A New Approach to Measurement of Effective Residual Ink Concentration of Deinked Papers

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ABSTRACT

The measurement of effective residual ink concentration (ERIC) in recycled papers is prone to errors. TAPPI Provisional Method T 567 pm-97 is based on application of the Kubelka Munk (KM) theory to diffuse reflection from papers measured once with the black backing and again with a thick backing of the same papers. At high opacities the two results become indistinguishable, leading to an undetermined value for ERIC when the full KM theory is applied. This is handled by use of an approximate value for the KM scattering coefficient to remove the ambiguity. However, the approximate value may be in error by 10%. An alternate approach avoids the uncertainty inherent in the approximation by applying the KM theory to the measurement of diffuse reflection and transmission in single sheets. The measurement is valid at any opacity for which the percentage transmission through the sheet is accurately determined in the near-infrared spectral region. Coefficients of variation (COV) are as low as or lower than those from the standard ERIC measurement throughout the range of interest. They decrease with increasing opacity to a low of 8% for a sheet having 1000 ppm ERIC, compared to a COV of 16% for the standard measurement based on an average value of scattering coefficient. The proposed method promises to be a superior way to monitor deinking in recycled papers.

INTRODUCTION

Ink removal is one of the most important steps in recycling of mixed recovered office paper, old magazines, and old newspapers. Ink removal efficiency of a recycling operation is characterized by the brightness increment of the final paper over that of feed stock. Final paper brightness has been used as a product specification of recycled papers. However, the brightness measure has deficiencies in quantifying ink-removal efficiency and the amount of residual ink in deinked pulp because paper brightness depends on additional factors, such as pulp refining, pressing, calendering, and formation. Jordan and Popson [1] developed a near-infrared reflectance technique to measure residual ink concentration in paper made of deinked pulp using Kubelka-Munk theory [2]. The technique measures reflectance at an infrared wavelength (~950 nm) from a paper sample over a black backing, \( R_0 \), and reflectance from a thick stack of paper from the same sample, \( R_s \). The Kubelka-Munk constant \( k \), the specific absorption coefficient of the sample, can be calculated from the two measured reflectance values, \( R_0 \) and \( R_s \). It is directly related to the residual ink concentration in the paper sample when measured at a near-infrared wavelength where the absorption from lignin and dyes can be ignored [1]. According to Kubelka [3], the specific absorption coefficient is

\[
k = S \frac{(1 - R_\infty)^2}{2R_\infty}
\]

where

\[
S = \left[ \frac{R_\infty}{w(1 - R_\infty^2)} \right] \ln \left[ \frac{1 - R_0/R_\infty}{1 - R_0/R_\infty} \right]
\]

\( S \) is the specific scattering coefficient, and \( w \) is the basis weight. The technique has been adopted by TAPPI as provisional test method T 567 pm-97 [4] to measure effective residual ink concentration (ERIC) of deinked pulp. The technique works fairly well except for the large standard deviations encountered in measuring papers of high opacity resulting from high basis weight, ash content, or ink concentration (high ERIC values). This causes concerns...
in interlaboratory data comparison [1]. These concerns are magnified through the use of several different kinds of spectrometers to measure ERIC in practice, some of which (like most UV-Vis spectrometers) don’t extend into the infrared. Low measurement accuracy for high-ERIC papers occurs primarily because the denominator of the logarithmic function in Equation (1b) approaches zero as \( R_0/R \) approaches unity. The condition \( R_0 = R \) defines a singular point. In tests of opaque papers, measurements of \( R_0 \) and \( R \) become statistically indistinguishable, resulting in an indeterminate value for \( S \) in Equation (1b) and forcing use of an approximate value. This anomaly in ERIC measurements using Kubelka-Munk theory motivates the present study. The objectives of the study are

1) to analytically and experimentally quantify errors in ERIC measurements resulting from application of the TAPPI provisional test method [4] and
2) to demonstrate a complementary method for ERIC measurements that can be applied to high opacity papers without resorting to an approximate value for \( S \).

METHODOLOGY

In the TAPPI provisional method [4] for measurements of deinked paper based on the work of Jordan and Popson [1], ERIC is the residual ink concentration determined as the ratio between the specific absorption coefficient, \( k \), of the deinked paper and the absorption coefficient of black ink, \( k_{ink} \). Neglecting the absorption by lignin at infrared wavelengths greater than 950 nm,

\[
ERIC = c_{ink} = \frac{k}{k_{ink}} \times 10^6 \text{ (ppm)}
\]  

(2)

where \( k_{ink} = 10,000 \text{ m}^2/\text{kg} \), a default value, and the Kubelka-Munk coefficient \( k \) is determined from two reflectance measurements using Equation (1). (For simplicity, Equation (1) will be used to refer jointly to Equations (1a) and (1b).)

