

## FUNDAMENTAL STUDY FOR QUANTITATIVE ANALYSIS OF THE FLUORESCENT WHITENING AGENT (FWA) CONTENT OF PAPER AND PROCESS WATER

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Fluorescent whitening agents (FWAs) are the most widely used functional chemicals for the manufacture of printing and writing grades of paper. FWAs are used as internal or external additives for the surface treatment on the size press and coater. In spite of the extensive use of FWAs, no method has been established to analyze the FWA content in process water and paper products. Samples are typically exposed to UV light in order to detect the presence of FWAs. This method is based on the fluorescence exhibited by FWAs under a UV-lamp. The observation of fluorescence with the naked eye is highly subjective. Thus, it is essential to develop a more scientific and objective to the quantitative analysis of FWA optical effects. Water and paper samples containing FWAs were prepared in a laboratory. Quantitative analysis was carried out with a spectrofluorometer, a spectrophotometer, and an image restoration microscope. Using these analytical instruments, fluorescence was observed. Regression equations were obtained from the relationship between the fluorescence intensity and the FWA optical effects of the samples.

*Keywords:* Fluorescent whitening agent (FWA); UV-lamp; Quantitative analysis; Spectrofluorometer; Spectrophotometer; Image restoration microscope

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### INTRODUCTION

The optical nature of a paper product is one of the most important factors affecting a customer's choice. Among the numerous ways to enhance the optical properties of papers, the use of fluorescent whitening agents (FWAs) is often the most straightforward and effective approach to enhance brightness. FWAs are widely used in the paper industry as internal and surface-sizing additives (Weaver 1997).

In general, the effect of FWAs is determined by the change in the brightness of paper products. This is a logical approach because we are interested in the enhancement of brightness using FWAs. Consequently the FWA content of paper products and process water has not been quantitatively analyzed in detail thus far; however, this is essential to evaluate the effectiveness of FWAs in practical situations. A conventional method to detect the presence of FWAs in a paper product, which is usually carried out in paper mill, involves the observation of the product under a UV-lamp in a dark environment. If the paper product contains FWAs, the visible bright blue light re-emitted by FWAs under UV light can be easily observed with the naked eye. Thus, this method enables the

papermakers to determine the presence or absence of FWAs in a sheet of paper. However, the quantitative analysis of FWA, which is essential for the effective use and monitoring of FWAs, cannot be achieved by using only an UV-lamp. By monitoring the amounts of FWAs in the stock, the process water and paper products, we can achieve a greater understanding of paper processing and control the amount of FWAs in paper products. Because sanitary paper products are generally manufactured by recycling printing grade paper, they contain some amount of FWAs. A number of Korean consumers believe that the FWAs present in sanitary products are health hazards. To address this concern, paper manufacturers should develop a technique to eliminate FWAs or reduce the FWA content of sanitary paper products. A systematic approach to FWAs content measurement is required to control FWA content not only of sanitary paper product but also of printing grade paper.

Two analytical methods have been proposed by some researchers and paper-makers to detect FWAs in paper products: one is an extraction method and the other is an optical measurement. The extraction measurement is generally carried out after extracting the paper using water and pyridine solution (Croce et al. 1981) or other solvents (Ciba-Geigy). Although several solvents have been reported for the effective removal of FWAs from paper, solvent extraction is not suitable for commercial use (Sam Won Industrial Co., Ltd. 2000). The concentration of the extracted FWAs in the solvents is usually determined using UV-spectrophotometers. The complete extraction of FWAs from paper is not possible. However, it is possible to obtain a reasonable estimate of the amount of FWAs extracted by using this method.

The optical measurement is based on the fluorescence or the ISO brightness exhibited by FWAs. To analyze FWAs with optical method, the intensity of the emitted fluorescence or the difference between the paper brightness with and without UV-light is measured. The optical methods do not require any pre-treatment of test specimen, and they consume less time than the extraction method. However, careful selection and maintenance of a light source are required to ensure that the light is properly incident at a constant intensity (TAPPI 1998), and the quenching effects caused by many cationic polymers on the fluorescence or brightness must be considered (Crouse and Snow 1981; Roltsch and Lloyd 1987; Hubbe 2008). Moreover, the relationship between the amount of FWAs in the sample sheet and the optical measurement outputs, including fluorescence and brightness, must be established for quantification. This relationship has not been investigated thus far.

