A NOVEL METHOD FOR DETERMINING AMOUNT OF INK PRINTED ON PAPER USING X-RAY FLUORESCENCE SPECTROSCOPY

Hitomi Hamada, Toshiharu Enomae, Masato Kato* and Fumihiko Onabe

Paper Science Laboratory, Graduate school of Agricultural and Life Sciences, The University of Tokyo, Tokyo, JAPAN, e-mail: hitomi@psl.fp.a.u-tokyo.ac.jp

**Digital Archives Research Center, Ryukoku University, Shiga, JAPAN*

ABSTRACT

With the view of quantifying amounts of ink printed on paper for offset printing, a newly developed technique using an X-ray fluorescence method was applied. In this technique, the content of copper included in a cyan-ink printed on paper was evaluated from an intensity of its peak in the X-ray fluorescence spectrum. A cyan-ink, one of the four colors of process inks (C, M, Y and B_k), is often used in printability tests. By the X-ray fluorescence method, mass of ink, preferably at large amounts, on paper can be measured precisely for a short period of time, though they are not proportional to the print density. As an application of this technique, the X-ray intensities of the elements contained in printed samples with and without print mottles were measured and mapped using an X-ray fluorescence microanalyzer. From the results of this measurement, it was suggested that the distribution of coating components near the surfaces is one of the important factors affecting ink mottling. The amount of ink transferred was found to decrease with increasing the smoothness of paper in the case of offset printing. As the amount of ink transferred reflects the properties of paper, it is expected that the X-ray fluorescence based quantifying method of ink on paper assists in estimating the printability of a variety of printing papers.

INTRODUCTION

There are two major known methods to quantify amounts of ink on nip-printed paper, one is to measure the amount of ink transferred by weighing the ink roll before and after printing; the other is to measure the print density using a spectrophotometer. However, the graph in the article[1] on ink receptivity of coated paper permits to interpret that the print density was not proportional to the amount of ink transferred over 1 g/m^2 ink amount. Lepoutre[2] reported that there were the exceptions of the supercalendered coating and the latex-covered coating though the optical density of the prints was only a function of the quantity of ink deposited for a variety of coatings other than that at low inking levels.

In this study, a novel technique to quantify amounts of ink on nip-printed paper using an X-ray fluorescence method was developed. For this technique, a particular attention was focused on a cyan-ink, one of process inks, often used in printability tests. The novel technique by an X-ray fluorescence method was found to measure precisely amounts of cyan-ink transferred on paper for a short period of time.

EXPERIMENTAL

Samples

Woodfree paper (65 g/m^2, Mitsubishi Paper Mills Limited, Japan) and coated paper (uncalendered, about 10 g/m^2 coat weight, 65 g/m^2 basis weight) both commercially available were supercalendered at 50 ℃, for 2 nips under linear pressures of 19.6, 49, 98, 147 and 196 kN/m. Twelve kinds of paper samples with several levels of smoothness were prepared. Bekk smoothness (Oken, Modified Bekk method, Digital EY type, KRK, Japan) and 75 ° sheet gloss (Glossmeter GM-26D, Murakami Color Research Laboratory, Japan) of the papers were measured. Printing on the papers with several levels of smoothness were conducted on a universal printability tester (MPT 8000, KRK, Japan) with a conventional process cyan-ink (TK high echo, Tack 9.5, Toyo Ink, Japan) for offset. Printing on groundwood paper (53 g/m^2, Dai-ni paper, Japan) and recycled paper (60 g/m^2, Oji Paper, Japan) were also conducted under the same conditions. The amount of ink transferred was measured by weighing the ink roll before and after printing and was found to range from 1.0 to 10 g/m^2.

Quantifying method of amount of ink transferred by X-ray fluorescence analysis

The X-ray fluorescence spectrum of each sample having several different amounts of ink transferred, which are known by weighing the ink roll, was measured using an X-ray fluorescence analyzer (MESA-500, Horiba, Japan) under conditions of 50 kV tube voltage, 74~240 μA tube currents, 5 mm diameter for scanning area and 250 s for scanning time. Figures 1 and 2 are examples of the X-ray fluorescence spectrum of printed and unprinted surfaces. The X-ray intensity of Cu-Kα at 8.04 keV is proportional to the content of copper included in a cyan-ink. A process cyan-ink used conventional is composed of Cu-phthalocyanin (Fig. 3) [3]. The calibration line for converting the X-ray intensity of copper to the amount of ink transferred was derived. The X-ray intensity of copper was evaluated as a value of a difference between counts per time and per current at 8.04 keV for printed and unprinted surfaces.