We propose to take a different and simple experimental approach to determine the Kubelka-Munk coefficients \( k \) and \( S \) in this study. This new approach measures reflectance \( R \) at the incident surface and transmission \( T \) at the back surface from the same paper sample without back reflectance or remounting [5].

For the case of a single specimen measured in isolation (i.e., where no radiation is returned to the specimen by reflection at the back surface) the solution of the KM equations for the light reflected from the front surface is

\[
R = \frac{\sinh(Sb)w}{a \sinh(Sw) + b \cosh(Sw)}
\]  

(3)

where \( a = k/S + 1 \) and \( b^2 = a^2 - 1 \). Transmission at the back surface is

\[
T = \frac{b}{a \sinh(Sw) + b \cosh(Sw)}
\]  

(4)

The inverse equations expressing \( S \) and \( k \) in terms of \( R \) and \( T \) are

\[
S = \frac{2R}{w \cdot \sqrt{(1 - T^2 + R^2)^2 - 4R^2}} \sinh^{-1} \left[ \frac{1}{2T} \sqrt{(1 - T^2 + R^2)^2 - 4R^2} \right]
\]  

(5)

and

\[
k = \frac{(1 - R)^2 - T^2}{w \cdot \sqrt{(1 - T^2 + R^2)^2 - 4R^2}} \sinh^{-1} \left[ \frac{1}{2T} \sqrt{(1 - T^2 + R^2)^2 - 4R^2} \right]
\]  

(6)

These results, derived in Reference [5], agree with Equation (1) when appropriate substitutions are made. A singularity occurs when \( T = 0 \). The singularity is consistent with that of Equation (1) since a paper for which \( T = 0 \)
must also have \( R_0 = R \). However, when \( T \) is small but finite, differences between \( R_0 \) and \( R \) will be on the order of \( T^2 \), and therefore much harder to measure accurately than \( T \) itself. This translates into greater ERIC measurement accuracy using Equation (6) in place of Equation (1).

Although characterization of optical properties using measurements of \( R_0 \) and \( R \) is fairly standard in the paper industry, there are many examples from paper [6], medicine and biology [7–9], paint [10], mineralogy [11, 12], and general instrumentation technology [13] where measurements of \( R \) and \( T \) are described. However, this is the first application we know of that applies the measurements to residual ink concentration.

For opacities above 97%, corresponding to \( T \) less than about 10%, Equation (1) is approximated as

\[
k = \bar{S} \left[ \frac{(1 - R_0)^2}{2R_{\text{m}}} \right]
\]

where \( \bar{S} \) is an average value of scattering coefficient based on the idea that scattering should not be expected to change in a sheet as absorption changes. (See, however, the discussion of the interaction between \( k \) and \( \bar{S} \) in the Foote effect [14, 15].) This approach removes the logarithmic singularity in Equation (1) when \( R_0 = R \); however, determination of the best value for \( \bar{S} \) in a sampling of recycled newsprints was found to be uncertain by about 10% [1].

ERIC values may be calculated by combining Equation (2) with any of the Equations (1), (6), or (7), depending on the data available. Using the default value \( k_{\text{ink}} = 10,000 \text{ m}^2/\text{kg} \), \( \text{ERIC(ppm)} = 100 k \). The three methods for determining ERIC will be referred to as the \( RT \) method, Equation (6), the \( R_0 R \) method, Equation (1), and the \( \bar{S}R \) method, Equation (7).

The main advantage of the \( RT \) method is that \( T \) can usually be measured more accurately in absorbing papers than differences between \( R_0 \) and \( R \). A secondary advantage is that it only requires measurement of a paper’s reflectance at the incident surface and transmittance at the back surface. No sample remounting is required to measure the two properties. The \( R_0 R \) method requires measurement of a paper twice to know its properties: first, as a single sheet; second, as part of an opaque stack of paper from the same sample. Remounting is required to perform the test. Because of the inhomogeneity of ink and fiber distribution in paper, the two measurements introduce variability unless perfectly repeated alignment and contact between papers in the stack is maintained from test to test. At high opacities, the precision of the \( R_0 R \) method is significantly compromised when the variability in reflectance measurements is amplified by the singularity in Equation (1b).