In this study, optical measurements were carried out to develop the instrumental methodology for the quantitative analysis of FWAs in model solutions and paper samples, excluding other affecting factors on the fluorescence, such as the effects of polymers, fillers, and so on. Paper samples containing only known amounts of FWAs were prepared in a laboratory. The fluorescence emission of an FWA solution having a known concentration was measured using a spectrofluorometer. The fluorescence emission and indices (Malthouse and Popson 1995) of paper samples containing FWAs then were determined using a spectrophotometer and an image restoration microscope. The FWA content of the paper samples was determined on the basis of the change in their adsorption on paper stocks. The relationships between the fluorescence indices or emissions of these paper samples and their FWA contents were plotted. The quantitative analysis of

the FWAs present in the solutions and paper samples was carried out on the basis of the regression equations.

## **EXPERIMENTAL**

### **Materials**

Bleached hardwood kraft pulp (Hw-BKP) was used to make handsheets dyed with FWAs. Three types of FWAs, including disulpho FWA (D-FWA), tetrasulpho FWA (T-FWA), and hexsulpho FWA (H-FWA) classes of commercially available products were used. Powdered FWAs were dissolved in distilled water to prepare FWA solutions with known concentrations before experiments. These solutions were used as an internal additive. Polydiallyldimethylammonium chloride (poly-DADMAC) at a concentration of 0.001 N was used to determine the charge density of FWAs and cationic demand of the pulp supernatant. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to control the pH of the pulp suspension and solution that contained FWAs.

### **Preparation of FWA Solutions and Handsheets Containing FWAs**

D-, T-, and H-FWAs were dissolved in distilled water with vigorous mixing to prepare 1.0% solutions. These FWA solutions were then diluted to 0.005 - 0.100% with distilled water.

Hw-BKP was beaten to  $450 \pm 5$  mL CSF using a laboratory Valley beater, and then diluted to 1.0% consistency for handsheet preparation. Handsheets with grammage of 80 and 100 g/m<sup>2</sup> were produced using FWAs. D-FWA and T-FWA were added to the pulp suspension and mixed for 2 min. Then, handsheets with grammage of 80 g/m<sup>2</sup> were produced. The handsheets were wet pressed and dried using a laboratory wet press and cylinder dryer at 120 °C, respectively. The dried handsheets were conditioned at 23 °C and 50% RH, and then analyzed.

### **Analysis of FWA Solution Using Spectrofluorometer**

The fluorescence spectra of FWAs in the aqueous phase were measured using a QuantaMaster spectrofluorometer developed by Photon Technology International. Using the spectrofluorometer, the intensity of fluorescence can be measured as a function of wavelength. The intensity of the fluorescent signal and dominant wavelength are obtained. The measurements provide a clear picture of the excitation and of the emission spectra of FWAs (Vaarasalo 1997).

The spectra of fluorescence excitation and emission were measured by employing a 1.0 nm slit opening to keep the maximum fluorescence emission from exceeding the measurable range. FWA solutions were placed on 12 × 45 × 4 mm quartz cuvette. All measurements were carried out in the surface reflection mode by measuring the light reflected from the cuvette surface. Fluorescence excitation and emission spectra were measured with UV light (wavelength: 320-420 nm and 400-800 nm, respectively) at 1 nm resolution.

### Analysis of FWA Adsorption on the Cellulosic Fibers

To determine the FWA content of the handsheets, the content of adsorbed FWA was determined by charge neutralization titration (Harris 1997). After the addition of FWAs, the pulp suspension was stirred at 600 rpm for 2 min. It was then filtered using a Büchner funnel with a Whatman GF/C paper to collect the filtrate containing unadsorbed FWAs. The cationic demand of the filtrate and zeta-potential (ZP) of the fibers were determined using a particle charge detector (PCD) and Magendans SZP 04, respectively, developed by Mütek. The charge density of the FWAs was measured at the same pH as that of the pulp suspension used for handsheet formation. After the cationic demand ( $D_{\text{cationic}}$ ) of filtrate and charge density ( $D_{\text{charge}}$ ) of the FWAs (Table I) were measured, and the amount of unadsorbed FWAs ( $\text{FWA}_{\text{unadsorbed}}$ ) in the pulp suspension was determined. Next, the amount of adsorbed FWAs ( $\text{FWA}_{\text{adsorbed}}$ ) was calculated by subtracting the amount of unadsorbed FWAs from the amount of added FWAs. The adsorption of the FWAs was expressed as the amount of FWA adsorbed per unit weight of oven-dried fibers (o.d. fibers). The equation used for the calculation of adsorbed FWA is given in Eq. 1.

