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Classification and Identification of Color Photocopiers By FT-IR and GC/MS

REFERENCE: Mizrachi N, Aizenshtat Z, Levy S, Elkayam R. Classification and identification of color photocopiers by FT-IR and GC/MS. J Forensic Sci 1998;43(2):353–361.

ABSTRACT: Colored toner samples and counterfeit money processed from color photocopiers were collected from the same six manufacturers. Through infrared spectroscopy, a spectral match between the standard toner prowder and the toner extracted from the respective copies counterfeit banknote and documents was achieved. The results allowed the identification of the manufacturers and models, except for one manufacturer for which only partial identification was obtained. The toners were characterized and classified into different groups. Characterization or elimination of the toner extracted from counterfeit money processed by suspected photocopiers, is foreseen through building a transpose library of infrared data. Gas chromatography/mass spectrometry results showed that it can be used as a complementary method.

KEYWORDS: forensic science, questioned documents, colored toners, photocopiers, counterfeit money, fourier transform infrared spectroscopy, gas chromatography, mass spectrometry, criminalistics

Color photocopiers provide an efficient and dangerous means to counterfeit documents and money as well. The cases involving photocopied documents have significantly increased over the last years. In the absence of a suspected photocopier, the questioned document examiner is confronted the difficult problem of classification and identification of the source of the copy. The significant increase in the number of questioned document cases involving color photocopies has lead to the development of several different analytical methods for the classification and identification of photocopying toners (1). Although the physical characteristics of the photocopiers have been discussed (2), chemical analysis of the toners appears to be a useful addition to their physical classification. Since the toners are mainly compositions of organic resins, polymers and copolymers, mixed with either carbon black or pigments, the toners can be easily analyzed using known and established analytical destructive and nondestructive techniques. Py-GC/MS (3,4), FT-IR spectroscopy (5,6), DRIFTS (7,8), and microspectrophotometry have been used. In some of the infrared techniques (7,8), reproducible results were obtained, which make possible the differentiation of toner samples obtained from different photocopiers. Although Kemp and Totty (9) observed some differences in the infrared spectra between the toners prior and post thermal fixation on the paper, these differences were attributed to the fusion during the fixation process by the photocopier. Most of the methods were focused on black toners, while Mazzella and co-authors (8,10) discussed analytical work done on colored toners together with the black ones. The problem addressed here was whether FT-IR and GC/MS spectra of the post fixation colored toners can be distinguished among various brand of photocopiers. Since the toners in the present work appear to be registered patents, we did not try to track them down by identifying their constituents. However, we tried to find out their unique differences in order to classify them.

Forty eight colored powder toners of 12 series were obtained representing 6 manufacturers. After the thermal fixation process 16 toners of the photocopies were obtained for analysis (Table 1). In addition, 3 copies of ink jet printers were processed for the declared trials.

Materials and Methods

Toner Samples

Four color samples for each photocopy sample were obtained from the company representatives in Israel (Table 1). These toners represent most of the toners available in the Israeli market. No further information was provided. All the analyzed photocopies were copied on the same model. The specified toner recommended by the manufacturer was used. The toner samples to be analyzed by FT-IR and GC/MS were respectively either gently scraped or extracted from the photocopies. For the recognition of the paper's contribution to the infrared spectra, we have used scraped paper as a reference.

The raw toner powder, the scraped photocopies of the same brand and model, and the scraped reference paper were analyzed by FT-IR. A small amount of each (1.5 or 2 mg for each), was added to KBr (potassium bromide for infrared analysis), mixed thoroughly, and a pellet was made using a 13 mm KBr evacuable die.

For the GC/MS, the toners were extracted from 2 $\times$ 1 cm section with 1 mL of chloroform, concentrated by evaporation and the concentrated extract from each toner was injected into the GC/MS. The analysis of the samples were repeated a number of times from different parts of the photocopies, to assess the reproducibility of the method. Although the FT-IR spectra were displayed in the transmission format (%T), the absorbance spectra has been used for the purposes of building library data.

