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Preliminary Examination of Machine Copier Toners by Infrared Spectrophotometry and Pyrolysis Gas Chromatography

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ABSTRACT: Thirty-five photocopy toners and copies processed from machines using the respective toners were collected from five manufacturers. Through infrared spectrophotometry, a spectral match between the standard toner powder and the toner extracted from the respective copied document was achieved. Also toners were categorized into 18 different groups, of which 7 included more than 1 toner. Further specificity was achieved using pyrolysis gas chromatography, in which the toners in the seven different groups were distinguished from all others. Application is foreseen in an infrared spectrophotometer library search for peak match or functional groups or both to identify the toner of a questioned document, or matching or eliminating the toner from a questioned document with standards from suspect machines with pyrolysis gas chromatography.

KEYWORDS: questioned documents, photocopiers, spectroscopic analysis, chromatographic analysis

Occasionally anonymous letters, drawings, printed material, or other machine copies are submitted to the document examiner in an effort to determine the source of such a product. There has been considerable research previously conducted in identifying the physical class and individual characteristics of various machines from copies [*1-2*]. Our research approaches the problem from a different perspective, similar to the study done by Kemp and Totty [*3*].

The purpose of this project is twofold:

(1) to determine if dry toners from various indirect process copy machines could be analyzed by infrared spectrophotometry, and each one differentiated from all others, and

(2) to determine if the toner could be extracted from a photocopied document, run on the infrared spectrophotometer, and would be consistent with or match the spectra of raw toner powders from the same copy machine.

The second step is the crucial part of this research. If there is consistency between toner powder and toner extracted from a copied document, then raw toners could be collected

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from various companies, a spectra developed, and a library established. An unknown machine copy, which is the questioned document, might be matched in terms of class characteristics by extracting the toner from the paper and performing a library search for peak match or functional groups or both. Where similarities were found, the individual spectra then could be compared by hand to the questioned document spectra to determine if a match could be made.

This project is limited to the indirect copy process. Reference is made to a preliminary report on differentiating between the zinc oxide coated papers by extracting the photoconductive surface layer, and running the extraction on an infrared spectrophotometer. In this particular research the resin extracts were categorized into 14 different spectra out of 50 papers, and further differentiation was achieved on the basis of pH, ultraviolet examination, paper weight, and thin-layer chromatography [*4*].

The first experiment attempting to match raw toner powder with a photocopied document was conducted for the Kodak Ektaprint® 150 copier using Kodak Ektaprint K toner, and the Xerox® 3100 copier using Xerox 6R189 dry imager. A small amount of raw toner powder, approximately 1.5 to 2.0 mg for each machine, was added to KBr (potassium bromide for infrared analysis), mixed thoroughly, and a pellet was made using a KBr evacuable die. Each toner pellet was run on the infrared (IR) spectrophotometer to see if the Kodak toner differed substantially from the Xerox toner. From the resultant spectra, considerable variation in terms of wavelength, relative size and shape of the peaks, and location were noted.

Some experimentation was done at this point to determine what kind of solvent would be suitable for removing the toner from the copied material. It was decided that acetone generally was adequate, although pyridine also was used. Infrared spectra were run with KBr and acetone, and then with KBr and pyridine. Neither solvents registered significantly in terms of affecting the outcome of the analysis.

To avoid paper contamination, an extraction from a "test" paper also was run. Cascade OD/Xerographic paper, widely distributed in the Rocky Mountain area, was used. It is a sulfite pulp with titanium dioxide for brightness and opacity, and with fillers and other additives to insure a smooth, dust free surface. The extraction from the paper alone, using pyridine as the solvent, showed a very slight variation of pattern at approximately 1450 to 1470 cm^{-1}, which would have to be taken into consideration when comparing extracted toner from this and other paper products.

The toner then was extracted from each of the two documents copied on the respective machines using acetone as the solvent. A concentration of the dissolved toner was added to the KBr, dried, and then each pellet was prepared and run. Lo and behold! The Kodak product matched the Kodak toner, and the Xerox product matched the Xerox toner (Figs. 1 and 2).