A disadvantage of the \( RT \) calculation is that it becomes error prone at low ERIC values for which Equation (6) approximates

\[
k \approx \frac{1 - R - T}{w}
\]

As the numerator becomes small in comparison to the variation in \( R + T \), the ERIC coefficient of variation (COV) increases. Therefore, the present technique suffers in measuring low-opacity samples just as the \( R_0 R \) method suffers in measuring high opacity samples. The two techniques are complementary to each other. However, the superiority of the \( R_0 R \) method does not show until ERIC values are below 150 ppm, a level of deinking near the clean limit of commercial practice, while the \( RT \) method works well from the first stages of ink removal to the commercial range. The \( \bar{S}R \) method is found to be intermediate to the \( RT \) and \( R_0 R \) methods with respect to COV, when reasonable allowance is made for the uncertainty in the estimated scattering coefficient \( \bar{S} \) [1].
EXPERIMENTAL

Samples
In this study, five samples consisting of five specimens each were measured for ERIC by the three methods of Equations (1), (6), and (7). Samples were chosen to span a wide range of ERIC values and opacity. Three samples with the highest values were 65 g/m² handsheets from a laboratory recycling trial. Recycled thermomechanical pulps with different degrees of residual ink were used. ERIC values were in the range 500 to 1200 ppm. Samples with lower ERIC values (150 to 200 ppm range) included a handsheet from repulped kraft copy paper with residual ink from laser printing, and a commercial newsprint sample of lower basis weight (50 g/m²). The range of sample opacities was 81.7% to 98.7%. Samples from the recycling trial were also measured by Technidyne Corporation (New Albany, Indiana) using their Master Color Touch instrument manufactured to meet the requirements for ERIC measurement [4].

Each of the handsheet samples was represented by five specimens, approximately 5 x 6 cm², taken from equivalent handsheets. Commercial newsprint specimens were 5 x 5 cm² and all came from the same unprinted page of a directory. The handsheet samples had a distinct two-sided roughness associated with the mold that was used. Other differences were minimized to increase sensitivity of experiments to the test method as opposed to within-sample variations.

Testing and Data Analysis
The experimental setup is shown in Figure 1 and described in detail in Reference [5]. A single detector was used to measure the reflected light \( R \) and, after repositioning, the transmitted light \( T \). \( R \) and \( T \) were measured for each sheet. Each of the five sheets in a sample was measured sequentially to complete a test. To develop statistics for calculation of the COV of a test, tests were conducted five separate times at varying intervals.

![Figure 1. Experimental arrangement for measurement of paper reflection and transmission.](image)

For comparison with TAPPI Provisional Measurement T 567 pm-97 [4], reflectance was also measured for sheets individually and as backed by four other sheets from the same sample. In this case, reflectances were noted as \( R_i \) and \( R_s \), respectively. Each sheet in the sample was measured alone and on top of the stack to complete a test. Eventually 50 pairs of values represented each sample: five per specimen per test method.

For determination of \( k \), averaged values of reflection and transmission measurements were used with the appropriate Equations (1), (6) or (7). With \( k \) expressed in units of m²/kg, ERIC in ppm was 100 x \( k \). For each sample, the ERIC COV was determined from the sum of the squares of the standard deviations of the reflection and transmission measurements, weighted according to the partial derivatives of the defining equations with respect to those
variables. The formulae are quite complicated, as may be inferred from examination of Eq. (6), for example. The results are contained in the Appendix to Reference [5].

RESULTS AND DISCUSSION

Table 1 is a summary of average ERIC and $S$ values for each sample as measured by each method, along with the opacity for the samples. Also given are values determined by a commercial instrument, determined at Technidyne. Commercial results were determined using the $SR_\infty$ method with a constant value for the scattering coefficient, $\bar{S} = 50 \text{ m}^2/\text{kg}$, consistent with the findings of Jordan and Popson [1]. Results for the three methods of this report all track commercial ERIC values well, though they consistently have lower values. Results from the $R_0 R_{\infty}$ method have the largest offset from commercial, reflecting the smaller scattering coefficients measured with this method. The biggest discrepancy is for the highest opacity sample, 98.7%. The ERIC result for the $R_0 R_\infty$ method applied to this sample is disallowed by the TAPPI provisional standard [4], since the opacity exceeds the 97% limit of the standard. This is appropriate, since 12 of the 25 individual tests of sheets from this sample gave values for which $R_{\infty} > R_0$. Even the (allowed) 96.1% opacity sample had this unphysical result for 2 of the 25 individual tests.