It is known that yellow, magenta, cyan, and black (quadrichromatic) are used for printing the picture in layers, hence the 4 colored toners have to be analyzed and considered as a mixture. The

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Received 24 March 1997; and in revised form 29 May and 1 July 1997; accepted 2 July 1997.

TABLE 1—*List of the photocopiers and models prior and post fixation of toners.*

Manufacturers	Models	Prior Fixation	Post Fixation	Remark†
CANON	CLC 1	*	*	
	CLC 200	*	*	clc 300,350, Agfa xc 305
	CLC 300		*	
	CLC 350		*	
	CLC 500	*	*	clc 550
	CLC 550		*	
	CLC 700	*	*	clc 800
	CLC 800			
	CLC 10‡		*	ink injection
	Bubble Jet‡ Al		*	ink injection
XEROX	5765	*	*	
	5775	*	*	
RICOH	NC 100	*	*	
	NC 5006	*	*	Gestetner 2706
	NC 8015	*	*	
KONICA	9028	*	*	
GESTETNER	2706	*	*	Ricoh 5006
AGFA	XC 305	*	*	Canon clc 300
OLIVETTI	C 8000‡		*	as for clc 10

*The toner samples were analyzed.
†Additional models which use the same toner.
‡Models of ink jet injection, not included in the list of the 6 manufacturers.

infrared spectra of the 48 toner samples, which were obtained separately from 12 series of toners were used for the 16 types of copiers from 6 different companies. The infrared spectra were of high quality and showed good reproducibility. Money bills and other colored documents were photocopied on the 16 different types (brand or models) of the copiers.

Apparatus

The infrared spectra were recorded using a Nicolet Magna-IR model 550 FT-IR spectrometer. The spectra were collected from 32 accumulated scans at a resolution of 4 cm^{-1}. A deuterated triglycine sulfate detector (DTGS) was employed and spectra were collected between 4000 and 400 cm^{-1}.

The data for GC/MS were generated using a Hewlett-Packard (HP) 5890 gas chromatograph connected to an HP 5970B Mass Selective Detector (MSD), operated in the scan mode, and controlled by an IBM computer using 3.11 version Window software. The instrument performs 70 electron volt EI ionization MS. A DB-5 bonded-phase fused silica GC column, 15 m by 0.25 mm internal diameter with a 0.25 μm film thickness of poly (5% diphenyl-95%-dimethylsiloxane) was used. Split injection (1 μL) was done at 220°C, at split ratio of 1:9. The column temperature was programmed from 50° to 290°C at a rate of 25°C/min. He gas was used as a carrier, with flow rate of 1 mL/min.

Results and Discussion

FT-IR

The spectra of the toner samples of the different photocopiers were compared in order to see whether the pigment provide a significant effect to the spectra. The comparison of the spectra obtained for 4 colored toners of the same manufacturer did not reveal any marked differences (Fig. 1). The same similarity and reproducibility are valid as well to the colored toners collected from the other companies (Fig. 2). These results confirmed our primary assumption that the amounts of the pigments in the toner and its contribution to the spectra are minor. Equal weights (25% w/w of each of the 4 colored toners) were then mixed together, the spectra obtained for these showed very minor differences in comparison to the single toner of the same brand (Fig. 3).

It was possible to use the scraped area of the photocopies from the different copiers indicating feasibility of database and infrared spectra library for the photocopying toners prior and post thermal fixation. This technique enabled us to identify and classify the photocopier and its copies, based on the mixture of all 4 colors.