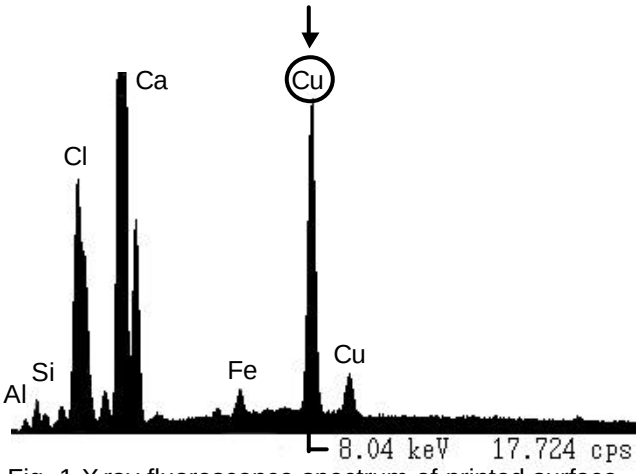

Fig. 1 X-ray fluorescence spectrum of printed surface

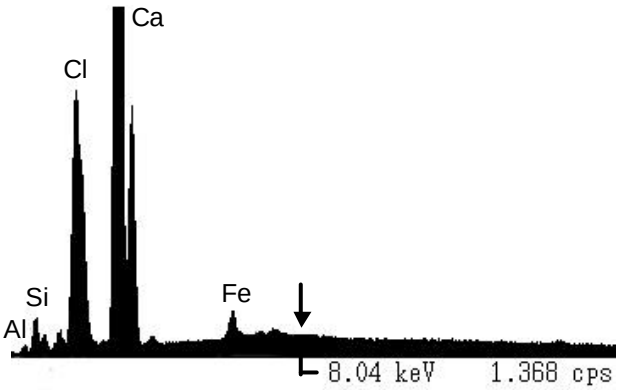

Fig. 2 X-ray fluorescence spectrum of unprinted surface

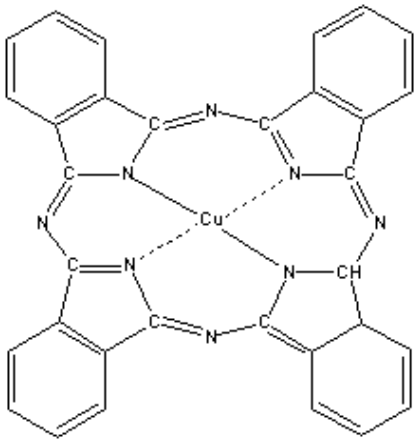

Fig. 3 Pigment Blue (Cu-phthalocyanine)

Comparison between X-ray fluorescence method and optical density measurement

The X-ray fluorescence method was compared with the optical density measurement. Seven kinds of coated papers with several different levels of lightness were prepared. Coating colors were preliminaly formulated with 70 pph of kaolin clay (UW-90, Engelhard, USA), 30 pph of calcium carbonate (Brilliant-15, Shiraishi kogyo, Japan) and 10 pph of binder latex (LX407G, Nippon Zeon, Japan). Two types of pigment latex, anionic hollow sphere pigment (HP-1055, Rohm and Haas, Japan) and anionic filled one (V1004, Nippon Zeon, Japan) were added separately to this color. The amounts of pigment latex were 5, 10 and 20 pph. The coatings were drawn down on one side of a base sheet (Woodfree paper, 65 g/m^2, Nippon Paper Industries, Japan) with a wire bar using a sheet-fed coater equipped with a synchro-starting dryer (PM9040MC, SMT, Japan). The coat weight was targeted at 9 g/m^2. The coated papers were dried at 120 ℃ for 10 s, and supercalendered at 50 ℃ under a linear pressure of 49.1 kN/m. Printing on coated papers was conducted on a RI printing tester (Ishikawajima Sangyo Kikai, Japan) with a conventional process cyan-ink for offset. RI printing tester permits comparison of every sample within the same run under the same conditions of nip pressure, speed and ink volume on a plate.

