 °C) was analyzed by a commercial temperature-programmed desorption mass spectrometer, EMD-WA1000K, ESCO, Japan. The evaporated pressure was  $1.59 \times 10^{-9}$  KPa.

## 2.4. Surface profile measurement

The thickness of the ink layer on the paper and the depth of the hole made by SIMS were measured by using a contact-type stylus profilometer, Tencor P-15, KLA, USA.

## 2.5. Observation by FIB-SEM

Analyses using a focused ion beam (FIB) (FB-2000) in combination with a scanning electron microscope (SEM) (S-5000) were performed. These instruments, manufactured by Hitachi Ltd., Japan, were used at an acceleration voltage of 5 kV. Before performing FIB cutting, the sample surfaces were coated with Pt and carbon (C). Surface observations of paper samples was performed at an acceleration voltage of 10 KV.

## 2.6. Particle size distribution

Particle sizes of pigment was observed by laser diffractometry method, UPA150, Microtrac Ltd.

## 3. Results

### 3.1. Preliminary analysis by temperature-programmed desorption mass spectrometer

Before introducing a printed sample to the high-vacuum conditions ( $10^{-8}$  to  $10^{-9}$  KPa) of SIMS, it must be confirmed that no glycerin evaporates from the sample. The preliminary analysis of the evaporation of glycerin was carried out by using a temperature-programmed desorption mass spectrometer, which is an apparatus that performs qualitative analysis by measuring the mass spectrum of a sample as it is heated and decomposed

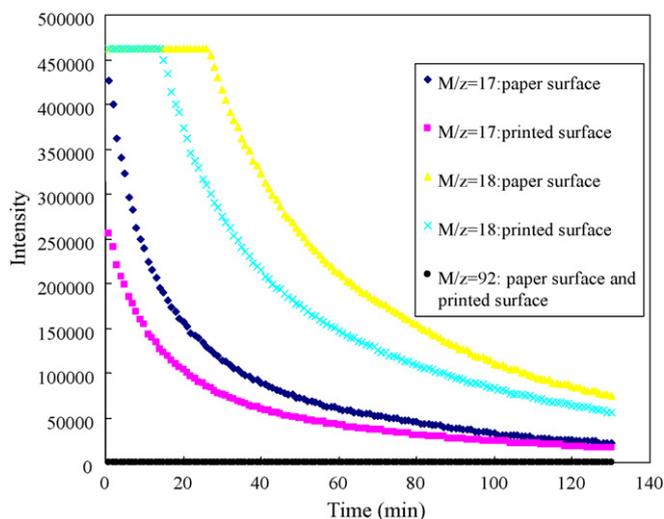


Fig. 1. Volatility of ink set on paper measured by mass spectroscopy during temperature programmed desorption.

under high-vacuum conditions. In this analysis, the existence of glycerin under high vacuum and room temperature (between 22 °C and 24 °C) was determined. Fig. 1 shows the changes in several mass spectrum peaks with time for the printed and the blank paper A samples. The intensity of the glycerin peaks appearing regularly at  $m/z=92$  was constantly zero for the printed samples as well as the blank sheet. In the spectra for both the printed