Table 1. ERIC values and Kubelka-Munk scattering coefficients by different methods. The $SR_\infty$ method uses $S$ values from the $RT$ method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Opacity (%)</th>
<th>$RT$ Method</th>
<th>$R_0 R_\infty$ Method</th>
<th>$SR_\infty$ Method</th>
<th>Commercial</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ERIC</td>
<td>$S$</td>
<td>ERIC</td>
<td>$S$</td>
<td>ERIC</td>
</tr>
<tr>
<td>News</td>
<td>81.7</td>
<td>181</td>
<td>45.0</td>
<td>127</td>
<td>40.8</td>
</tr>
<tr>
<td>Kraft</td>
<td>83.2</td>
<td>189</td>
<td>30.0</td>
<td>149</td>
<td>28.3</td>
</tr>
<tr>
<td>Trial 1</td>
<td>94.6</td>
<td>519</td>
<td>47.9</td>
<td>417</td>
<td>39.7</td>
</tr>
<tr>
<td>Trial 2</td>
<td>96.1</td>
<td>702</td>
<td>50.1</td>
<td>558</td>
<td>40.4</td>
</tr>
<tr>
<td>Trial 3</td>
<td>98.7</td>
<td>1106</td>
<td>51.7</td>
<td>939</td>
<td>43.8</td>
</tr>
</tbody>
</table>

Figure 2. Effective residual ink concentration (ERIC) measurements using the $RT$, $R_0 R_\infty$, and $SR_\infty$ methods, contrasted with opacity measurements.

Figure 2 is a plot of ERIC and opacity values from Table 1. Also shown are error bars associated with the use of the $RT$ and $R_0 R_\infty$ methods. The error bars represent the standard deviation in the results of a single test as determined from the precision analysis of Reference [5]. Half-error bars are shown to avoid overlap: upward bars refer to the $RT$ method, and downward bars refer to the $R_0 R_\infty$ method. Error bars associated with the $R_0 R_\infty$ method are much
larger at high opacity, owing to the singularity in the defining Equation (1). At the highest opacity of 98.7%, the $R_o R$ method is clearly inappropriate for this reason. However, residual effect of the singularity remains at opacity 96.1% (Trial 2). Care must be exercised in using the $R_o R$ method in the vicinity of 97% opacity. At 94.6% opacity (Trial 1), the error bars for both the $RT$ and $R_o R$ methods are comparable, but the latter produces a smaller ERIC owing to smaller values for the scattering coefficient. This tendency of the $R_o R$ method to produce smaller scattering coefficients than the $RT$ method was observed for all samples. The average reduction was 13%. Better agreement between scattering values calculated from the two methods is reported by Knox and Wahren [6]. However, for their four most opaque samples, values of $S$ calculated from $R_o R$ data were 8% lower than calculated from their version of the $RT$ method.

Figure 3 is a theoretical plot of the COV of ERIC as a function of ERIC for all three methods of calculation, based on the precision analysis of Reference [5]. In generating the curves, the COVs of the measured variables were assumed to be 4% for the reflectances $R, R_o$, and $R_e$, and 5% for the transmission $T$. These are close to the values for our actual data. We used 10% as the COV of $S$, inferred from the size of error bars in data by Jordan and Popson [1]. The slight change of slope in the $RT$ curves near ERIC = 500 ppm is a mathematical artifact of the precision analysis. It reflects a change in variables in the defining Eq. (6) from $T$ to $A = 1 - R - T$, where $A$ is the fractional amount of the incident radiation absorbed by the sample. The precision analysis gives a lower COV using the variable $A$ for low ERIC values, and the variable $T$ for high ERIC values [5].

![Figure 3](image_url)

Figure 3. Coefficient of variation (COV) of effective residual ink concentration (ERIC) values as a function of ERIC.

An increase in ERIC COV at low ERIC values occurs for all methods. It reflects the decreasing denominator in the COV calculation. There are no ERIC values on the graph for which the $SR_o$ method provides the lowest COV. The $R_o R$ method is best for ERIC values less than 150 ppm, and the $RT$ method is best for higher ERIC values. In the absence of the $RT$ method, Figure 3 shows the superiority of the $SR_o$ method over the $R_o R$ method for all ERICs above 250 ppm.