$$\text{FWA}_{\text{adsorbed}} = \frac{\text{FWA}_{\text{added}} - (D_{\text{charge}} \times D_{\text{cationic}})}{\text{o.d. fibers}} \quad (1)$$

**Table 1.** Charge Density of FWAs

pH	D-FWA (meq/g)	T-FWA (meq/g)
5.5	-2.3	-4.9
7.5	-2.8	-5.0

### Analysis of FWA in Paper Using Spectrophotometer

An Elrepho spectrophotometer equipped with D65, C, and A illuminants was used for the measurement of the optical properties of paper. The CIE whiteness, ISO brightness, and fluorescence indices of papers can be measured using this spectrophotometer. When the CIE whiteness and fluorescence index of whiteness were measured, D65 illuminant was used, and when ISO brightness and fluorescence index of brightness were measured, C illuminant was used according to ISO 11475 and ISO 2470, respectively. The measurements of fluorescence indices were performed by inserting a UV cutoff filter in front of the light source of the spectrophotometer. Then, CIE whiteness and ISO brightness with and without UV components were measured. All of the measurements were carried out at 10 points of a handsheet. The CIE whiteness, ISO brightness, and the indices were expressed as the average data for a handsheet.

### Analysis of FWA in Paper Using Image Restoration Microscope

The fluorescence emission of FWAs was measured using a DeltaVision RT image restoration microscope developed by AppliedPrecision. This image restoration microscope is equipped with an arc mercury lamp, filter, and fiber optics that ensure constant

illumination intensity. The images magnified by a factor of 200 ( $512 \times 512$  in size) were captured and analyzed using software installed in the image restoration microscope. The fluorescence emission at a wavelength of 457 nm was measured after exposing the sample to excitation UV light with a wavelength of 360 nm. The maximum, minimum, and mean fluorescence emissions were determined by image analysis. 0.1% ND and 0.035 exposure were employed as the measurement conditions. The  $15 \times 15$  mm square samples were cut out from the handsheet and fixed to the slide glass for the measurement. Fluorescence emission measurement was carried out at 10 points of a handsheet, and final fluorescence emission was expressed as the average data for a handsheet.

### Regression Equations for Quantitative Analysis

The fluorescence index (FI) was plotted as a function of FWA content, and regression equations were obtained with the least-squares method (Cho et al. 2001) for quantitative analysis of FWAs. The relationship between fluorescence emission and FWA content was also examined and the regression equation was determined with the same method. The regression equations obtained for water and papers were linear and exponential, respectively.

## RESULTS AND DISCUSSION

### Regression Equations for FWAs in Solution Using Spectrofluorometer

Regression equations were obtained for quantitative analysis of FWAs in water. It was found that there was a linear relationship between fluorescence excitation and emission (Fig. 1). In this study, the regression equation between fluorescence emission and FWA concentration was obtained and used for the quantitative analysis of FWAs in water.