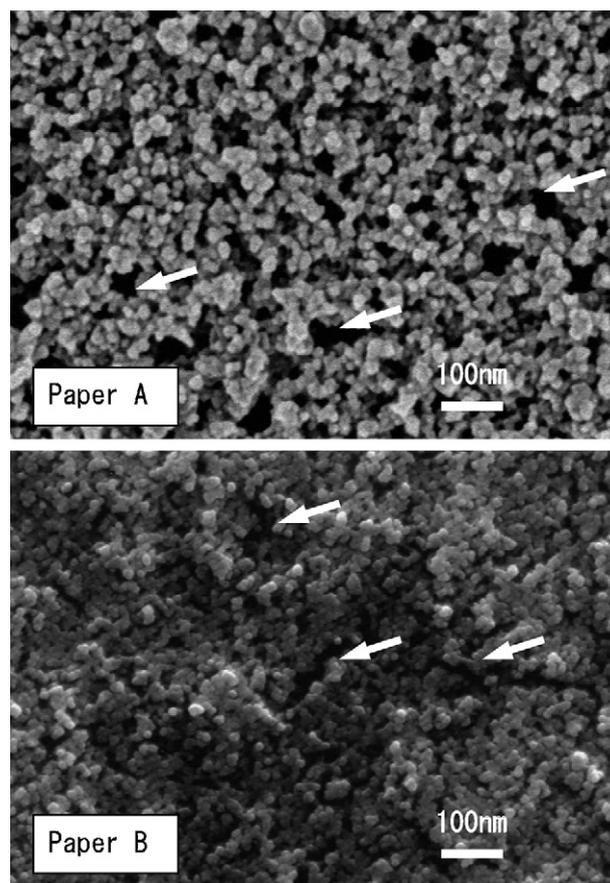
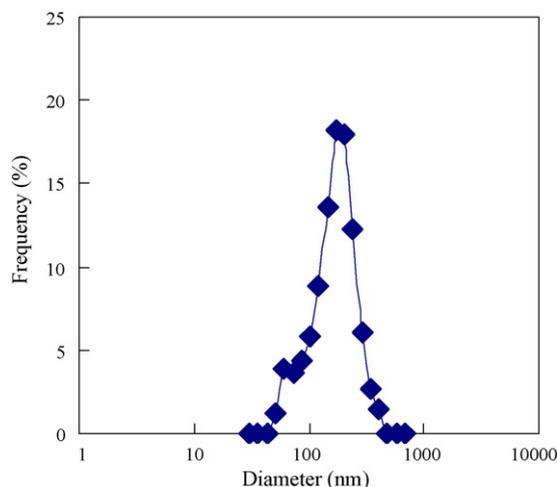


Fig. 2. Scanning electron micrographs of paper A and B with large voids on surface indicated by arrows.

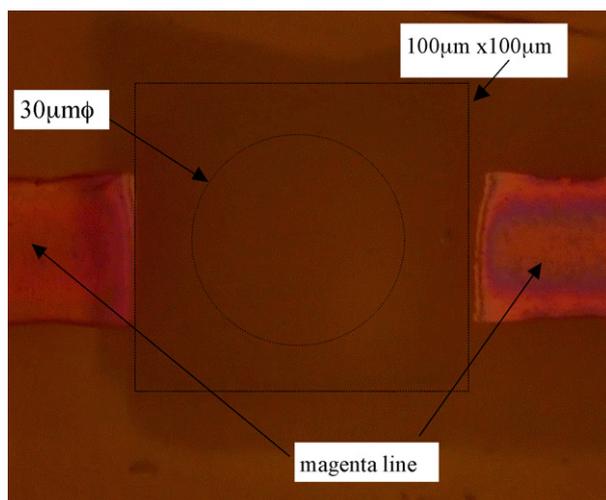


**Fig. 3.** Particle size distribution of ink pigment determined by laser diffractometry method.

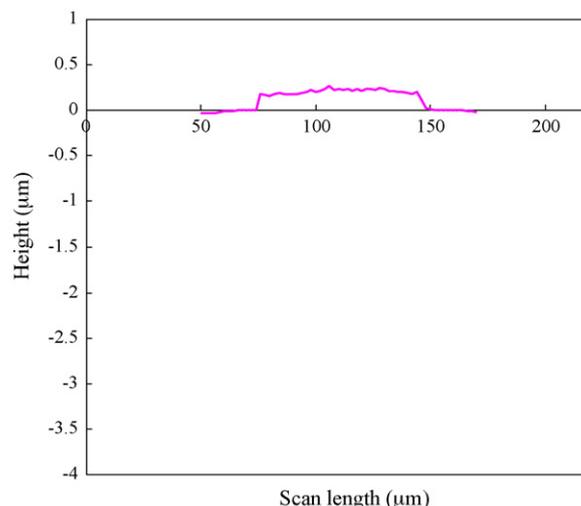
and blank samples, the detected peaks at  $m/z = 18$  and 17 are attributed to water ( $H_2O$ ) and the hydroxyl ion ( $OH$ ), respectively. They are generated from the water contained in the paper under the vacuum conditions. The peaks at  $m/z = 18$  remained at a plateau until approximately 30 min from the beginning because the signal overshoot the detection range. Based on this measurement, it was confirmed that the glycerin in the printed samples does not evaporate and can be analyzed under high-vacuum conditions by using SIMS.