The amounts of cyan-ink printed on the coated papers prepared were determined by the X-ray fluorescence method. The spectral distribution of printed and unprinted surfaces were measured using a spectrophotometer under the conditions of D 65 diffuse illuminant / 2 ° normal observer. Lightness (L^*) was derived from the spectral distribution by basic equations[4]. The following equation gave the differences of optical density between printed and unprinted surfaces.

$$\Delta D = \log L^*_g - \log L^*$$

,where L^*_g is lightness of unprinted surface and L^* is lightness of printed surface

Application for ink mottling analysis

Two kinds of cyan prints with coated papers (about 10 g/m^2 coat weight, 105 g/m^2 basis weight) prepared under different drying conditions, i.e. a poor print with print mottle (Fig. 4 A) and a good print (Fig. 4 B), were compared. Surface roughness of unprinted parts of the prints was measured using a stylus profilometer (SE-3, Kosaka laboratory, Japan). The X-ray intensities of copper and elements (Ca, Al and Si) contained in the prints were measured and mapped using an X-ray fluorescence microanalyzer (EAGLE Ⅱ, EDAX, Japan). The measuring conditions of mapping were

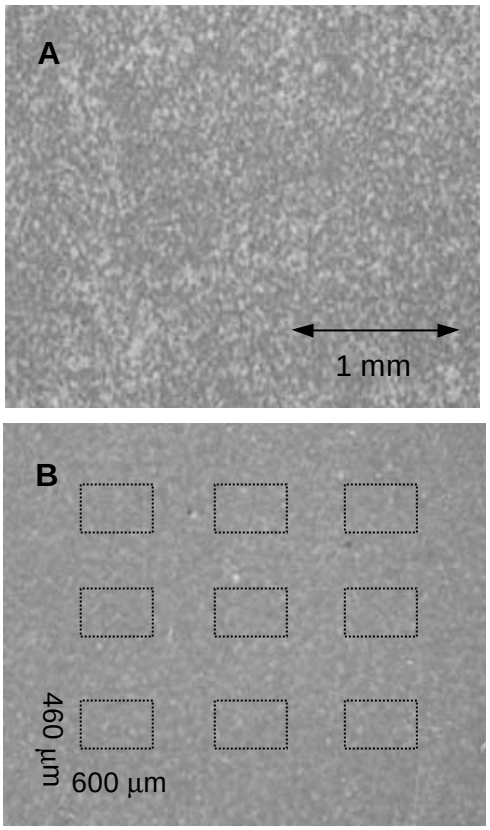

Fig. 4 Poor (A) and good (B) printed surfaces observed by stereo microscope with 9 rectangular parts showing measured area using FE-SEM/EDX

40 kV tube voltage, 900 μA tube current, 512×400 pixels and 400 ms scanning time for one pixel. With the view of analyzing an area closer to the printed surfaces, the X-ray intensities of elements contained in the prints which were platinum-coated in advance for providing electric conductivity were measured with nine areas of 600×460 μm^2 of each print (Fig. 4) using an FE-SEM (S-4000, Hitachi, Japan) with EDX (EMAX-5770X, Horiba, Japan) at 20 kV accelerating voltage, 0.20 nA probe current and 500 s scanning time.

RESULTS AND DISCUSSION

Relationship between smoothness of paper and amount of ink transferred

Figure 5 shows that the smoothness increased by supercalendering for both coated and uncoated papers. The smoothness of coated paper was higher than that of uncoated paper at the same linear pressure. The smoothness of coated paper increased as linear pressure increased up to 150 kN/m and above this value it decreased. This fact indicates that flocs in the paper became protruded on the paper surface. Therefore, the smoothness of paper decreased at high pressures. Figure 6 shows that the sheet gloss of the coated paper increased with increasing the smoothness and then leveled off. This is probably due to a decrease in refractive index caused by the collapse of coating at high pressures. The refractive index of the substance is one of the factors affecting gloss. The amount of ink transferred decreased with increasing the smoothness of papers as shown in Fig. 7. This result is consistent with those obtained by other authors[5,6].