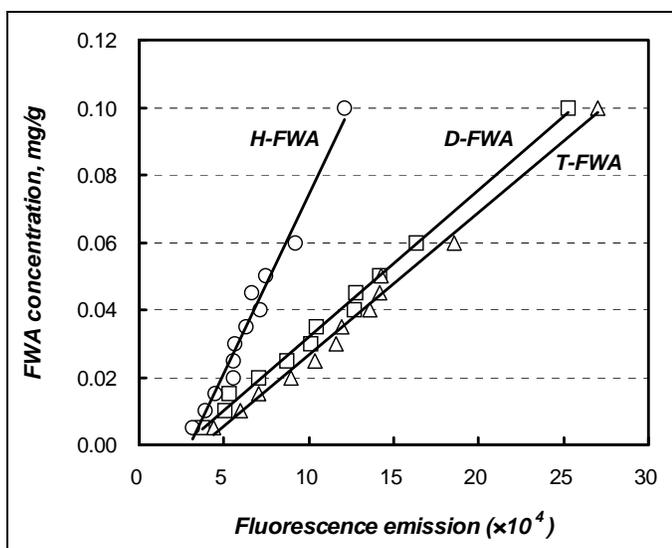


Fig. 1. Relationship between fluorescence emission and concentration of FWAs

The peak excitation wavelengths were different depending upon the types of FWAs. In the case of D-FWA and H-FWA, a peak excitation wavelength of 340 nm was used for quantitative analysis. A peak wavelength of 337 nm was used to analyze T-FWA solutions. Measurements of fluorescence emission were carried out with FWA solutions with concentrations ranging from 0.02 to 0.10 mg/g. The emission wavelengths used were 440 nm for D-FWA and H-FWA, and 438 nm for T-FWA, which were the wavelengths where fluorescence showed peak emission spectra. Figure 1 illustrates the relationship between the concentration of FWAs and fluorescence emission.

As the concentration of FWAs increased, fluorescence emission increased linearly. The coefficients of determination for D-FWA, T-FWA, and H-FWA were greater than 0.9, irrespective of the type of FWAs. The linear regression equations used for quantitative analysis are presented in Table 2.

**Table 2.** Regression Equations for the Quantitative Analysis of FWAs in Solution

Regression equation : $y = a \times x + b$ [where, y : concentration of FWA (mg/g), x : fluorescence emission]					
FWA type	Emission wavelength	Excitation wavelength	a	b	R <sup>2</sup>
D-FWA	440 nm	340 nm	$4.40 \times 10^{-7}$	0.012	0.99
T-FWA	438 nm	337 nm	$4.24 \times 10^{-7}$	0.016	0.99
H-FWA	440 nm	340 nm	$1.07 \times 10^{-6}$	-0.032	0.98

### Adsorption of FWAs on the Cellulosic Fibers

Paper samples dyed with D-FWA and T-FWA were manufactured, and their FWA content was determined through the adsorption analysis of FWAs. Two sets of experiments were carried out to determine the amount of FWAs in the paper. First, zeta potential analysis of fiber stock was measured to find the contact time required for maximum adsorption of FWA onto fiber. Secondly, analysis was made to determine FWA content.

Figure 2 shows the zeta potential of fibers dyed with D-FWA as a function of contact time. The initial ZP of fibers was negative, because the fibers in the pulp suspension carry negatively charged carboxyl groups (Bley and Winter 1997). When D-FWA was added into pulp suspension, zeta potential of fibers became more negative during the first 2 minutes of addition. This indicates that negatively charged FWAs adsorbed onto fibers during this period. When the contact time was longer than 2 minutes, the zeta potential of fibers reversed and started to increase toward positive charge. This seemed to be because D-FWA adsorbing on the fiber surface started to penetrate into the pores present on fibers by diffuse movement (Cho et al. 2001) as the contact time increased. Koethe et al., who investigated the effect of contact time on the surface charge of fibers, showed that as contact time increased the surface charge of fibers declined because of the penetration of polymers into the pore present on the fiber surface (Koethe

et al. 1993). Moreover, Crouse et al. reported that minimal contact time was required to ensure uniform distribution of adsorbates (Crouse et al. 1981). In this study, the contact time between internal FWAs and fibers was kept constant at 2 minutes to prevent the diffuse movement of FWAs.

Figure 3 presents the ZP of fibers as a function of D-FWA addition. As the addition of D-FWA increased, the ZP of the fibers moved to negative charge. This indicated that as the addition of D-FWA increased, the amount of adsorbed D-FWA increased. An increasingly negative ZP of fibers indicated that the adsorption of D-FWA on fibers increased as the contact time progressed. Amounts of adsorbed D-FWA and T-FWA are presented in Fig. 4.