### 3.2. Surface analysis of paper samples and particle size of ink pigments

Fig. 2 shows photographs of paper samples A and B. It is observed that both the samples have void structure and particles of silica pigment are round and less than 30 nm in diameter. Large voids were formed in places as indicated by arrows. However, particle diameter of ink pigments were distributed approximately 50–400 nm as shown in Fig. 3. This fact indicates that most of ink pigment particles are not possible to intrude into voids between silica particles, but partly possible to drop into large voids on the paper surface.



**Fig. 4.** Surface photograph of the sample by SIMS analysis.

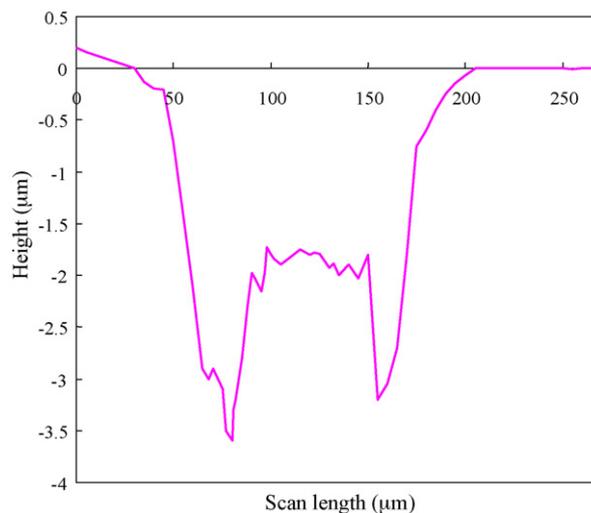


**Fig. 5.** Surface profile of magenta ink dot on paper A.

### 3.3. Analysis by SIMS

#### 3.3.1. SIMS analysis of samples using magenta ink

Fig. 4 shows the result of the SIMS analysis of a sample on which a linear continuous pattern is drawn with magenta ink containing d8 glycerin. Figs. 5 and 6 show the height of the ink layer and the depth of the hole produced by SIMS, as measured by the contact-type profilometer, respectively. The thickness of the ink layer and the depth of the hole are estimated to be approximately 0.25 and 1.8  $\mu\text{m}$ , respectively. Figs. 7–9 show the results of the SIMS analysis as a function of the time after printing. SIMS etches the pigment ink layer by spattering Cs ions along the z-direction perpendicular to the paper plane and carries out time-resolved detection of secondary ions. The secondary ions focused on in this work included six species:  $^{13}\text{C}$ ,  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{18}\text{O}$ ,  $^{63}\text{Cu}$ , and  $^{30}\text{Si}$ . The  $^{13}\text{C}$ ,  $^1\text{H}$ , and  $^{18}\text{O}$  secondary ions were included in the pigment quinacridone, the binder of the coating layer, and the high-boiling-point organic compounds. On the other hand, a part of the  $^{18}\text{O}$  and all of  $^{30}\text{Si}$  ions were included in the silica used as the coating layer of the paper sample. In the figures, the vertical axis represents the secondary ion intensities and the horizontal axis, the spattering time. The data at 0 s correspond to information about the top surface of the sample.



**Fig. 6.** Depth profile of magenta ink dot on paper A after etching.

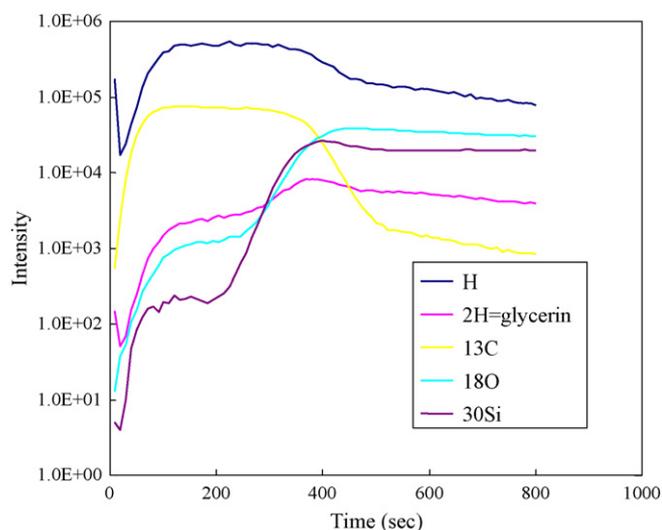


Fig. 7. Intensity of secondary ions from magenta ink dot on paper A 24h after printing.