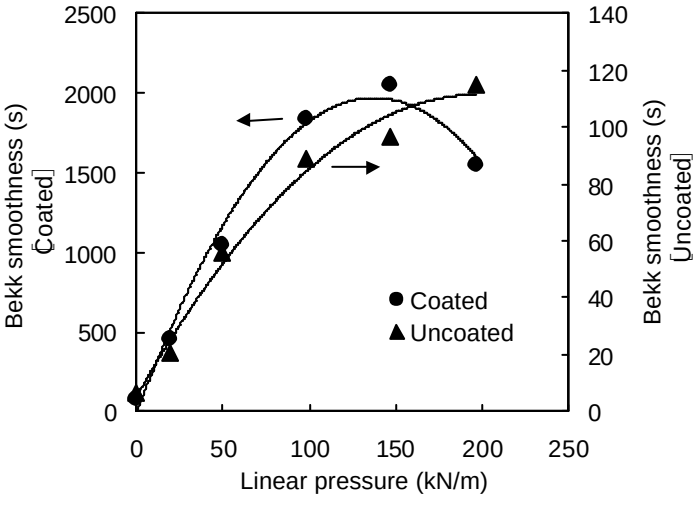

Fig. 5 Smoothness increase by supercalendering for A2 coat and uncoated woodfree papers

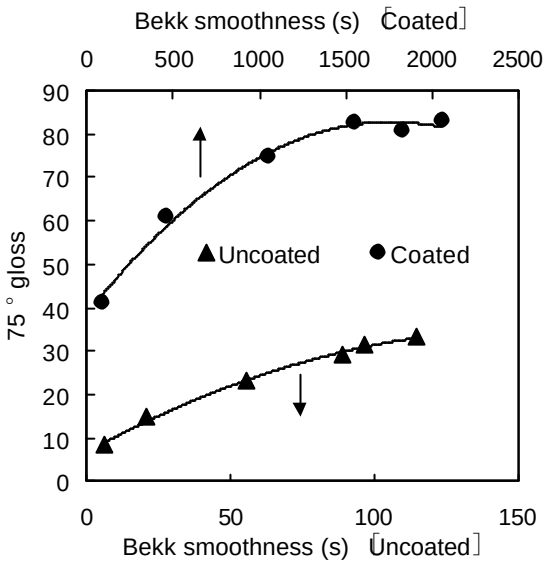

Fig. 6 Gloss measured in MD vs Bekk smoothness

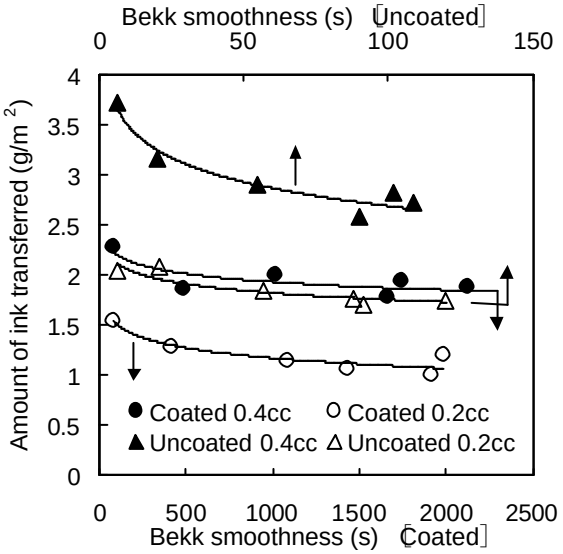

Fig. 7 Ink transfer depending on smoothness of paper

Quantifying method of amount of ink transferred by X-ray fluorescence analysis

Figure 8 shows that the proportional relationship held between X-ray intensity of copper and amount of ink transferred, which had been measured gravimetrically, irrespective of the kind of printed papers. For each kind of paper used in this work, almost the same gradient values and high correlation coefficients were derived as shown in Table 1. These results suggest that the X-ray intensity of copper is not influenced by paper whether the paper contains a large amount of inorganic components or not, and therefore this method can be applied to most of the conventional printed papers. It follows that the amount of cyan-ink printed can be determined by measuring the X-ray intensity of copper in an X-ray fluorescence spectrum. Using this method, we can measure precisely the amount of cyan-ink transferred on paper for a short period of time. It is considered that this method can be applicable for measuring the amount of some major color inks including inorganic elements, i.e. Cl and Fe.