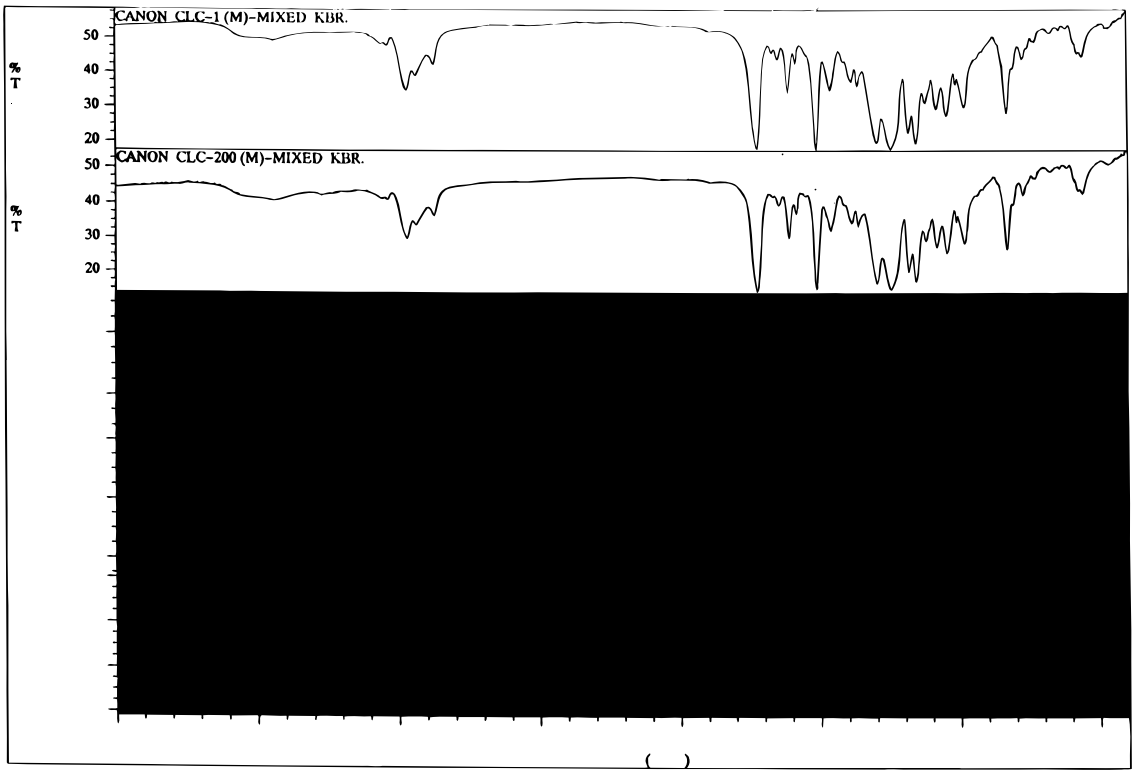
Figure 2 and Fig. 4 exhibit the fact that the thermal fixation of the toners has very little influence on the total infrared spectra of the toners. Hence, a database library was built. This library, can be used for the classification of color-copiers according to different toners used by different manufacturers (one should be careful to follow the manufacturer's specifications).

