Determination of Toner Content by Diffuse Reflectance for Office Paper Recycling Studies

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Waste office paper, photocopied or laser printed, has recently increased along with office automatization. In waste office paper, toner ink is used as the printing medium in place of conventional oil ink. Since toner ink cannot be saponificated by alkali and be decolored by bleaching, different from the case of oil ink, toner remains on regenerated paper as black specks. Although cascade recycling of waste office paper is compelled at present, the demand for low-grade paper is limited. From such circumstances, a new separation process for waste office paper is demanded to achieve parallel recycling. At the first stage of separation studies, the sharpness of separation is evaluated using small separators to obtain fundamental data. In a lab-scale separator, the sample amount of one feed is generally a few grams. However, the sample amount used for brightness, ERIC, and image analysis that are generally used to evaluate the efficiency of deinking are not small for lab-scale tests of these analyses. This paper describes an investigation of a sheet preparation method by a small amount of sample under 0.5g and compares the precision of toner content determination of spectroscopic analysis and image analysis from the viewpoint of separation evaluation. The easiness and convenience of the operation using only general-purpose equipments has also been set as a principle purpose. From the viewpoint of an analysis that yields high precision with a small amount of sample in short time, the method calculating the absorption coefficient from diffuse reflectance in the visible region is the most rational method in this study.
Keywords: Office Paper recycling, Ink determination, Toner ink, Spectroscopic analysis

Introduction

In paper recycling, to evaluate fiber-ink separation for usual waste paper such as newsprint, brightness is usually measured. However, because toner ink is used in waste office paper, photocopied or laser printed, brightness does not necessarily become a quality indicator. As a toner particle consists of lots of fine carbon or magnetite particles covered with resin, it cannot be hydrolyzed in alkali by saponification and be decolored by bleaching different from the case of conventional oil ink [1-4]. So, toner remains on regenerated paper as black specks, and the specks decide the market value of it.

Recently, ERIC (effective residual ink concentration) method of the Tappi standard [5] and image analysis [1,6] are used to determine the concentration of residual toner specks. Although these are excellent methods that measure weak ink absorption, several grams of sample must be prepared at least in these standard methods which are industrial testing methods. Generally, when studying separation techniques in a laboratory, the sharpness of separation is evaluated using small separators to obtain fundamental data for practical use. The sample amount of one feed for the smallest separator which is used at the first stage of a separation test is about 1g. So, the sharpness of separation to evaluate deinking properties must be examined by a very small amount of separated product.

In our previous paper [7], a sample preparation method using under 0.5g of sample was investigated. In this paper, using a small amount of sample under 0.5g, the precision of toner content determination of image analysis and several spectroscopic analyses were compared to analyze under substandard sample conditions. The easiness and convenience of the operation using only general-purpose equipments has also been set as a principle purpose for lob-scale recycling study.

Experiment

Preparation of Disintegrated Samples

The printed samples were prepared by printing on arbitrary areas of one side of paper (NBC-Ricoh:My Recycle Paper New, used fiber is blended at 70%, 65g/m²) with a laser printer (Canon:Laser Shot B406E). Although many toner products on the market are nonmagnetic type, a printer using magnetic toner (Canon:CRG-EPKS II) was used here to enable the evaluation of assay precision of both image and spectroscopic analysis by ICP analysis. The printed samples were cut at sizes according to the thickness of the sheeted sample to be prepared. The sample for each thickness was mixed with 20ml of 8%-NaOH solution and was soaked in that solution for 12hr. Then beating was carried out for 5min. at a fixed speed using an agate mortar. Next, this mixture with the beaten sample inside was poured into a 200ml beaker, adjusted to 150ml by the addition of 8%-NaOH solution, irradiated by ultrasonic wave for 5min. and stirred by a stainless impeller (rotation diameter:50mm) at 500r.p.m. for 10min. After repeating irradiation of ultrasonic wave for 5min. and agitation for 10min. twice, ultrasonic wave was irradiated for 5min. again. Finally, the sample suspension was filtrated by an alkali-resistant membrane filter under reduced pressure, and the disintegrated sample was washed 3 times with water.