To avoid charging in the ion beam, the top surface of the sample is coated with Pt in advance. Therefore, little sample information is provided by the data obtained in the time range 0–60 s because the signals are generated in the Pt layer. After approximately 60 s, the Pt layer is passed and the top surface of the ink layer is exposed. The depth range of 60–300 s corresponds to the quinacridone layer because the intensities of  $^{13}\text{C}$  and  $^1\text{H}$  are constant. The secondary ion intensities of  $^{13}\text{C}$  and  $^1\text{H}$  have their first inflection points at approximately 300 s, and then decrease for 300–500 s constantly. They also have a second inflection point at approximately 500 s, and then they decrease gradually until the end. On the other hand, the intensity curve of  $^{30}\text{Si}$  has its first inflection point at approximately 200 s; subsequently, it has a second inflection point at approximately 400 s, which remains constant after 500 s until the end. The secondary ion  $^{18}\text{O}$  is included in the quinacridone, glycerin, and silica of the coating layer. The intensity of  $^{18}\text{O}$  has its first inflection point at approximately 200 s and a faint second inflection point at approximately 450 s, which decreases slightly after 500 s. This result shows that the depth range of 200–500 s is not a clear boundary (NCB range). Small ink-pigment particles may intrude into the

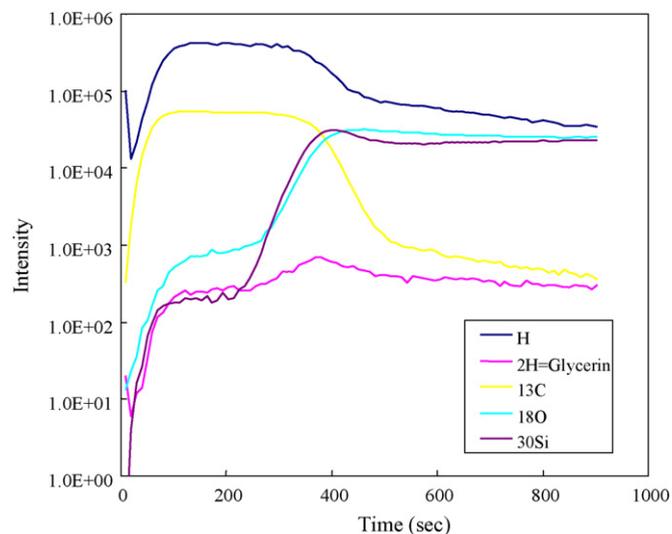


Fig. 9. Intensity of secondary ions from magenta ink dot on paper A 7 days after printing.

micropores of the coating layer of the paper sample because there is no distinct transition in the  $^{18}\text{O}$  intensity curve in this time range. In this analysis, the ion intensity of deuterium ( $^2\text{H}$ ) is important because it represents the glycerin distribution. Glycerin consists of C, H, and O. Sector-type SIMS cannot distinguish between the ions of non-deuterated glycerin and the ions of other organic compounds. However, as deuterated glycerin is used in this analysis, it can be said that the ion intensity of  $^2\text{H}$  corresponds to that of glycerin. The natural abundance ratio of  $^2\text{H}$  is 0.015%, and the ion intensity of  $^2\text{H}$  in glycerin clearly differs from that of natural  $^2\text{H}$ . The background natural  $^2\text{H}$  intensity was below  $1.0 \times 10^{-8}$ . The peaks of  $^2\text{H}$  corresponding to concentrated glycerin can be observed in the depth range of 200–500 s, which is the NCB range for this paper sample. Most of the glycerin present in the magenta ink is found in this range. This indicates that there is some shielding effect acting on glycerin when it is transferred from the ink layer to the paper coating layer. The intensities of  $^{30}\text{Si}$  and  $^{18}\text{O}$  become constant after 500 s, but the intensities of  $^{13}\text{C}$  and  $^1\text{H}$  decrease after 500 s, at a constant rate. It is supposed that the paper coating layer has an over coat of resin components, which are contained in the coating layer or