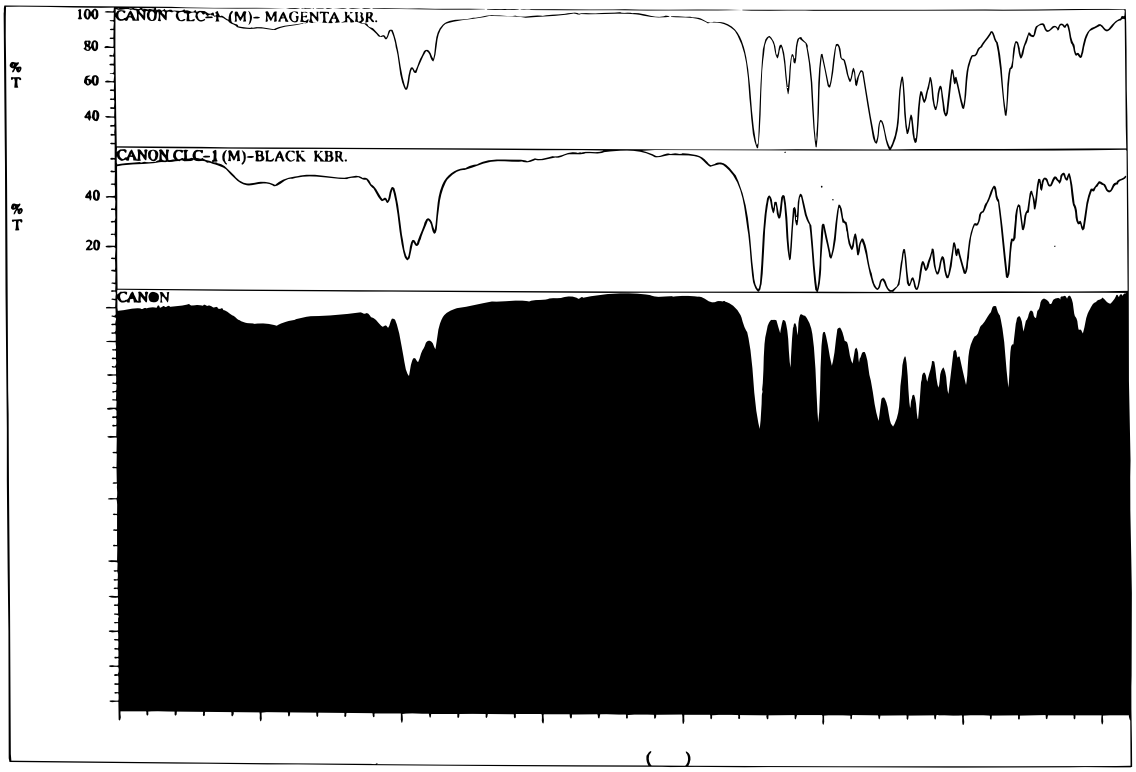
An exception was the type of Canon CLC 200. Its photocopy spectrum was different from that of the original toner, although the same toners are used for other types of Canon (CLC 300, & CLC 350), whose spectra are similar prior and post fixation (Fig. 5). This fact can be explained as caused due to different conditions of the fixation process that might exist in this particular model CLC 200 (extra heat, pressure or both).

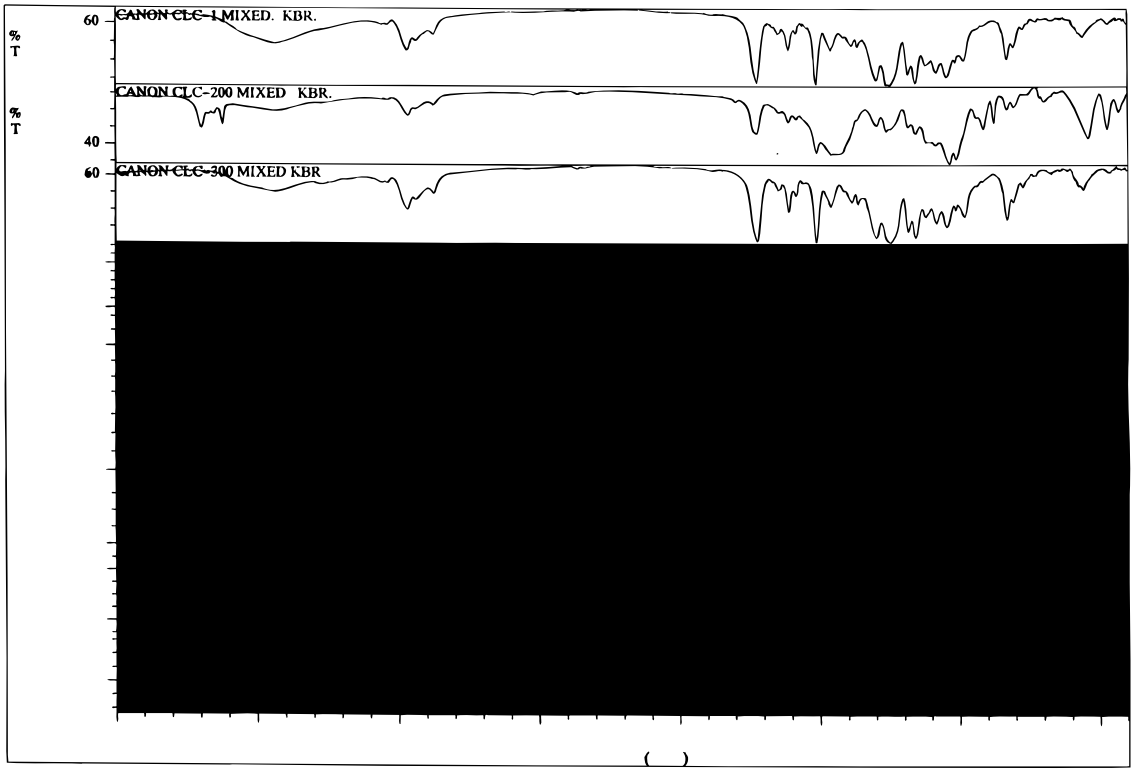
The spectra and their degree of similarity can be influenced by the depth of the scraping and the quantities of the fibers (cellulose) scraped from the paper together with the toners (Fig. 6). In this technique it is almost impossible to prevent the scraping of the fibers together with the toners. Three possible solutions for this problem are suggested as follows: a) scraping the fibers as a background from a white area. b) The extraction of the photocopies were analyzed after the solvent's evaporation. However, with this technique not all the constituents were extracted. On the other hand, this technique was useful for the preparation of samples that were used for the GC/MS analysis to compare volatile constituents existing in the toners. c) Scraping the layers of the toners stepwise from the clean toner through the toner + paper to "clean" paper, will show the contribution of the paper to the spectra. The spectrum of the last step will be almost free of the influence of the toner. The toner is thermally fixed on the surface of the paper almost without creating any chemical bonding with the cellulose fibers. Since it is difficult to find a white area on the counterfeit money or other colored photocopies for mathematical subtraction (Fig. 7), the third technique is preferable when using FT-IR.