Sheet Preparation

Sheet preparation was carried out by the following method [7]. The disintegrated sample was mixed with 10ml of 1%-PVA (polyvinyl-alcohol) which is a wetting agent for toner. The mixture was poured into a 100ml measuring cylinder and the whole quantity was adjusted to 100ml by ion-exchanged water. To obtain representative data of toner concentration, it is important that toner and fiber are dispersed in the pulp suspension. Because the isoelectric points in zeta potentials of toner and fiber were almost the same value around pH3, the suspension was adjusted to pH7 to avoid homo-coagulation and hetero-coagulation of toner and fiber. The sample stirred with a glass stirrer was transferred into a funnel (filtration diameter:36mm) set to a cellulose acetate type membrane filter (pore size: 0.2μm, diameter: 47mm) and was filtered under reduced pressure by a vacuum pump. To make a smoother surface at the filtration process, a polypropylene disk having a smooth surface (diameter:36mm, thickness:1mm, density:0.91g/cm^3) was floated on the suspension. As the filtration suspension level goes down, the disk lowers along with it as shown in **Fig.1**. Then, dehydration and compression of the sheeted plane were promoted by suction of the pump. Next, the sample which became sheet-like was detached altogether with the filter.
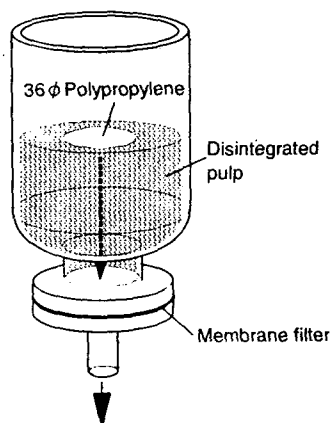

Fig.1 Filtration of disintegrated sample using a polypropylene disk.

A 47mm diameter water-absorbing paper was placed on the sample and then pressed by a hydraulic press at 2MPa for 5min. Then, the water-absorption paper was removed and the sample was dried at 60°C for 20min. Finally, after taking off the filter, the sheeted sample for measurements were made by pressing the sample at 2MPa for 5min. again in order to remove the deflection caused by drying. The correlation between the weight and thickness of the sheeted samples was r^2=0.999 (**Fig.2**). The sheeted samples prepared by this method had almost the same density.
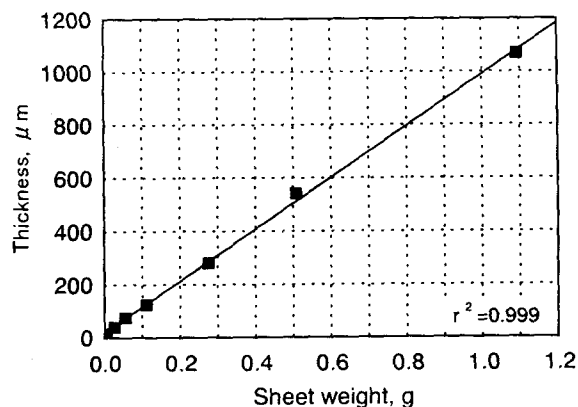

Fig.2 Relation between weight and thickness of sheeted samples.

Image Analysis

Image analysis was used to measure the toner area ratio of a sheeted sample. The sheeted sample was set to a reflecting microscope and the image information from a video camera connected to the microscope was taken into a personal computer. Then the toner area ratio of the sheeted sample was determined by an image analyzing software (Mitani:Winroof). Measurements were carried out for 35mm^2 of measurement area and at 1pixel=2.36μm considering the original toner particle size which were 10μm.

