A method for measuring the mass of nondispersible ink

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ABSTRACT: A rapid and accurate method, based on successive elimination of non-ink components in a repulped stock of recycled paper, has been developed to quantify the mass of nondispersible ink in the photocopied and laser-printed papers. By this method, selective chemical actions are used to successively remove the nonfibrous material such as the filler and the fibrous components, leaving the ink component intact. The reliability of the technique is supported by the results of infrared spectrophotometric analysis of the isolated ink. This method should be useful for determining toner ink in recovered papers.

KEYWORDS: Deinking, infrared spectroscopy, mass, measurement, printing ink, recovered papers, reprographic papers, toners.

To evaluate the efficiency of a deinking process, which consists of removing ink and other objectionable nonfibrous contaminants from a slurry of recycled paper, a reliable method to determine residual ink in a pulp is required. Deinking efficiency can be characterized by brightness measurement or absorption coefficient of the deinked paper *(1)*. However, the results of these measurements, which depend greatly on the amount and the size of ink particles *(2)*, cannot be used to quantify ink concentration.

Image analysis *(3–8)* is a useful tool for evaluating effectiveness of deinking chemicals and equipment. However, the information derived from this technique is not necessarily accurate and reliable unless care is taken in sample preparation and calibration of instrument, according to Seldin *(8)*. Besides, image analyzers measure the size and shape but not the mass of ink particles. The amount of residual ink, particularly the fine particles, has a significant effect on optical properties of recycled papers *(2)*. Hence, a complementary method, which allows quantifying the residual ink by weight, is needed to evaluate the efficiency of a deinking process.

The objective of this work is to develop a method that can determine the mass of residual ink in photocopied and laser-printed papers.

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Experimental

Principle of method

The principle of the proposed method is based on progressive elimination of undesirable components, which in this case are fibrous material and other non-ink contaminants. In essence, the eliminatory process consists of, for example, filler removal, delignification, and dissolution of carbohydrates. Care is taken to minimize chemical damages to the ink component. The mass of the residual ink is determined in the usual way, and its particle size distribution may be further studied by an image analyzer.

Procedure

Preparation of sample. White ledger paper (75 g/m^2, 21.5x28 cm) suitable for photocopying was used. Sample sheets were first dried at 105°C to measure their weight prior to printing by xerographic or laser processes. Some sample papers were printed with xerographic ink (Sharp-PPC-SF-880NT1), and others were printed by means of a laser printer using HP-TONER-92275A. All the sample papers were printed with

identical text. The printed sheets were redried at 105°C to determine the mass of the transferred ink.

The printed paper of about 4.5 g, presoaked and torn into a 3x3 cm size, was disintegrated at 0.5% consistency at 45°C for 5 min by means of a hand blender (Braun Multipractic). Sodium hydroxide (0.5% ovendry paper) and sodium silicate (2%) were used in the disintegration process. After filtration washing (Whatman No. 42), the pulp was diluted to 1 L, including 10 mL of nitric acid (4 N), in a 2-L beaker heated to about 80°C with continuous stirring for 10 min. The suspension was filtered (Whatman No. 42), and the remainder was washed with hot distilled water by filtration. The nitric acid treatment helped reduce the ash content in the pulp.

Delignification. The pulp treated with nitric acid was well mixed in a 2-L beaker containing 795 mL water, 100 mL potassium permanganate (0.1 N) and 100 mL sulfuric acid and allowed to stand for 20 min; sodium thiosulfate was then added until the red color of potassium permanganate disappeared. The delignified pulp containing ink particles was alternatively washed with 0.1 N sulfuric acid and distilled water by filtration (Whatman No. 934-4H).