As part of a study involving pulp from 27 newsprint deinking lines in 1998, (and 18 lines in 1999), Haynes found that the top quartile of participants produced pulp with an average ERIC value of 235 ppm [16, 17]. Although the $R_o R$ method is comparable in accuracy to the $RT$ method at these levels, it appears that commercial deinked pulp is never clean enough to take advantage of the anticipated superiority of the $R_o R$ method’s accuracy at low ERIC levels. The $RT$ method is clearly the best choice for monitoring the ink-removal process from start to finish. Over the
domain shown in Figure 3, it is even superior to the $\tilde{SR}$ method without the need for use of an approximate value for $S$.

When the model used to produce the solid curves in Figure 3 is carried forward to larger ERIC values than appear on the graph, the singularity in the $RT$ method begins to have an effect. The corresponding ERIC COV eventually exceeds that of the $\tilde{SR}$ method when ERIC is about 5000 ppm. The estimated opacity at which this happens is 99.999%. The basis for the estimate is the formula for opacity that results from equating the right-hand sides of Equations (5) and (1b) near their singularities $T = 0$ and $R_0 = R_e$, respectively. Using the approximation $\sinh^{-1}(x) \approx \ln(2x)$ for large $x$ in Equation (5), we find that the two equations produce equal scattering coefficients when

$$\text{Opacity} = 100\% \times \frac{R_0}{R_{\infty}} = 100\% \times \left(1 - \frac{T^2}{1 - R^2} \right)$$

(9)

The modeled values $T = 0.003$ and $R = 0.268$ provide “five-nines” opacity, $S = 50 \text{ m}^2/\text{kg}$, ERIC = 5000 ppm, and ERIC COV = 11%. At this low value for $T$, the main source of measurement variation is likely to be electronic noise. The model also predicts that the minimum COV associated with the $RT$ method is 5% occurring near 2700 ppm ERIC. These large values for ERIC are not likely to be encountered in practice, but they show the strength of the $RT$ measurement approach. It is robust to 99.999% opacity versus 97% opacity for the $R_0 R_e$ method of the provisional standard [4].

CONCLUSIONS

The basic functions derived in the Kubelka-Munk theory of two-light-flux propagation in diffusing media are reflection and transmission, $R$ and $T$. Many authors have used measurements of $R$ and $T$ to solve for inverse variables of absorption $k$ and scattering $S$ [6–13]. These measurements, done correctly with diffuse illumination and detection using integrating spheres, tend to be complicated. Partly for that reason, commercial instruments designed to measure $k$, $S$, or related variants such as opacity and color, frequently use a geometry based only on reflection. This cuts design complexity in half, simplifies calibration, and eliminates the potential need for moving parts. All this leads to lower cost, higher reliability instruments that can perform multiple functions. At the same time, it places restrictions on the range of samples that can be measured accurately.

Measurement of ERIC in recycled pulp is a case in point. TAPPI provisional method T567 pm-97 [4] recognizes the inability to make a correct diffuse reflectance measurement of ERIC when opacity is above 97.0% at the 950-nm wavelength of interest. In the present study, this value of opacity is reached at ERIC values ranging from about 800 to 900 ppm. The ERIC COV at the limiting opacity ranges from 40% to 80%, dependent on the scattering coefficient. This means that a handsheet producing an ERIC of 243 ppm can, as we observed on retest, also produce a value of 871 ppm. Such a test result encourages the use of an approximate scattering coefficient at opacities greater than 97%. This limits the utility of ERIC to that of a differential measurement.

We have developed and implemented a demonstration test for measuring reflection $R$ and transmission $T$ from a single sheet. The result is used to calculate an ERIC value that is increasingly accurate as opacity increases. For example, recycled newsprint measuring 800 ppm has a standard deviation of about 80 ppm. This level of accuracy facilitates the process of ink removal in recycled pulps by limiting the need for repeat testing. The fact that an assumed scattering value is not needed increases the confidence that changes in fillers and fines are not influencing the result. At 10% accuracy, ERIC values in the literature will command greater attention because they will be less subject to mill-to-mill variations.

The objective of this paper is to alert the recycling industry to limits in a common test that have not received much attention in recent years and to show a feasible alternative for going beyond those limits. In the future, the Kubelka-Munk inverse solutions for $k$ and $S$ (Eqs. (1) or (5) and (6)) may be replaced by software such as DORT2002 [18–20]. This software exchanges the two-flux Kubelka-Munk model with a many-flux model that can be adapted to experimental setups like that of Figure 1. As a result, it may not be necessary to augment setups with costly
hardware to get acceptable ERIC measurements. We suggest that refinement of the \textit{RT} method developed here deserves incorporation into methods and provisional methods such as T567 pm-97. It may prove useful whenever diffuse reflection geometries are limited because of high sample opacities.

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**REFERENCES**