Spectroscopic Analysis

A spectroscopic colorimeter (Minolta:CM-3500d) was used for reflectance and transmittance analysis in the visible region. The light source of this colorimeter is a xenon lamp. The measurement conditions were; the d/8 system (diffusion irradiation 8 degrees light reception), irradiation diameter: 36mm, wavelength range: 400-700nm.

A Fourier transform type infrared spectrophotometer (Nicolet:Magna760) was used in the near infrared. The light source of this spectrophotometer is a tungsten halogen lamp. PbS was used for the detector, and quartz for the beam splitter. The measurement wavelength range was between 909-2381nm and 1024 times were integrated for each spectrum.

ICP Analysis

The quantity of Fe contained in magnetic toner was determined by an ICP emission spectrophotometer (Seiko Instruments:SPS4000) in order to evaluate the assay precision of image and spectroscopic analyses. After weighing the magnetic toner used in the laser printer, iron oxide contained in it was obtained by combustion of the resin part at 800°C for 1hr. The iron oxide was dissolved by 5%-HCl until no residue remained, and then the Fe concentration was measured by the ICP. After the Fe content of the magnetic toner was determined in this way, the printed office paper too was subjected to combustion

and then dissolved by 5%-HCl. Then, the toner content of the paper was obtained by determining the Fe content with ICP. The correlation of the ICP calibration curve was $r^2=0.999$. This analytical method using ICP is possible only for magnetic toner

Results and Discussion

Relation of Toner Content and Toner Area by Image Analysis

Toner specks in waste office paper are often measured directly by image analysis. Sheeted samples of about $500\mu m$ were prepared by 10 pieces of 0.5g paper which had been printed at an arbitrary area. The relationship between toner content and toner area ratio of the sheeted samples are shown in Fig.3(a). The toner content and toner area ratio showed a linear relation with the correlation of $r^2=0.976$. This r^2 value is not sufficient enough to allow the use of this calibration curve for the evaluation of separation.
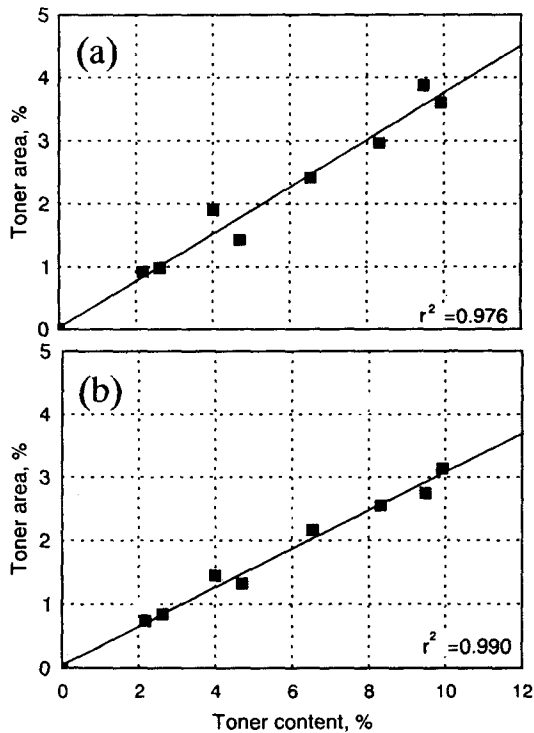

Fig.3 Relation between toner content and toner area ratio by image analysis before and after maximum size correction.
(a) before correction (b) after correction