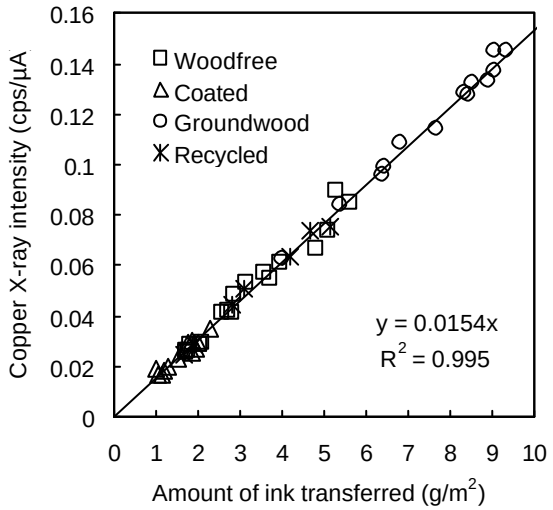

Fig. 8 Calibration line for converting X-ray intensity of copper to amount of ink

Table 1 Relationship between X-ray intensity of copper and amount of ink transferred

Kind of paper	Gradient	Correlation coefficient
Woodfree	0.0153	0.969
Coated	0.0152	0.900
Groundwood	0.0154	0.986
Recycled	0.0153	0.985

Comparison between X-ray fluorescence method and optical density measurement

Figure 9 shows the changes of the differences in optical density between printed and unprinted surfaces as a function of the amount of ink on paper. The differences in optical density were not proportional to the amount of ink on paper measured by the X-ray fluorescence method. Lightness of the coated paper formulated with hollow sphere pigment is high, since the large interface area provides high light scattering[7,8]. The prints with coated paper with high lightness showed higher optical density when the amounts of ink on paper were the same. Slight differences of the amount of ink, e.g. about 0.05 g/m^2, could not be measured by the differences of optical density. It has been reported that the print density was not proportional to the amount of ink transferred in the case of the prints at relatively large ink amounts[1] and with some kinds of coatings[2]. However, the quantification method of the amount of ink transferred by X-ray fluorescence analysis is

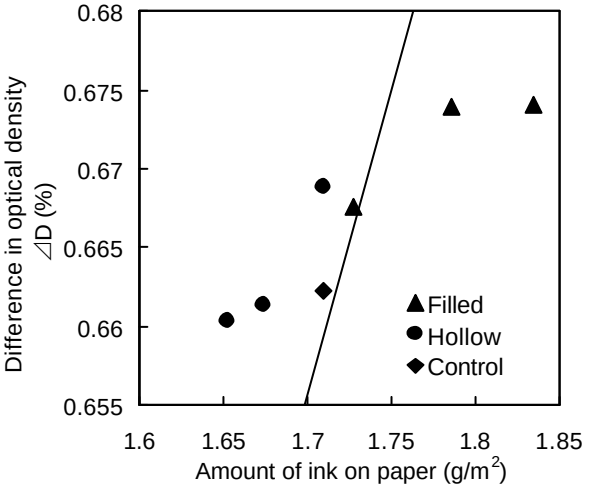

Fig. 9 Changes of optical density vs. amount of ink on paper

especially suitable for measurement of the large amount of ink transferred, and is applicable to almost all the prints.

Application for ink mottling analysis

Figure 10 shows the surface roughness of unprinted parts of the poor print and the good print. The surface roughness of unprinted parts of the good print was higher than that of the poor print in the wavelength range up to 300 μm. For the good print, more concaves with about 10 μm diameter were observed on the coated paper surfaces by SEM observation. It seems that these small concaves caused to increase the surface roughness. However, surface roughness of both prints showed almost the same values at about 250 μm wavelengths that were reported as affecting printability. This suggests that surface roughness of base paper do not affect mainly print mottling.

Figure 11 shows the results of mapping analysis of copper and other elements like Ca, Al and Si of coating components contained in the prints measured using an X-ray fluorescence microanalyzer. The correlation between the distribution of X-ray intensity of copper and the print mottle was not obtained from the mapping analysis. This is because the differences in ink amount between shadow and highlight parts were very small at a low inking, and then sufficient X-ray intensity was not obtained. Tables 2 and 3 show the X-ray intensity of elements contained in the prints measured using an X-ray fluorescence microanalyzer and FE-SEM/EDX, respectively. The X-ray intensity of copper of the good print was higher than that of the poor print. These results suggest that all of the amounts of ink transferred of the good print were higher than those of poor print.