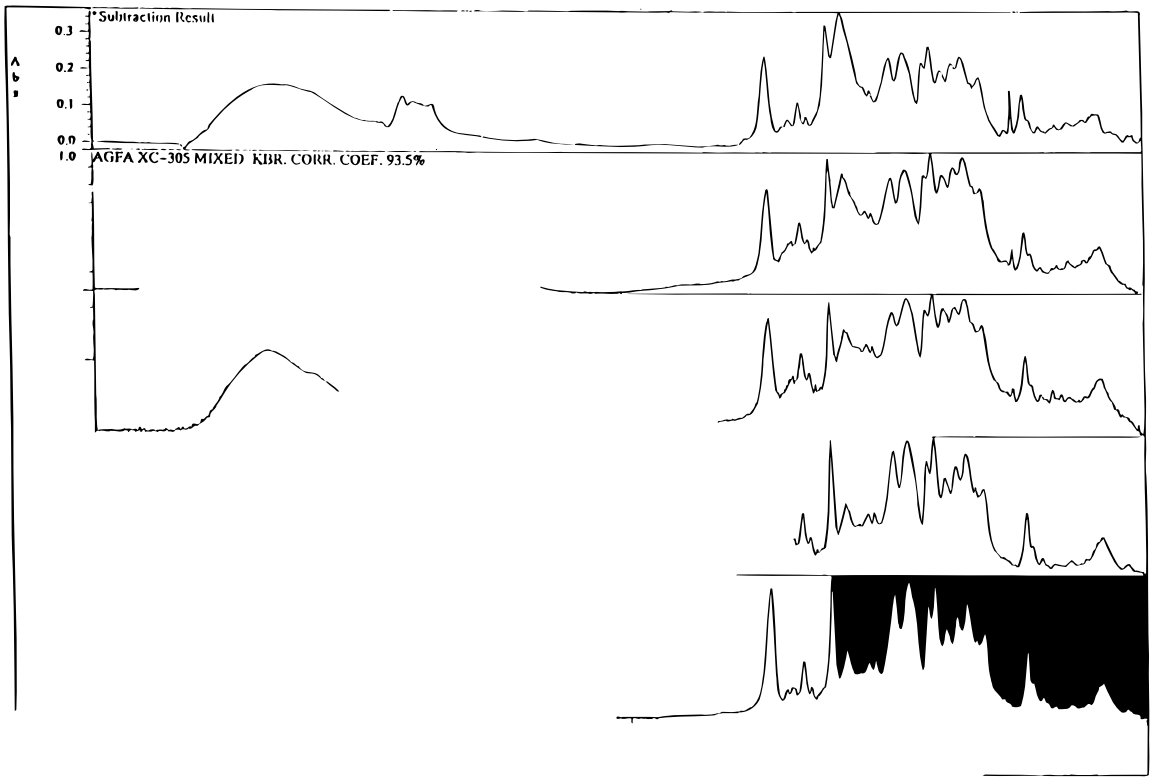
The results of the toners prior and post fixation analyzed by FT-IR technique are summarized in Fig. 8. This flow chart is a convenient way to look at the different models within a given company and compare them with different models in other companies. Models (in each and every group) which were listed perpendicularly have similar spectra, while models which were listed horizontally have different spectra. In conclusion with this technique 7 different groups were listed in the prior thermal fixation, however, 8 different groups were identified for the post thermal fixation (not including the ink jet injection).