The size distribution of toner specks measured in this image analysis is continuous in smaller particle size range, but becomes discontinuous in the larger particle size range (Fig.4). The precision of toner determination by image analysis must be lowered by casual appearance of larger size toner specks. So, changing the maximum size for calculation in image analysis to a smaller size is tried. The

r^2 value is gradually higher by this calculation method, and is improved to $r^2=0.990$ at $34\mu m$ of maximum size (Fig.3(b)). Although the difference of 0.990 and 0.976 is not enough to be recognized as significant in the 10 plots evaluation (n=10), these results suggest that the toner appearance frequency in each size range has an influence on the relative toner concentration.
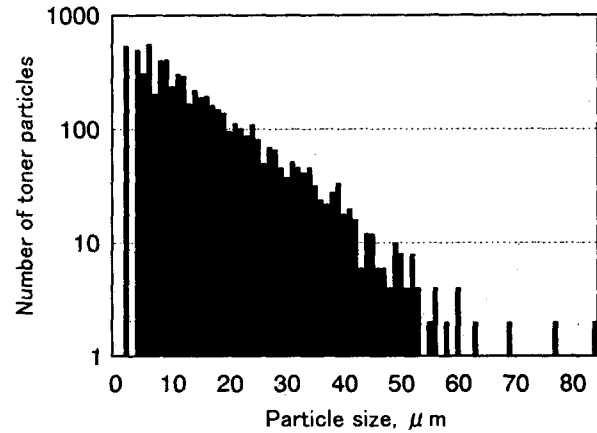

Fig.4 Number of toner particles in each toner size by image analysis. (toner content: 9.47%)

Relation of Toner Content and KM Function in the Visible Region and the Near Infrared Spectra

When identifying the absorption component of a powder layer by the reflectance spectra, the Kubelka-Munk theory (KM theory) [8-10] which is described as the following equation has been usually applied.

$$F(R_\infty)=K/S=(1-R_\infty)^2/2R_\infty \qquad (1)$$

where K (the absorption coefficient) and S (the scattering coefficient) are the energy loss proportion of incident light lost by absorption and rear diffusion, respectively, and R_∞ is the diffuse reflectance of the powder layer which has infinite thickness $(d=\infty)$. Generally, $F(R_\infty)$ is called the KM function. When the sample conditions of KM theory such as thickness conditions $(d=\infty)$ are satisfied, a linear relationship is obtained between $F(R_\infty)$ and the concentration of the absorption component, because total reflectance can be considered to consist of diffuse reflection only.

The reflectance of sheeted samples, which were prepared in the same way as for image analysis, were measured. Fig.5(a) and Fig.5(b) show the relationship between the $F(R_\infty)$ and the toner content in the visible region and in the near infrared, respectively. Each plot in these figures shows the mean values of 6 replicates. The r^2 between the toner content and $F(R_\infty)$ is 0.991 in the visible region and 0.987 in the near infrared. These r^2 values are recognized as the same level as the r^2 by image analysis in the 10 plots evaluation. These results suggest that the sample thickness $(500\mu m)$ made by 0.5g of disintegrated

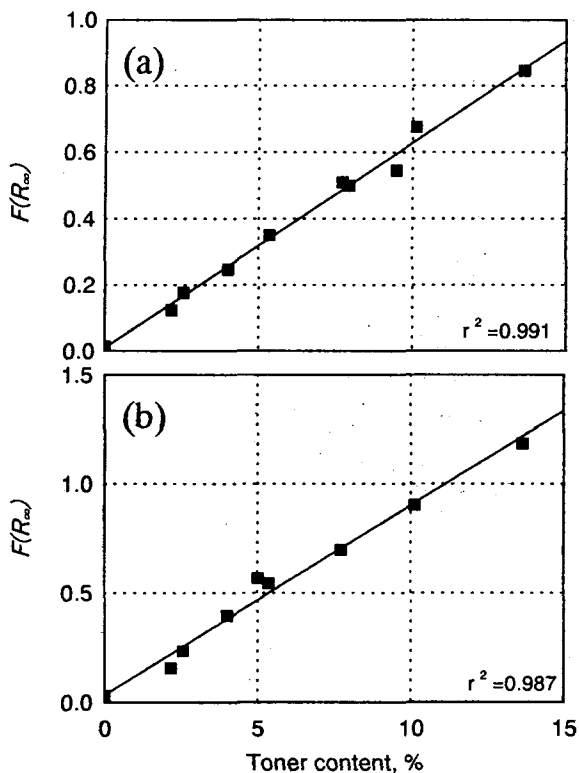sample is not enough to satisfy the sample conditions of KM theory.