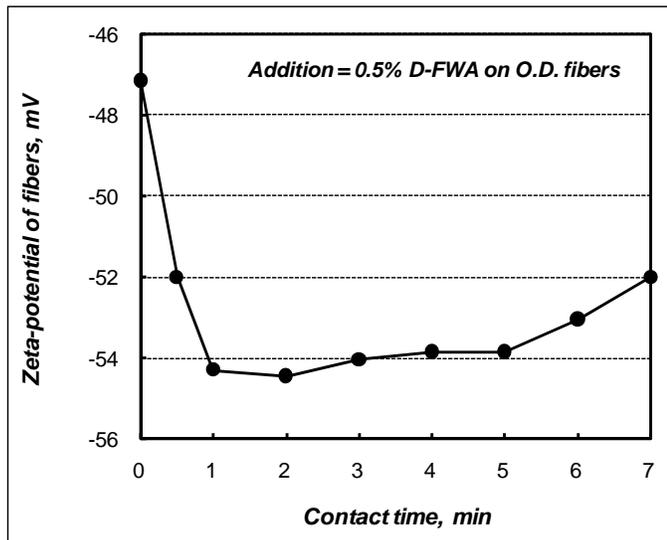


Fig. 2. Zeta potential of fibers as a function of D-FWA addition

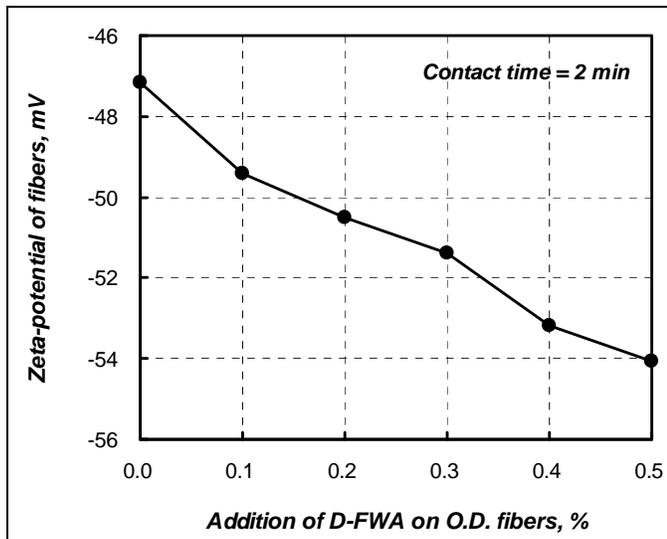


Fig. 3. Zeta potential of fibers as a function of D-FWA addition

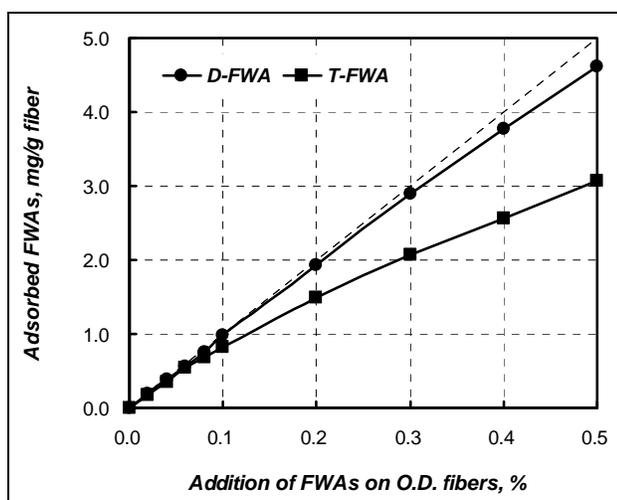


Fig. 4. Adsorption of FWAs on fibers as a function of FWA addition

### Regression Equations for FWAs in Model Papers Using Spectrophotometer

The FWA content in handsheets dyed with FWAs and the fluorescence phenomena were analyzed using the spectrophotometer. Figures 5 and 6 illustrate the FWA content in papers as a function of the fluorescence index. The FWA content increased exponentially as the fluorescence index increased. This indicates that the relationship between the FWA content and the fluorescence index was nonlinear. Exponential regression equations with three constants,  $y = y_0 + a \times \exp(b \times x)$ , showed the highest coefficient of determination for quantitative analysis. The regression equations derived for the quantitative analysis of FWAs in papers using the spectrophotometer are presented in Table 3. In all cases, the coefficients of determination were greater than 0.9, indicating that fairly precise estimation of FWAs in the samples can be obtained from these equations.

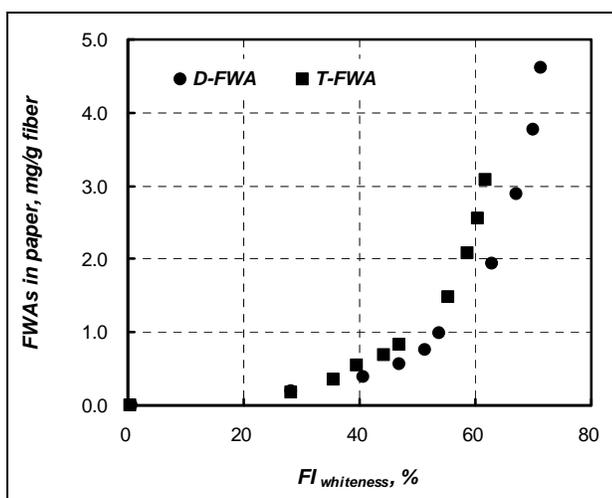


Fig. 5. Relationship between FWA content and fluorescence index ( $FI_{whiteness}$ )