The number of the analyzed samples post fixation is greater than those of prior fixation since some toners were used for more than one model of the photocopiers as recommended by the manufacturers (see Table 1).

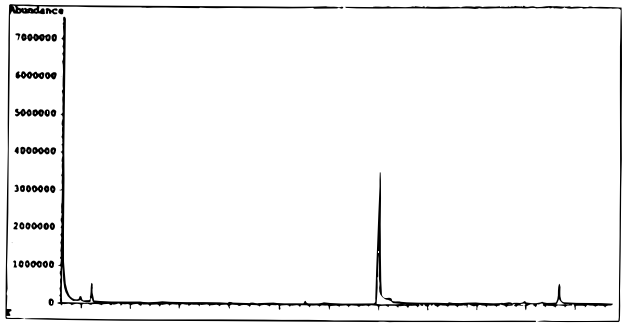

CANON CLC-1 (M)-MIXED KBR.
CANON CLC-200 (M)-MIXED KBR.
%T
%T
50
40
30
20
50
40
30
20


CANON CLC-1 (M)- MAGENTA KBR.
CANON CLC-1 (M)-BLACK KBR.
CANON
%T
%T
100
80
60
40
40
20

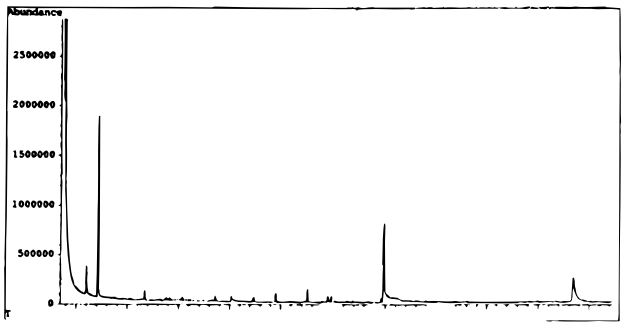

%
T
60
CANON CLC-1 MIXED. KBR.
%
T
CANON CLC-200 MIXED KBR.
40
60
CANON CLC-300 MIXED KBR


*Subtraction Result
0.3
0.2
0.1
0.0
1.0
AGFA XC-305 MIXED KBR. CORR. COEF. 93.5%

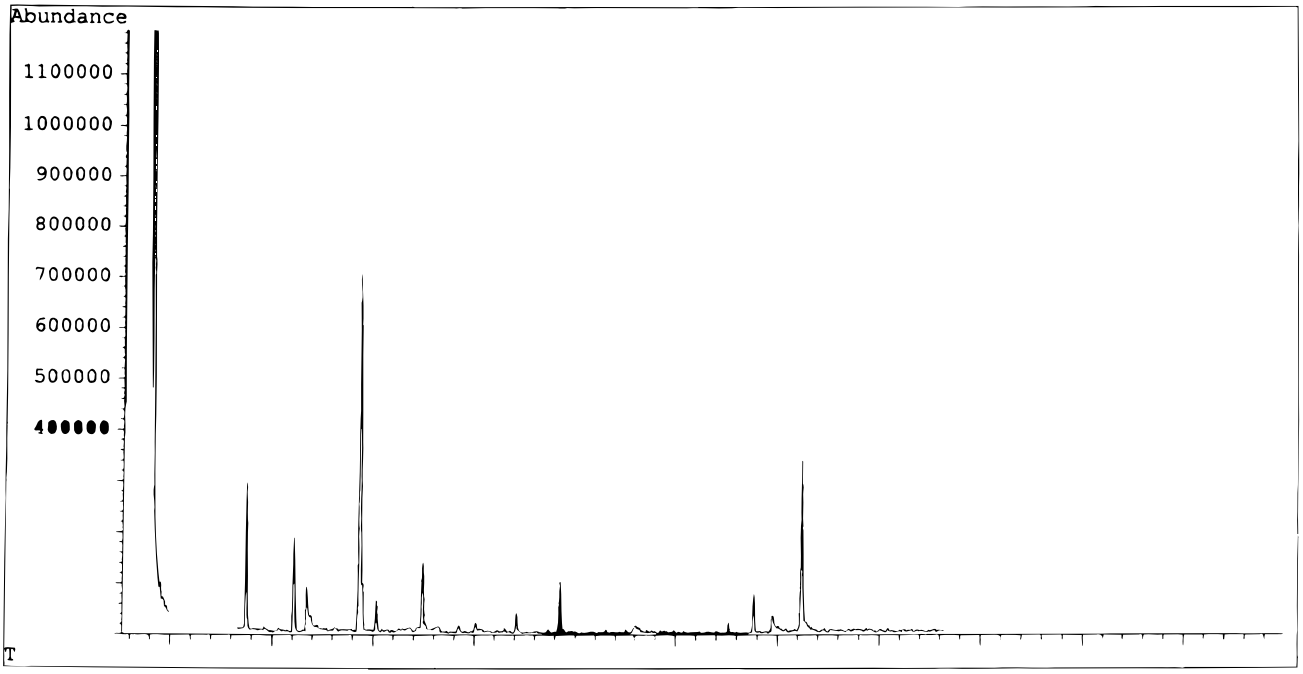
a)


Abundance
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0

b)


Abundance
2500000
2000000
1500000
1000000
500000
0

a)


Abundance
1100000