Fig.5 Correlation between toner content and $F(R_\infty)$ converted from total reflectance in the visible region and in the near infrared.
(a) visible region (b) near infrared

Relation of Toner Content and Absorption Coefficient in the Visible Region and the Near Infrared Spectra

According to the equation of Kubelka, S can be mathematically obtained from Eq.2 by using the reflectance measured with a white and black backing.

$$R=[1-Rg(a\text{-}bctgh(bSd))/[a\text{-}Rg+bctgh(bSd)]] \qquad (2)$$

where $a=(S+K)/S$, $b=(a^2-1)^{0.5}$ and Rg is background reflectance. From this calculation, the absorption coefficient (K) also can be calculated by equation of Kubelka [9, 10]. Recently, the ERIC measurement [5,7] is used as a standard method for flexo ink determination. The ERIC value is calculated with K measured at 950nm in the near infrared region. In this study, K were measured in the visible region, the near infrared, and at 950nm by a small amount of sample, and the assay precision was compared. The sample of 150μm thickness prepared by 0.15g of disintegrated pulp which has enough low opacity is used for these measurements. The relation between toner content and K in the whole visible region, in the whole near infrared, and at 950nm are shown in **Fig.6(a)-(c)**,

respectively. The mean values of 6 replicates of measurement are shown in the figures. Even when the sample amount is relatively small, such as 0.15g, the r^2 of these methods reach 0.998 in all cases. However, under substandard sample conditions and the evaluation by 10 plots in this study, the original advantage of the ERIC measurement at 950nm is not expressed and there is no difference between the assay precision at 950nm and that in the whole wavelength range of the visible region and the near infrared.
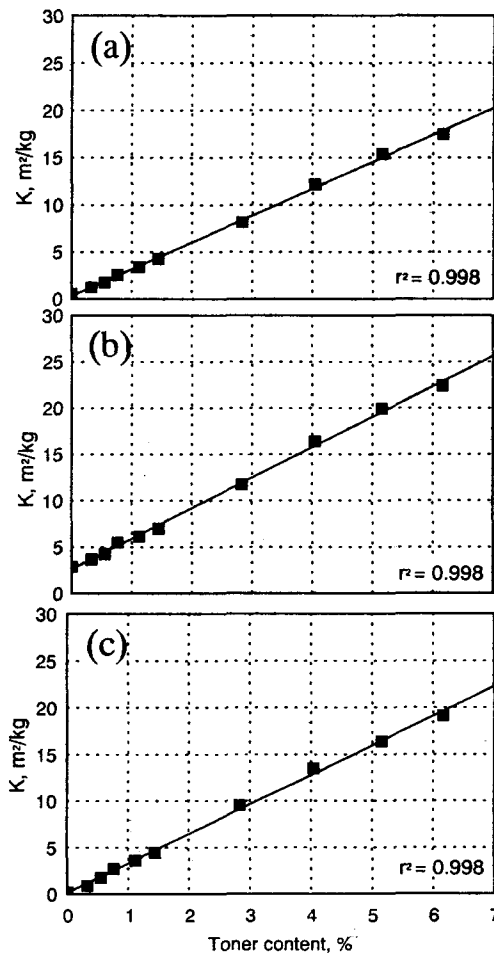

Fig.6 Correlation between toner content and absorption coefficient in the visible region and the near infrared.
(a): Visible region (400nm-700nm)
(b): Near infrared (909nm-2381nm)
(c): Near infrared (950nm)