The X-ray intensity of calcium of the good print showed higher values than that of the poor print. On the other hand, the X-ray intensity of aluminum and silicon of the good print showed lower values than that of the poor print (Table 2). In the results of FE-SEM/EDX, which provides surface analysis, the differences of the X-ray intensity between the good and poor print increased. These results indicate that calcium carbonate was rich at the parts close to the coating surface of the good print and clay was rich at those of the poor print. For these reasons, it is

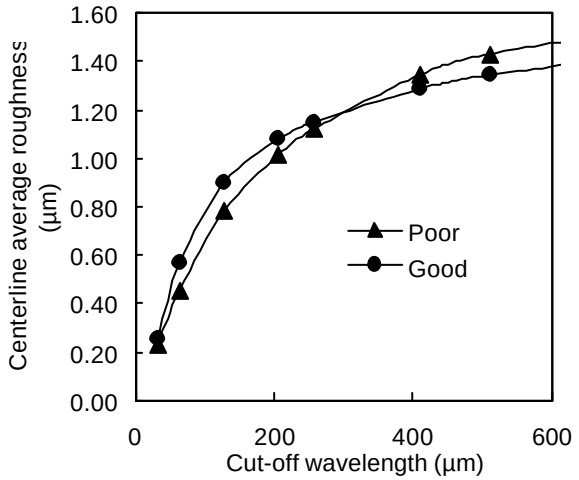

Fig. 10 Surface roughness of unprinted parts of the coated papers

Table 2 X-ray intensity (cps) of elements contained in prints measured by X-ray fluorescence microanalyzer

	Cu-Kα	Ca-Kα	Al-Kα	Si-Kα
Poor print	0.558	8.98	2.52	4.52
Good print	0.566	10.0	1.53	3.21

Table 3 Ratio of X-ray intensity of elements contained in prints to that of platinum measured by FE-SEM/EDX

	Cu/Pt	Ca/Pt	Al/Pt	Si/Pt
Poor print	0.062	9.91	18.71	18.18
Good print	0.074	22.97	11.15	12.43