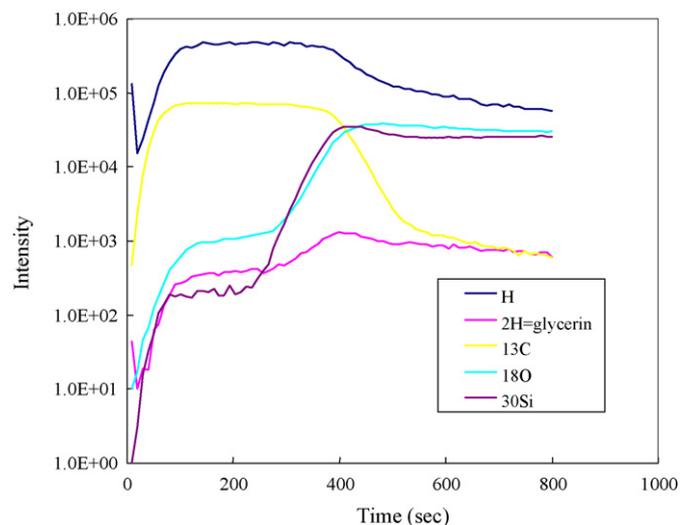


Fig. 8. Intensity of secondary ions from magenta ink dot on paper A 48h after printing.

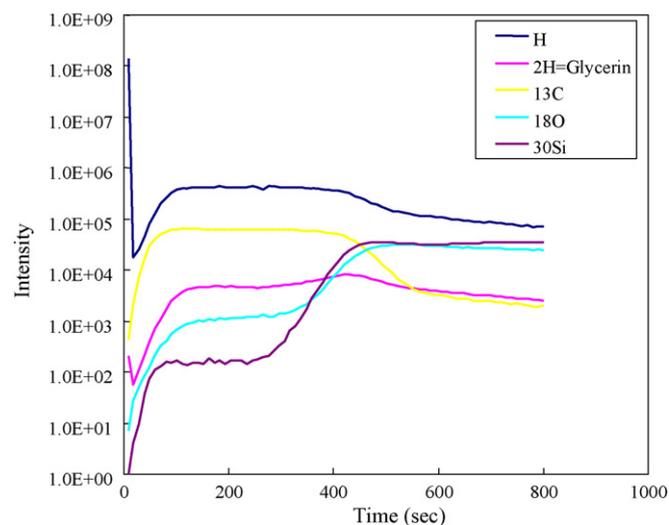


Fig. 10. Intensity of secondary ions from magenta ink dot on paper B 24h after printing.

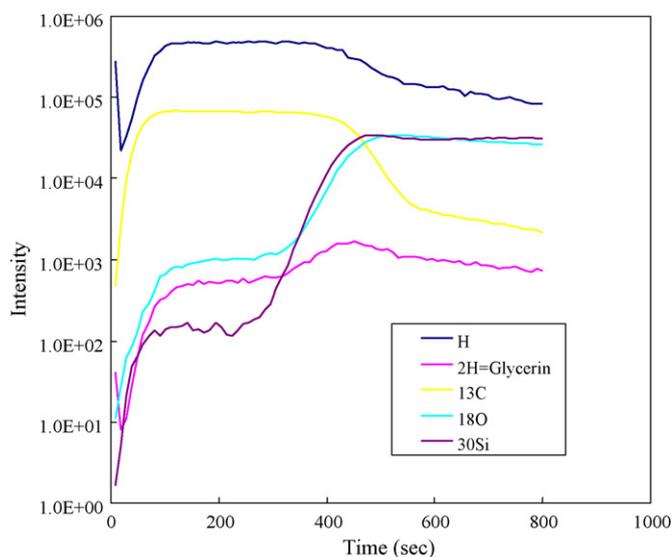


Fig. 11. Intensity of secondary ions from magenta ink dot on paper B 48 h after printing.

the formulated amount of the resin components are different from those in the bulk coating layer in the paper surface. To enhance the smoothness and hardness of the paper surface, post-treatment processes have been reported to be conducted in the production of commercial inkjet photo paper [7]. Therefore, it was possible that the resin components on the paper surface block the penetration of glycerin. At the same time, both the <sup>30</sup>Si and <sup>18</sup>O curves also had peaks at approximately 400 s. Hence, it was supposed that there is another coating layer with a high ratio of silica on the surface of the paper sample; however, from the observation of the cross-section of the coating layer (Fig. 15), there is no evidence of such a silica layer over the paper surface. This suggests that some other material containing silica is coated on the paper surface.