Relation of Toner Content and Absorption Coefficient by Transmittance Spectra

Usually, when K of a solution is measured, a transmitting spectrometer is used and light absorption is measured as the absorbance (A). If a transmitting spectrometer, which is the most popular spectrometer, can be used for toner concentration measurements, it is very convenient for lab-

scale recycling studies. However, for sheeted samples, since parallel transmittance obeys the law of Lamert-Beer and diffuse transmittance obeys the KM theory, analysis error may be larger than other determination methods. In this chapter, the transmittances of sheeted samples were measured and the possibility of using a transmitting spectrometer for toner determination was investigated. **Fig.7** shows the relationship between toner content and transmittance calculated according to the law of Lamert-Beer, by using 0.15g sheeted samples. The r^2 between the toner content and absorbance is 0.993. This r^2 value in this study can be recognized statistically as the same accuracy level as the values by image analysis (0.990) and by $F(R_\infty)$ measurements in the visible region (0.991) and the near infrared (0.987). These results show that the transmittance measurement shows lower assay precision than the K measurement by diffuse reflectance, but it can be used instead of image analysis and $F(R_\infty)$ measurements.
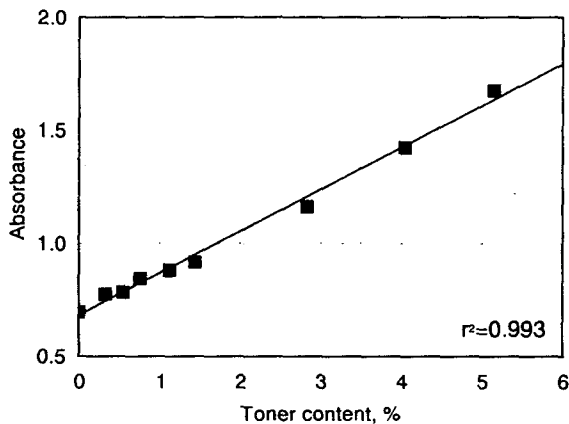

Fig.7 Relation between toner content and absorbance calculated from total transmittance.

Relation of precision and Operation Time

In this paper, to achieve good precision for toner determination by using a small amount of sample, some toner content determination methods such as image and spectroscopic analyses have been examined. Correlations from $r^2=0.976$ to $r^2=0.998$ were obtained from sheeted samples prepared by the same method. In the three methods of measuring K by diffuse reflectance, the r^2 values are highest in this study and extremely near to that of the calibration curve of ICP. However, when considering toner determination as an index for the evaluation of separation in recycling studies, the operation time also becomes an important factor because it is necessary to measure many samples conveniently. So, toner content determination methods that have been examined in this paper are summarized from the viewpoint of precision and operation time.

The time required in each stage from sheet preparation to data collection is shown in **Table 1**. Two kinds of samples were prepared, that is, the 500μm-thick (0.5g) sample corresponding to an infinite thickness for $F(R_\infty)$ and image analyses, and the 150μm-thickness (0.15g) sample for K

and transmittance analyses. Naturally, the 150μm sample requires a smaller amount but that is not the only advantage. Since filtration and drying can be done quickly in the case of the 0.15g sample, the total time of these two procedures can be shortened to less than 1/4 than that of the 500μm sample. The time required in each step may change according to the equipment and measurement condition used, but relatively speaking, it can be said that the operation time becomes longer in the order of visible region spectroscopy, near infrared spectroscopy, and image analysis.

Table 1 Operation time in each stage of data collecting.

Methods	Sample amount (g)	Operation time for one sample (min.)						
		Sheet preparation				Measure		Total
		Filt.	Press	Dry	Press	Mes.	Cal.	
IMn*	0.5	10	5	30	5	40	5	95
IMc*	0.5	10	5	30	5	40	10	100
KMv	0.5	10	5	30	5	5	5	60
KMn	0.5	10	5	30	5	30	5	85
Tv	0.15	1	5	8	5	5	5	29
Kv	0.15	1	5	8	5	10	5	34
Kn	0.15	1	5	8	5	60	5	84
K950	0.15	1	5	8	5	20	5	44

IMn: image analysis (normal calculation)
IMc: image analysis (correction of size distribution)
KMv: $F(R_\infty)$ measurement in the visible region
KMn: $F(R_\infty)$ measurement in the near infrared
Tv: Transmittance in the visible region
Kv: K measurement in the visible region
Kn: K measurement in the near infrared
K950: K measurement at 950nm
filt.: filtration, mes.: measurement, cal.: calculation
* The analysis time by measuring 20 images of 307,200 pixels.