It was then decided to pursue the experiment by collecting and analyzing both dry toners from various manufacturers and toner extracted from copies produced using the respective toners. The spectra would then be compared to determine if sufficient variation were present to differentiate each toner, from one manufacturer to another, and to insure that the product from each machine matched the powder toner. Obtaining a spectra match for each raw toner to toner developed by extraction from the copy would provide confidence in later extracting toner from an unknown document and knowing through such research that it was representative of the raw toner of a certain manufacture and type. Letters were sent to manufacturers of various copy machines requesting a sample of the toner and a copy from the machines using that toner. The companies responding thus far are AB Dick, Royal, Sharp, Minolta, and Ricoh. Of 35 toners run thus far, 18 different categories were established as follows:

(1) Sharp 74T and Sharp 72T;
(2) Xerox 6R189, AB Dick 62-6100, and Nashua for Xerox 3100;

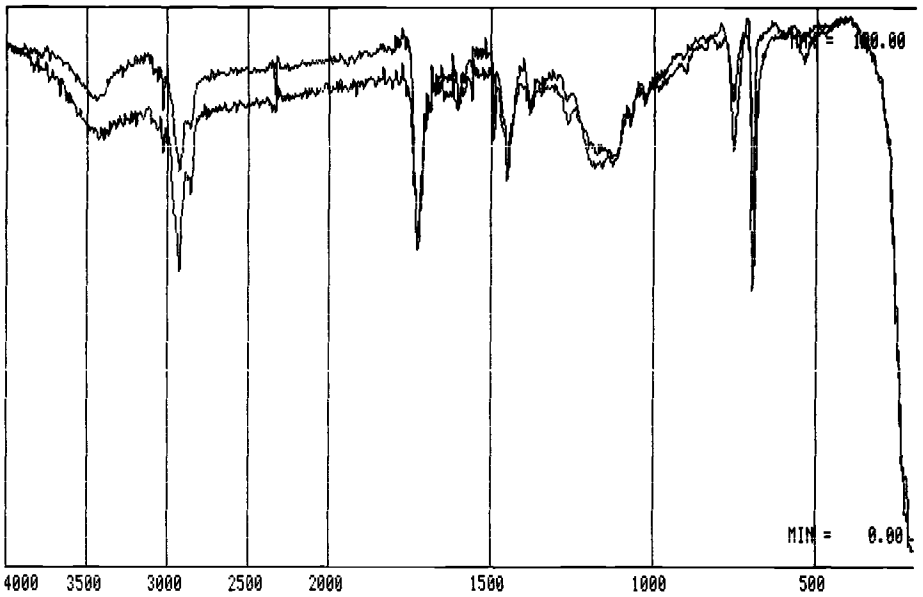

FIG. 1—*Kodak Ektaprint 150 copier with Ektaprint K. toner.* Top line—*Extraction from the copy.* Bottom line—*Standard toner in powder form.*