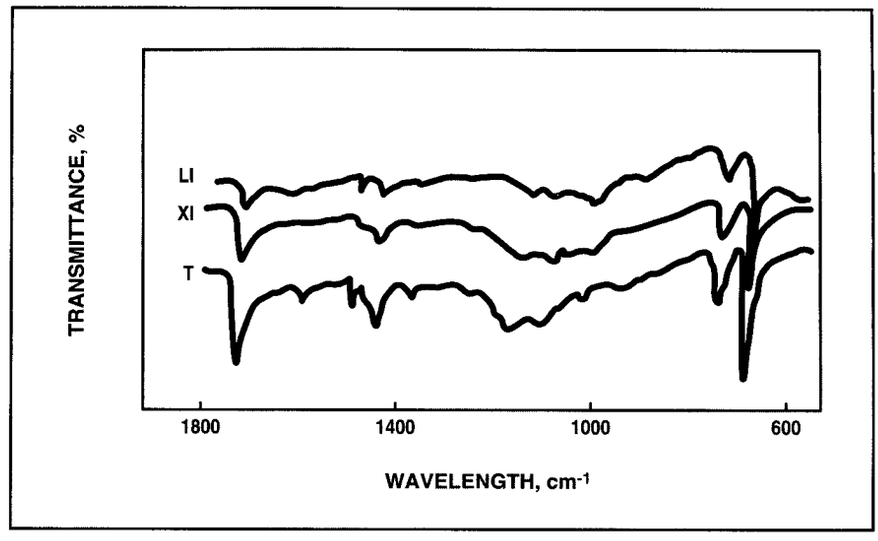
Dissolution of carbohydrates. The delignified pulp was slushed in ethanol, and a pad was formed on filter paper (Whatman No. 934-4H) by filtration. This pad was further washed with ethanol to remove any remaining water. The ethanol treatment helped improve the dis-persibility of the fibrous pad. After being dried with a hair dryer, the pad was torn into small pieces and treated with 1 M cupriethylenedi-amine at 0.5% consistency at 50°C with continuous stirring for 20 min.

After cooling to 20°C with running cold water, the solution was passed through a filter paper (Whatman No. 934-4H) that had been pretreated with hydrochloric acid (4 N), washed with distilled water, and dried to a constant weight. The remaining material was successively filtered with 1 M cupriethylenedi-amine, hot distilled water, 4 N hydrochloric acid, and distilled water. Each washing step lasted 5 min. After washing, the remainder of the ink and the filter were dried at 105°C, and the mass of ink was determined in the usual way.

I. Ash content in toner and printed paper

Sample	*Ash, %*
Unused toner	0.94
Unprinted paper	11.02
Unprinted paper (NHO_3 treated)	5.00
Laser-printed paper	11.90
Laser-printed paper (NHO_3 treated)	6.05

1. Infrared spectra of ink (T = toner, XI = isolated xerographic ink, LI = isolated laser ink)



Results and Discussion

Effect of NHO_3 on ash content

Table I shows that the ash content in the papers used in the experiments was reduced by nearly 55% after the NHO_3 treatment. The remainder of ash appeared to be completely removed during the steps following the pretreatment, and had no effect on the mass of the isolated ink as illustrated by the results reported in **Table II**. However, in papers containing clay or TiO_2, a complete removal of ash by this method may be difficult.

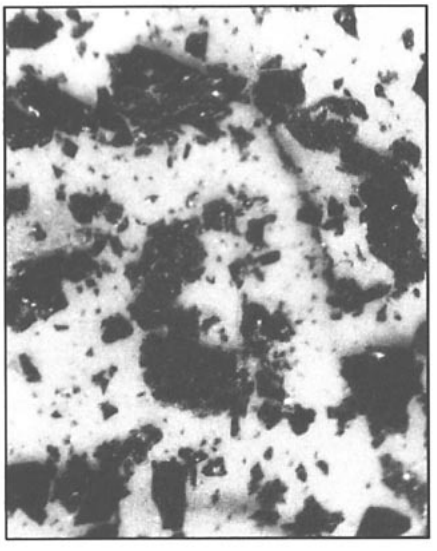
2. Partially disintegrated fiber-ink structure (laser ink magnified 60X)