Figs. 10 and 11 show the SIMS analysis results for paper sample B. Comparing this result with that for paper A, we observe that paper B has more residual glycerin. This tendency is the same as that in the previous analysis results using the Py-GC method [5]. It appears that the difference in the diffusion rate due to the prolonged wetting of glycerin over the coating pore surfaces causes

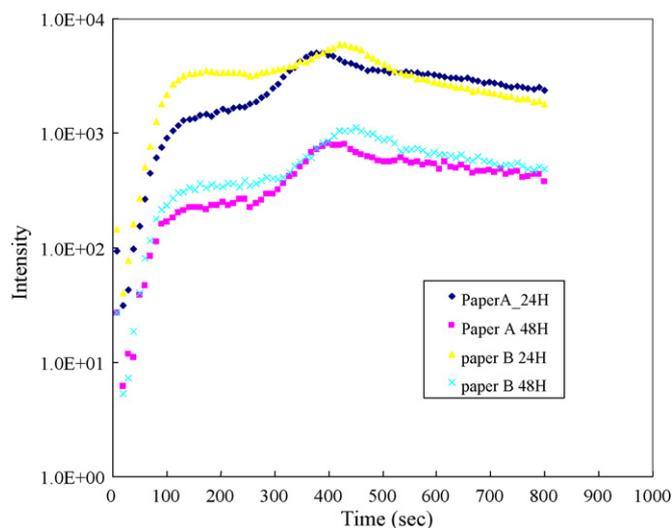


Fig. 12. Comparison in intensity of 2H ions from magenta dot between paper A and B.

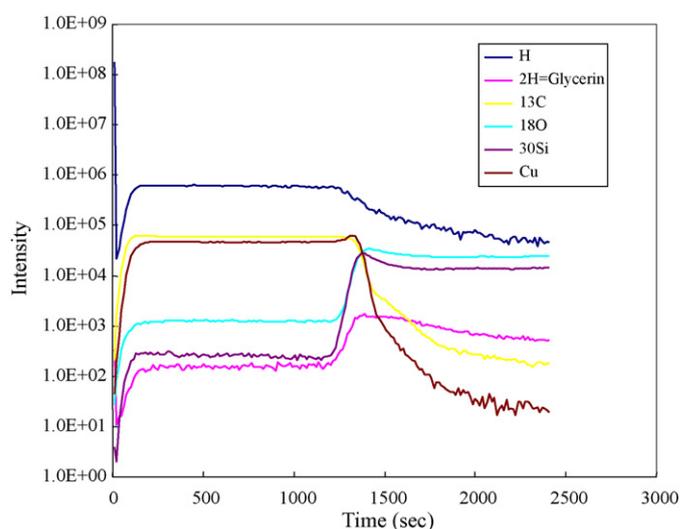


Fig. 13. Intensity of secondary ions from cyan ink dot on paper A 24 h after printing.

the difference in the residual glycerin distribution. In other words, the lower the wetting ability of glycerin over the coating pore surfaces, the more is the residual glycerin in the NCB range. Fig. 12 shows the relative intensities of <sup>2</sup>H to <sup>13</sup>C for both the papers at 24 and 48 h after printing. The peak of the residual glycerin distribution appears to be located in the NCB range. As observed from the peak shifts of approximately 450 s during the etching time and the decreased peak heights, the glycerin penetrated the coating layer during the second 24 h. In addition, the peak locations of <sup>2</sup>H for both the paper samples were different because of the different etching rates.

### 3.3.2. SIMS analysis of samples using cyan ink

Fig. 13 shows the result of the SIMS analysis for the sample printed with cyan ink containing d8 glycerin. The measurement was made 24 h after printing. Since the cyan ink contains C.I. PB15:3 as a pigment, the behavior of both the <sup>63</sup>Cu ions and the residual glycerin can be observed. As shown in Fig. 14, the thickness of the cyan ink layer is 0.5 μm approximately twice that of the magenta ink layer. In comparison with the amount of residual glycerin in the magenta ink layer (Fig. 7), the amount of residual glycerin in the cyan ink layer is smaller and that in the paper coating layer is larger. The reason for the smaller amount of residual glycerin in