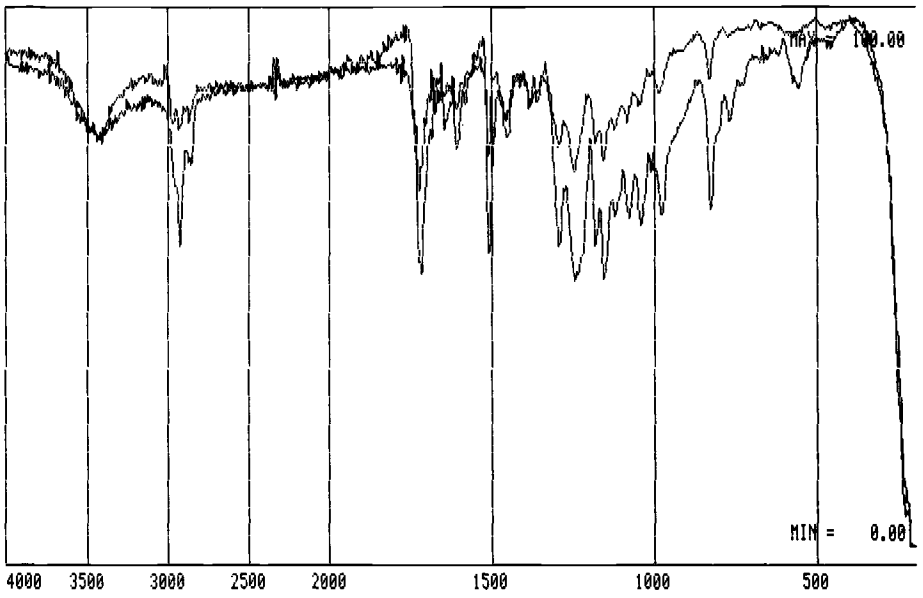

FIG. 2—*Xerox 3100 copier with Xerox 6R189 dry imager.* Top line—*Standard toner in powder form.* Bottom line—*Extraction from the copy.*

(3) Royal 3602/2502, Royal 3302, and Royal NTF 145;
(4) AB Dick 62-5500;
(5) AB Dick 62-2000;
(6) AB Dick 62-7202;
(7) Royal 130RRC;

(8) Minolta MT 8915-042, Minolta MT EP450, EP4502, and Minolta EP510;
(9) Kodak Ektaprint K;
(10) Royal 130 NTF and Royal 115 NTF;
(11) Sharp 75T, Sharp 76T, AB Dick 62-9616, AB Dick 62-9880, AB Dick 62-9820, AB Dick 62-9002, AB Dick 62-9902, and Kodak Ektaprint L;
(12) Minolta EP650Z MT, Sharp 90T, and Sharp 85T;
(13) Royal 1200 MC;
(14) AB Dick 62-6150;
(15) AB Dick 92-2635;
(16) Royal 110;
(17) Minolta MT EG301; and
(18) Ricoh.

The Kodak and Xerox material were taken from machines presently available at the Aurora Police Department.

These results demonstrate that the IR spectrophotometer can be used to break toners down into categories, at least. Certain limitations of this experiment were recognized at the onset. First of all, the IR spectrophotometer, while highly specific in its identification of compounds, lacks a certain specificity for the purpose of our analysis in that it analyzes the substance as a whole rather than breaking it down into its components. Its value in the forensic science laboratory is in differentiating between substances that have basically a different chemical formulation. Toner material manufactured for various makes of copy machines is primarily carbon black and resins, and may vary only quantitatively or in certain additives to enhance the quality of the image, and the binding properties. However, thus far, such analysis does separate the toners into manageable categories.

The next step in our research was to find a process to differentiate further the toners. Pyrolysis gas chromatography seemingly has provided that solution.[3]

Those toners in Category 11 listed above, the largest category, were chosen for experimentation and represented eight toners from three different manufacturers. The pyrolysis chromatogram did enable us to differentiate between all eight of the toners in Group 11, each one from all others.

We are continuing to collect and process both the toners from various manufacturers and the products from the machines, and will continue also to build our library. When it is as nearly up to date as possible, such information would be available to any other laboratory having similar facilities as the Aurora Police Department.

The application of this research is seen in receiving a machine copy as a questioned document and having no place to start in locating the machine and possible suspect. Where documents are 8½ by 11 or 11 by 14 in. in size, and the cover of the machine, another possible source of identification, is blocked by the document being copied, IR spectrophotometer analysis can be run of a small sample to narrow down the possible source of the toner. Then, pyrolysis gas chromatography can be performed, and the individual spectra match could be made to identify the copy toner used. If suspect machines can be located, the possibility of finding the actual machine could be made by attempting a match through trash marks or possibly drum or lens defects or both.

When a machine copy is received as a questioned document, along with products of suspect sources of machines, pyrolysis gas chromatography could be performed for each document to match or eliminate the questioned document from the standards.

At this stage of the research, the authors are continuing to establish the IR spectrophotometer library for raw powder toners. Using both IR spectrophotometry and pyrolysis gas chromatography, products from each machine are being compared to verify

[3]This process was suggested to the authors by Dr. Kent Oakes, Forensic Chemist Consultant for the Aurora Police Department.

consistency between the extraction from copies and raw toners, as well as the effects of paper on the results. The criminalist becomes the essential key to this type of document problem since the interpretation of results is his/her responsibility.

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