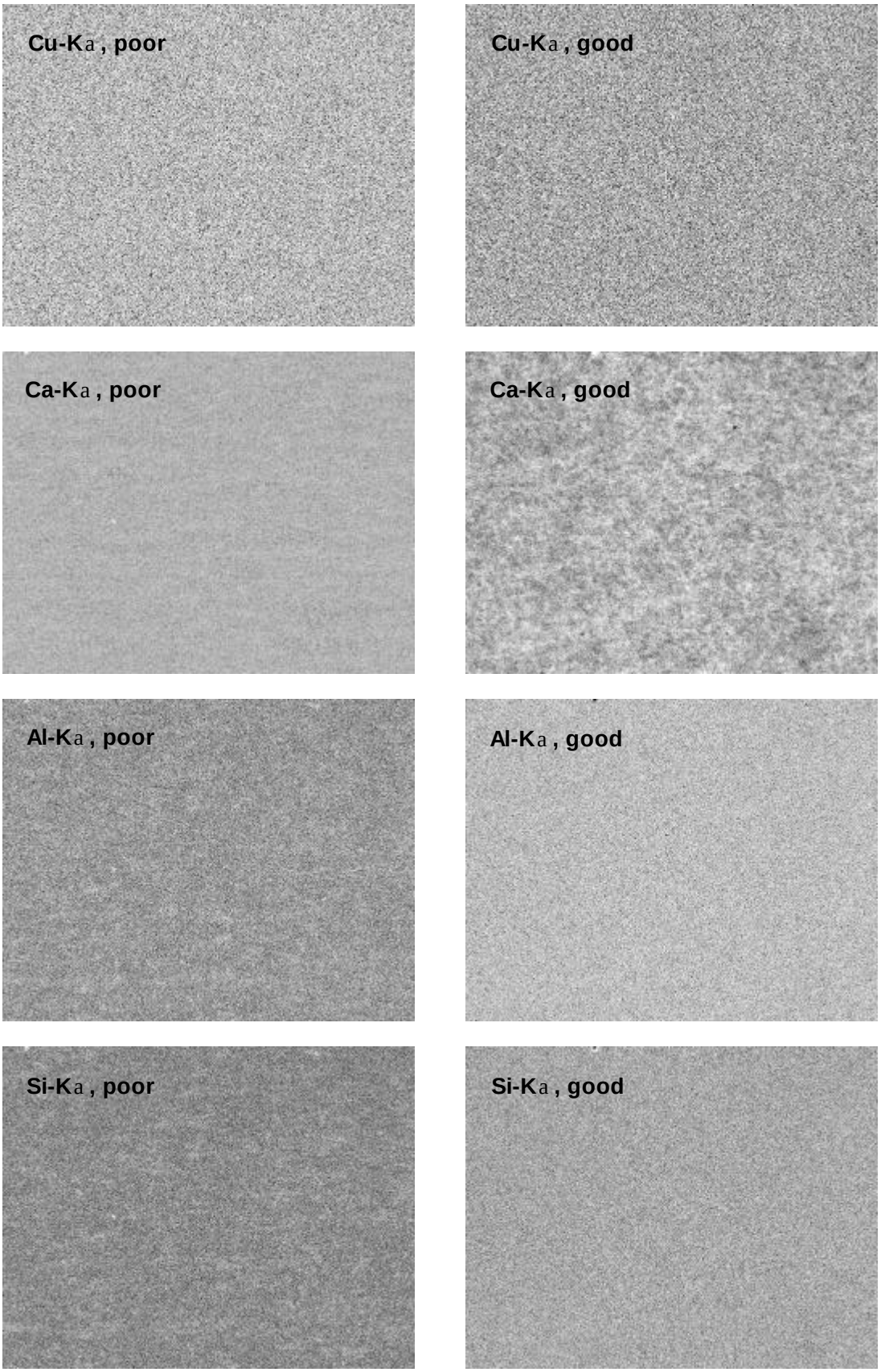

Fig. 11 Mapping images of the X-ray intensity of elements contained in prints measured using an X-ray fluorescence microanalyzer

indicated that when clay and/or binder is rich at the parts close to the coating surface, the decreased rate of penetration of a dampening solution for printing results in ink mottling. From the results, it is suggested that uneven distribution of coating pigments is one of the factors affecting ink mottling.

CONCLUSION

The quantifying method of amounts of ink transferred by X-ray fluorescence analysis was established for offset printing with process cyan-ink. In this technique, the content of copper included in a cyan-ink printed on paper is evaluated from an intensity of its peak in the X-ray fluorescence spectrum. The proportional relationship held between the copper content so measured and the amount of ink transferred, which had been measured gravimetrically, irrespective of the kind of prints. Using the calibration line to convert the X-ray intensity of copper to the amount of ink transferred, we can quantify precisely the unknown amount of cyan-ink printed for a short period time. This method is expected to apply to measuring the amount of some color inks including inorganic elements, i.e. Cl and Fe. It may be difficult to apply the X-ray fluorescence method to the analysis of ink mottling in the case of low inking levels, which the differences of ink amount between shadow and highlight parts were very small, used in this work. However, this X-ray fluorescence method is especially effective for prints with relatively large ink amounts, which is not proportional to the print density. From the results of the mapping analysis of the elements contained in prints by the X-ray fluorescence method, it is concluded that the distribution of the coating components near the surface affect the rate of penetration of a dampening solution for printing, which leads to ink mottling. The amount of ink transferred was found to decrease with increasing smoothness of base paper in the case of offset printing. As the amount of ink transferred reflects the properties of paper, it is expected that the X-ray fluorescence based quantifying method of ink on paper assists in estimating the printability of a variety of printing papers.

ACKNOWLEDGMENT

The authors wish to thank Mr. Hiroyuki Fukasawa, Fuji Industrial Research Institute of Shizuoka and Ms. Yoko Saito, Nippon Zeon Co., Ltd., for their help in the experiments. We are also grateful to Mr. Tatsuhide Tohara and Mr. Masanobu Kawabata, EDAX Japan K.K., for their contribution in the analysis using an X-ray fluorescence microanalyzer.

REFERENCES

1. Zang Y. –H. and Aspler J. S.：Journal of Pulp and Paper Science 24 (5) 141 (1998)
2. Lepoutre P., DeGrace J. H. and P. J. Mangin：Tappi 62 (5) 33 (1979)
3. Oshima S.： Japan Tappi 53 (5) 571 (1999)
4. Publication CIE No.15.2 (1986) COLORIMETRY, SECOND EDTION 4.
5. Wakabayashi H.：Paper & Pulp No.600 20 (1999)
6. Lepoutre P. and DeGrace J. H.：Paper Technology and Industry 19 (9) 301 (1978)
7. Hamada H., Enomae T., Onabe F. and Saito Y.： Proceedings of Pre-symposium of the 10th ISWPC, Korea, 1999, pp309-314
8. Hamada H., Enomae T., Onabe F. and Saito Y.： Japan Tappi 55 (11) 79 (2001)