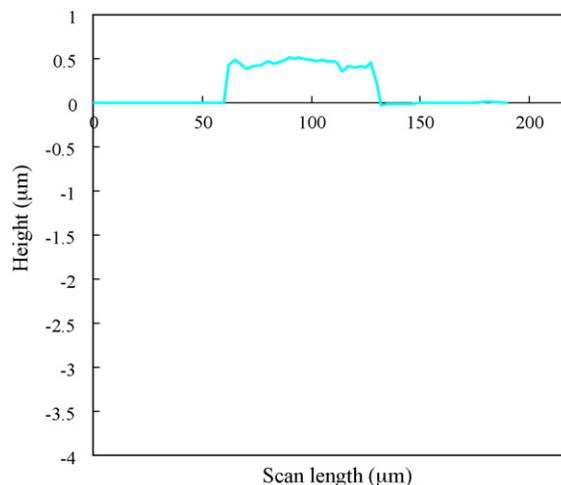


Fig. 14. Surface profile of cyan ink dot on paper A.

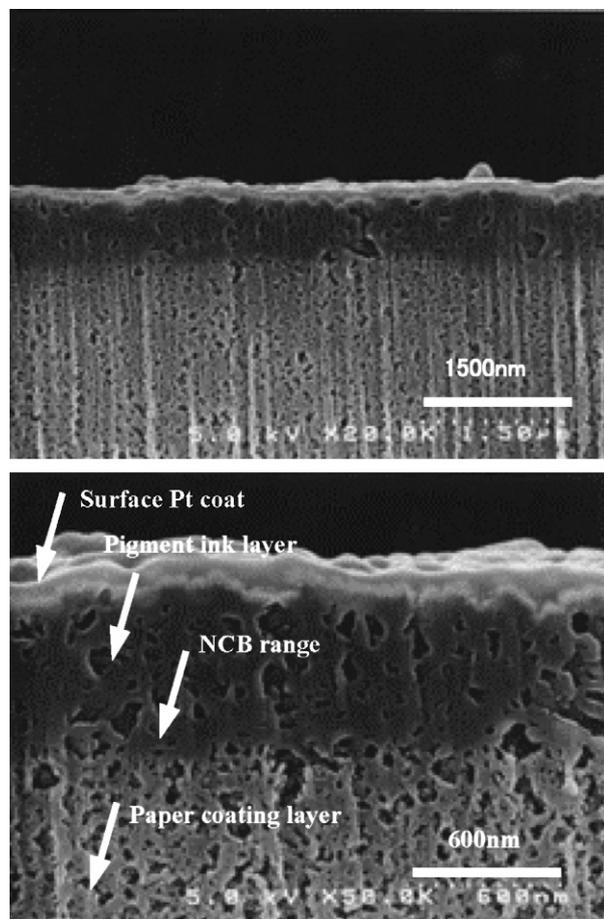


Fig. 15. Cross-section image of cyan ink dot on paper A.

the cyan ink layer is unclear. However, it is considered that glycerin cannot be retained in the cyan ink because half the height of the cyan ink dot implies that the cyan ink layer has more pores than the magenta ink layer for equal amounts of pigment in the inks.

The calculated porosity of magenta ink layer is 45.7% but that of the cyan one is 78.6%; hence, the porosity of the cyan ink layer is about 1.7 times larger than that of the magenta ink layer. The existence of a micro-filter cake at the bottom of the ink layer and at the boundary with the paper coating layer has been discussed in the references [8,9]. A transient increase in the intensity of the  $^{63}\text{Cu}$  ion is observed at the boundary, but an increase in the intensities of  $^{13}\text{C}$  and  $^1\text{H}$  ions is not observed. Therefore, the existence of a micro-filter cake is not clearly confirmed. Moreover, the existence of a micro-filter cake at the boundary is not clearly confirmed. Moreover, the existence of a micro-filter cake is not clearly confirmed. Moreover, the existence of a micro-filter cake at the boundary is not clearly confirmed.

#### 4. Conclusion

Ink-jet paper samples printed with inks containing d8 glycerin, namely that with all the hydrogen atoms replaced with deuterium atoms, as a stable-isotope-labeled compound was analyzed by using SIMS. The distribution of residual glycerin along the z-direction of the samples was obtained. This method could be applied to other printing methods such as offset printing using high-boiling-point solvents. Residual glycerin was locally distributed in the ink layer and at the boundary with the paper coating layer. Furthermore, the existence of a pigment filter cake could not be confirmed.

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