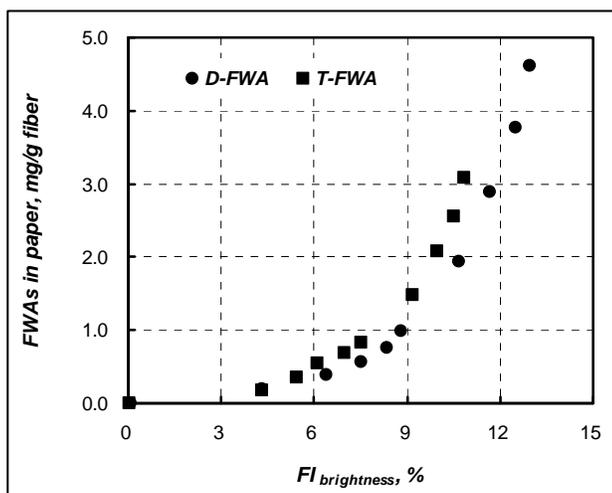


Fig. 6. Relationship between FWA content and fluorescence index ( $FI_{\text{brightness}}$ )

Table 3. Regression Equations for the Quantitative Analysis of FWA Optical Effects in Paper

Regression equation : $y = y_0 + a \times \exp(x \times b)$ [where, y : FWA content in paper (mg/g), x : fluorescence index (%)]					
FI	FWA	$y_0$	A	b	$R^2$
$FI_{\text{whiteness}}$	D-FWA	$1.35 \times 10^{-1}$	$4.00 \times 10^{-3}$	$9.90 \times 10^{-2}$	0.99
	T-FWA	$1.08 \times 10^{-1}$	$7.00 \times 10^{-3}$	$9.80 \times 10^{-2}$	0.99
$FI_{\text{brightness}}$	D-FWA	$2.40 \times 10^{-2}$	$3.80 \times 10^{-2}$	$3.70 \times 10^{-1}$	0.99
	T-FWA	$4.00 \times 10^{-2}$	$4.00 \times 10^{-2}$	$3.97 \times 10^{-1}$	0.99

### Regression Equations for FWAs in Model Papers Using Image Restoration Microscope

Images of handsheets dyed with internal FWAs were obtained using an image restoration microscope. The image magnification was 200 times, and the fluorescence emission was determined using image analysis software developed by AppliedPrecision. Figure 7 presents images of papers without and with FWAs, respectively. The image of paper without FWA presents an unclear picture of fibers, because there was no fluorescence emission from the paper. However, the image of paper with D-FWA showed the fluorescence emission, and the shapes of fibers could be observed. The intensity of the fluorescence emission was analyzed by the image analysis technique and the mean, maximum and minimum fluorescence emissions at 457 nm were determined. As the

addition of FWAs increased, the mean, maximum, and minimum fluorescence emission increased. In this study, the mean fluorescence emission was used when the regression equations were induced. The fluorescence emission did not increase linearly to the increase of FWAs when the addition of FWAs was greater than 0.3%. The relationship between FWA content and mean fluorescence emission was exponential, as shown in Figure 8. Regression equations for the quantitative analysis of FWAs in paper using an image restoration microscope are presented in Table 4. All of the coefficients of determination were greater than 0.9.