II. Mass of transferred ink before and after isolation

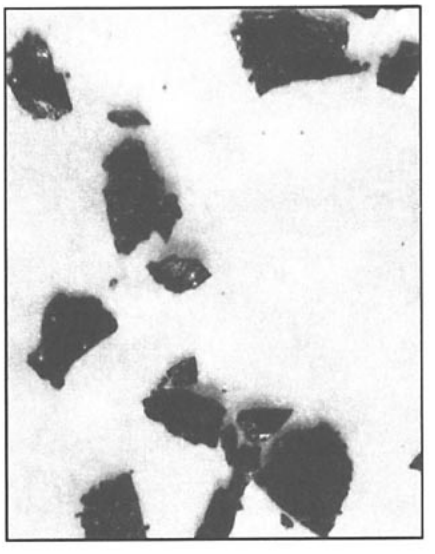
Printing method	Sample*	Ink mass, g/m² Before	After
Xerographic	1	0.50	0.45
	2	0.50	0.47
	3	0.50	0.47
	4	0.50	0.50
	Average (1-4)	0.50	0.47
	Std. deviation	0.0	0.0206
	Repeatability	0.0	0.0285 (6.08%)
	5	0.53	-
Laser	1	2.16	2.18
	2	2.16	2.21
	3	2.16	2.18
	4	2.16	2.16
	Average (1-4)	2.16	2.18
	Std. deviation	0.0	0.0209
	Repeatability	0.0	0.0289 (1.33%)
	5	2.13	-

*Samples 1-4: average of four single-side-printed; Sample 5: average of ten double-side-printed.

3. Isolated xerographic ink (magnified 75X)



4. Isolated laser ink (magnified 75X)



Infrared spectrophotometric analysis

Infrared (IR) spectrophotometric analysis (**Fig. 1**) of unused toner (Sharp PPS-SF-990NT1) and the isolated ink from xerographic-copied paper and laser-printed paper indicated that the three types of ink were indeed similar in spectrum. This means that there was little or no apparent structural changes of the main ink components incurred by the isolation process described.

Furthermore, no absorption of syringyl (e.g., 1230 cm^{-1}) or quaiacyl propane (e.g., 1270 cm^{-1}) of lignin appeared in the IR spectrum of the isolated ink, implying that the isolated ink was not contaminated with lignin that may be present in the wood-free ledger.

Microscopic observation

Laser ink or xerographic ink is difficult to dislodge from printed fibers during repulping; they are susceptive to forming mini-structures reinforced with fibers, as shown in **Fig. 2**. Formation of these resistant mini-structures is more evident in a slurry prepared from double-side-printed ledger. In this case, a more severe chemi-thermomechanical treatment would be required to completely separate the ink from the fiber surface and to reduce the size of ink particles suitable for flotation or washing.

Figures 3 and 4 show ink particles isolated using the proposed method. Observations using a stereomicroscope showed that there was no particular physical degradation of the ink particles during the isolation process discussed, and that there was no apparent contamination of fibrous material in the isolated ink mass.

Mass of ink on printed paper

Table II, which presents the mass of ink transferred from printers to the papers and the ink isolated using our proposed method, indicates that, in both printing processes, the mean values of ink mass obtained before and after isolation were not statistically different at a 0.01 significance level. The repeatability of the experimental values are quite good, showing the reliability of the technique used.

Table II also shows a standard deviation of 0.02 for repeated measurements of 0.50 g/m^2 of toner ink on printed papers, which is relatively good. However, in stocks which have been deinked with about 90% re-

moval efficiency, the accuracy of the method will substantially decrease when measuring residual ink of low levels.

It is interesting to note that the mass of ink transferred on laser-printed paper was approximately four times higher than that on xerographic-printed paper, although these two printing processes are similar *(4)*. This difference in ink concentration between these types of pulp cannot be detected by image analysis technique, although the size of ink particles in both cases may be similar. In addition, this observed characteristic may have an effect on the deinking behavior of these papers.

Conclusions

The initial concentration or mass of xerographic and laser ink in printed papers can be rapidly and accurately determined (in less than 120 min) by an eliminatory chemical isolation process. This process, which has a repeatability of about 6% or less, can be a useful technique for measuring the mass of toner ink in recovered paper stocks, as well as for preparing ink samples for image analysis.

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The financial assistance of the National Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Received for review Oct. 15, 1992.

Accepted Dec. 28, 1993.