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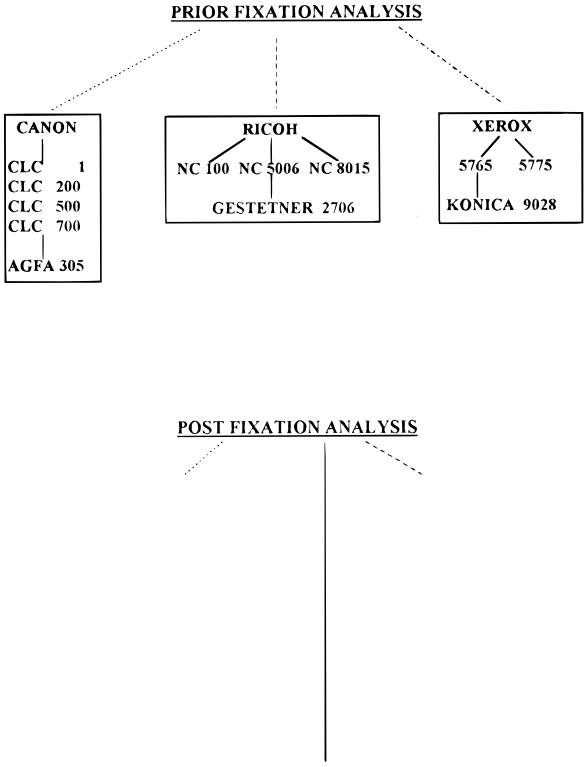
900000
800000
700000
600000
500000
400000
T



A number of declared trials that were given by the questioned documents' laboratory have indicated a 100% success rate using the FT-IR technique. Documents which were produced by ink injection printers were identified as not suitable to the collected database for the powder toners. However, collecting and introducing the data of these printers into the database source, a full success was achieved in a similar test (Fig. 7).

Acknowledgments

The authors would like to thank the company representatives in Israel for providing the toner samples and the photocopies for this study, and to Mr. H. Bretler from SICPA S. A. Company, Lausane, Switzerland, for his initial guidance.

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