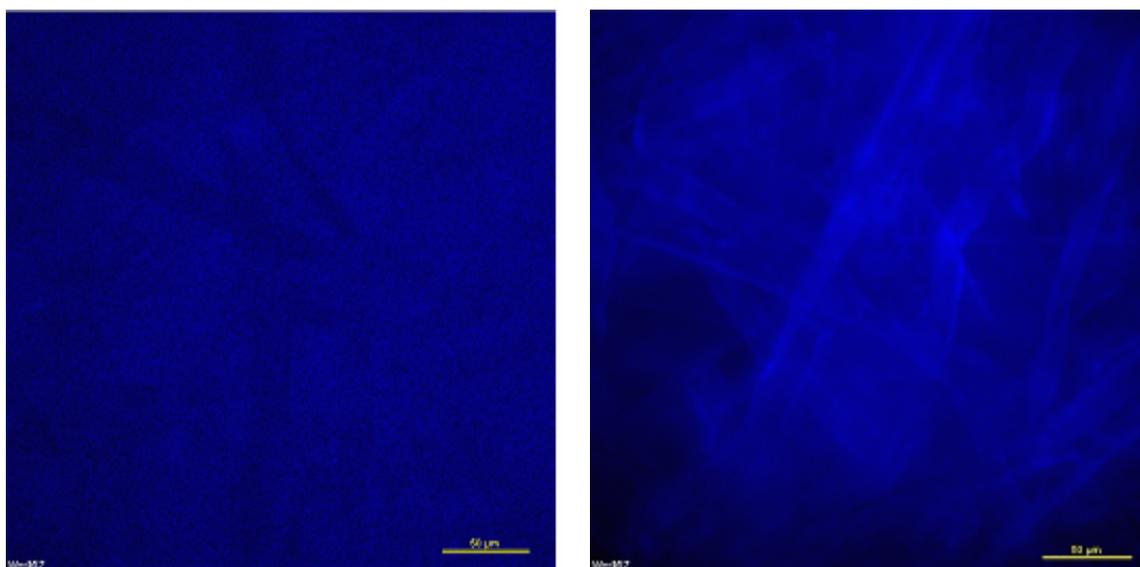


Fig. 7. IRM images of handsheets dye with 0.0% (left) and 0.5% (right) of T-FWA

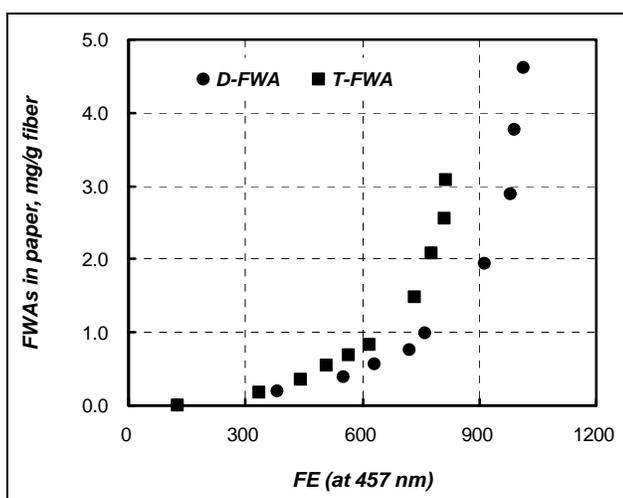


Fig. 8. FWA content in paper as a function of fluorescence emission

**Table 4.** Regression Equations for the Quantitative Analysis of FWA Optical Effects in Paper

Regression equation : $y = y_0 + a \times \exp(x \times b)$ [where, y : FWA content in paper (mg/g), x : fluorescence index (%)]					
	FWA	$y_0$	a	b	$R^2$
Fluorescence emission at 457 nm	D-FWA	$2.70 \times 10^{-1}$	$1.00 \times 10^{-3}$	$8.00 \times 10^{-3}$	0.98
	T-FWA	$1.21 \times 10^{-1}$	$9.00 \times 10^{-3}$	$7.00 \times 10^{-3}$	0.99

## CONCLUSIONS

In this study, three optical measurements were carried out to establish the methodology to analyze the FWA content of papermaking process water and paper samples. Test solutions and papers that contained only known amounts of FWAs were prepared in the laboratory, and their FWA contents were determined using analytical instruments, including a spectrofluorometer, a spectrophotometer, and an image restoration microscope. The fluorescence emission of the FWA solutions was measured using a spectrofluorometer. The relationship between the fluorescence and the FWA concentration was plotted, and linear regression equations were obtained. The FWA content of the paper samples was determined by the adsorption analysis of FWAs on the fibers. Fluorescence indices, such as  $FI_{\text{whiteness}}$  and  $FI_{\text{brightness}}$  were measured using a spectrophotometer. The fluorescence emission was determined using an image restoration microscope and image analysis. The fluorescence indices and emissions were plotted as a function of FWA content in paper, and exponential regression equations were obtained for the quantitative analysis. The coefficients of determination for the regression equations were greater than 0.9, which indicated that the FWA content of water and paper samples could be estimated using the regression equations.

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