The relationship between assay precision, operation time is shown in **Fig.8**. The big circle plot and small circle plot represent the results for 500μm-thick and 150μm-thick sample, respectively. From the viewpoint of an analysis that yields high precision with a small amount of sample in short time, the K measurement methods in all cases excel the other methods. Especially in this study, the method measuring K by calculation of diffuse reflectance in the visible region (Kv in Fig.8) seems to be the most rational one (**Table 2**). Also, the same level of assay precision as image analysis can be obtained from $F(R_\infty)$ and transmittance in shorter operation time. In office paper recycling studies, ERIC method and image analysis are usually used at present. However, under substandard sample conditions, researchers can select many other methods using reflectance and transmittance of sheeted sample to obtain the same assay precision.
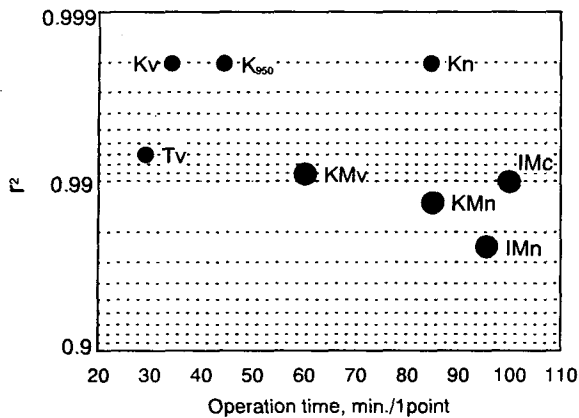
Fig.8 Relation between operation time and r^2

● 0.15g sample ● 0.5g sample
IMn: image analysis (normal calculation)
IMc: image analysis (correction of size distribution)
KMv: $F(R_\infty)$ measurement in the visible region
KMn: $F(R_\infty)$ measurement in the near infrared
Tv: Transmittance in the visible region
Kv: K measurement in the visible region
Kn: K measurement in the near infrared
K_{950}: K measurement at 950nm

Table 2 Analysis conditions and assay precision in the K measuring method in the visible region (Kv).

Sample amount (g)	Sheet preparation time (min.)	Measuring time (min.)	Total operation time (min.)	r^2 of calibration curve (n=10)	SEC* (%)	SEP** (%)
0.15	19	15	34	0.998	0.010	0.136

*SEC: standard error of calibration
**SEP: standard error of prediction obtained by cross validation

Conclusions

In this study, various toner determination methods have been investigated as an index for the evaluation of separation of waste office paper in the field of recycling study. Keeping in mind that only a small amount of sample and general-purpose equipments should be used throughout the operation, the precision of the analyses was examined. The results are as follows:

(1) The correlations between the toner content and $F(R_\infty)$ which had been converted from total reflectance in both the visible region and the near infrared were the same level as that by image analysis.

(2) The correlations between the toner content and transmittance was also the same level as that by image analysis. $F(R_\infty)$ and transmittance measurement methods can be used instead of image analysis as a toner content determination under substandard conditions using small amount sample.

(3) The methods measuring K in the visible region, in the near infrared, and at 950nm have high r^2 values of 0.998 in

all cases. Relatively speaking, the operation time becomes longer in the order as follows; visible region spectroscopy < near infrared spectroscopy < image analysis. In substandard conditions using small amount of sample, the method measuring K in the visible region is sufficient enough to use for the evaluation of separation, and the correlation of r^2=0.998 can be obtained by 34 min. of operation time using 0.15g of sheeted sample.

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